Optimising biological desulphurisation with the addition of humic substances

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Zusammenfassung

In diesem Beitrag wird eine mögliche Optimierung der biologischen Entschwefelung von Biogas durch den Einsatz von Löslichkeitsvermittlern vorgestellt. Als Löslichkeitsvermittler werden Huminstoffe untersucht.


Schlüsselwörter: Biogas, Entschwefelung, Huminstoffe

Summary

This paper presents a possible optimisation of biological desulphurisation of biogas with the addition of solubilisers. In this instance, humic substances were utilised as the solubilisers.

The whole process consists of a bioscrubber and a downstream bioreactor. In the bioscrubber the absorption is improved by the addition of humic substances. The downstream bioreactor acts as a regenerator of the washing liquid. An additional aim is to obtain elemental sulphur which can be used as fertiliser in agriculture.

In laboratory experiments the effectiveness of humates as solubilisers for the absorption of H₂S, as well as their quality for the application in the bioscrubber, were investigated. In steady state experiments the optimisation of absorption was carried out. These experiments showed that the humic substances “Humin-P” (potassium humate) and “Humin-S” (sodium humate) achieved significant improvements in comparison to pure water as washing liquid. In two laboratory bioreactors the regeneration of humic substances as well as their effect on the sulphur bacteria, Thiobazilli, was investigated.

Keywords: Biogas, desulphurisation, humic substances
1 Introduction

This paper deals with the optimisation of biogas treatment. Before using biogas, for instance in an incineration process, the sulphur content is removed in order to avoid an impact on the environment e.g. bad smells, corrosion and acid rain. Biogas has H₂S concentrations from 2000 to 5000 ppm. One option is the separation of H₂S and organic sulphur compounds by biological means. Thereby microorganisms oxidise H₂S to elemental sulphide and sulphate (SCHNEIDER 2007). Processes for this purpose have not yet been optimised.

An improvement of the effectiveness of gas scrubbers can be achieved by using adapted washing liquids. The idea of the optimisation of biogas treatment concerns the addition of solubilisers into the washing liquid of a bioscrubber in order to improve the absorption of H₂S. Bioscrubbers can also be built smaller, thereby reducing the costs. Humic substances haven’t been tested so far as solubilisers in the biogas treatment. As they are a natural product their use in this process will be a good optimisation of the treatment.

Besides, the biological regeneration of the bioscrubber aims to produce elemental sulphide, which can be used as fertiliser. Due to the declining atmospheric sulphur input, farmers have to fertilise regularly in order to ensure a sufficient sulphur supply and crop productivity (LUVENA S. A. 2003).

The solubilisers were tested in laboratory experiments for their application in the bioscrubber-system. In a pilot plant at a biogas power station site the effectiveness of this treatment will be tested.

2 Material and methods

A bioscrubber-system for the desulphurisation of biogas, containing a bioscrubber and a downstream bioreactor, is optimised by the addition of humic substances as solubiliser. In laboratory experiments the effectiveness of these solubilisers was analysed. Furthermore the regeneration of the solubilisers, their compatibility with the microorganisms and the characteristics of the biological hydrosulphide oxidation were determined.

The bioscrubber-system was built as a pilot plant at a biogas power station site. In this pilot plant the results of the laboratory experiments will be compared with the practical tests.

2.1 Bioscrubber

An improvement of the effectiveness of gas scrubbers can be achieved by using adapted washing liquids. Humic substances were investigated as solubility agents to improve the absorptive separation in bioscrubbers for the desulphurisation of biogas.

2.1.1 Humic substances as solubiliser

With the addition of solubilisers into the washing liquid the solubility of H₂S is improved. For the application in biological desulphurisation, the solubilisers should offer amongst others the following characteristics:
Humic substances fulfil these criteria. The prior-tested humic substances are a potassium humate (Humin-P) and a sodium humate (Humin-S) from the company Humintech. Humates are the salts of humic acids, they consist of 70-80% of humic acids and are completely soluble in water. Humic substances have been identified as good solubilisers for odorous substances (Niemeyer, Stegmann 2006).

Humic acids are large molecular chemical compounds and compose with fulvic acids and humin the third fraction of humic substances. The chemical reactivity results from numerous functional groups, especially carboxyl groups, phenolic and hydroxyl groups as well as carbonyl and amino groups. They provide the surface active properties of the humic acids and increase the solubility of organic compounds in water. Humic substances are formed through the chemical and biological humification of plant and animal matter and through the biological activities of microorganisms. (Ziechmann 1996; Humintech® 2002)

2.1.2 Steady state experiments

The effectiveness of humates as solubilisers for the absorption of H₂S was investigated in steady state experiments. In these experiments according to the head space method the reduction of H₂S in the gas-phase was analysed. For equilibrium purposes a sample bag, filled with biogas and washing liquid, was stored for several hours in the laboratory at a constant temperature. The measurements in the gas-phase were carried out by a mass spectrometer, a H₂S Data Logger called OdaLog or Dräger-test-tubes. The samples of the biogas were taken at source, directly at the biogas plant. The dosages of washing liquid in the sample bags were between 0.1 and 100 ml per litre biogas. The degree of reduction indicates the effect of the washing liquid.

In the experiments it turns out that only minimal amounts of humate solutions were necessary for a degree of reduction over 90%. Due to different initial concentrations of biogas (between 100 and 3000 ppm) and different concentrations of the used humate solution (between 0.5 and 4%) the necessary amount of humate solution alternated between 0.1 and 60 ml of humate solutions per litre of biogas. The pH value of the humate solutions was between 9 and 10. In comparison tests with alkaline water it needed more than 100 ml per litre biogas for this reduction. This shows the improvement of the absorption of H₂S by the addition of humic substances.

*Figure 1* presents the degree of reduction according to the wash volume of a 3.5% humate solution. This example shows that for a reduction of H₂S in the gas-phase less than 10 ml of the washing liquid per litre of biogas (content of H₂S: 1000 ppm) are necessary to reduce this to almost zero ppm.
Fig. 1: Reduction of H2S with varying volumes of washing liquid

The series of steady state experiments (variation of pH, temperature, type of humic substances and dilution of washing liquid) showed that the absorption of H2S from biogas is improved by the addition of humates.

To evaluate the ability of the humic substances as solubilisers further, the Henry coefficients are determined. The Henry coefficient is a common parameter to characterise the absorption capacity of a substance. The solubility of a gas (index i) in a liquid (index j) can be described mathematically according to Henry’s Law as follows:

\[
H_{i/j} = \frac{p_i}{x_j}
\]

or

\[
H_{i/j} = \frac{y_i}{x_j}, p
\]

The loadings \(y_i\) and \(x_j\) [mol/mol]) can be determined with the measurement of the \(H_2S\) concentration in steady state and the concentration of the untreated biogas. To achieve the best possible accuracy the Henry coefficient must be determined at the limit value of \(x_i = 0\) (GMEHLING, KOLBE 1988). This limit value can be estimated by a diagram where the ratio \(y/x_i\) is plotted versus the liquid loading \(x_i\). The axis intercept \(y_{(x=0)}\) of a linear smoothing function multiplied with the total pressure \(p\) yields to the searched Henry coefficient. *Figure 2* shows an example for the determination of the Henry coefficient at a temperature of 30 °C.
In this experiment the following Henry coefficients could be determined:

\[ H_{Humin-P} \approx 6.5 \text{bar} \]
\[ H_{Humin-S} \approx 14 \text{bar} \]
\[ H_{\text{H}_2\text{O}} \approx 550 \text{bar} \]

If interpreting the Henry coefficients it must be taken into account that in accordance with Henry’s law the gas solubility is inversely proportional to the Henry coefficient. That means that small Henry coefficients indicate high absorption. In comparison with water it appears that the humic substances promise very good absorption qualities. Theoretically the Henry coefficient of H\(_2\)S in water at a temperature of 25 °C is 560 bar (Sander 1999).

Due to the enormous difference between the Henry coefficient of the system H\(_2\)S/water and H\(_2\)S/humate solution, there must appear also other reactions with the H\(_2\)S in the humate solution than a simple absorption. One has to consider a chemisorption. By reason of the complexity and undefined structures of humic substances these reactions couldn’t be determined until now.

Figure 3 indicates the reactions of H\(_2\)S with the humate solution. First, it occurs the absorption in accordance with Henry’s Law. Secondly, the dissolved H\(_2\)S dissociates into HS\(^-\) and S\(^2-\). And thirdly, there is a reaction between the H\(_2\)S and the humic substances (HOM).
In the determination of the Henry coefficient the dissociation due to the alkaline pH value of the humate solution is considered and filtered out. The apparently very good Henry coefficient is not a consequence of the alkaline pH value of the humate solution. A further series of steady state experiments (variation of pH value and concentration of the humate solution) starts with the analysing the base of the very good reduction rates.

*Figure 4* demonstrates the dependence of the concentration of the humates in the washing liquid upon the required amount of washing liquid to achieve reduction rates of over 80%. Even with only 0.5 % Humin-P in the washing liquid the required amount of washing liquid is less than with an alkaline solution. Alkaline solutions with pH values between 8.5 and 13 were analysed.
Another series of experiments were carried out to underline the effect or non-effect of the pH value. The example of a steady state experiment with variation of pH, shown in table 1, underlines that the reduction of H$_2$S is more dependent upon the concentration of humates than upon the pH value. In table 1 are the concentrations of H$_2$S in equilibrium presented at different percentages of the Humin-P in solution and different pH values of the solution. The H$_2$S concentration in the biogas is between 1200 ppm and 1800 ppm (equal per each pH value).

Tab. 1: Dependence of pH value and concentration of Humin-P solution

<table>
<thead>
<tr>
<th>Concentration of Humin-P [%]</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 3</td>
<td>&gt;350</td>
<td>&gt;350</td>
<td>27</td>
<td>6</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>pH 4.5</td>
<td>&gt;350</td>
<td>&gt;350</td>
<td>213</td>
<td>146</td>
<td>144</td>
<td>82</td>
</tr>
<tr>
<td>pH 6.5</td>
<td>&gt;350</td>
<td>&gt;350</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>pH 11</td>
<td>&gt;350</td>
<td>&gt;350</td>
<td>62</td>
<td>2</td>
<td>6</td>
<td>1</td>
</tr>
</tbody>
</table>

The improvement of the absorptive capacity by the humate solution is not (only) based on the high pH value of the washing liquid. The specific interaction of the humic substances with the H$_2$S must be analysed in detail in further experiments.
2.2 Regeneration

The high requirements of separation effectiveness of gas treatment plants lead to the need for a high performance regeneration. Therefore the ability to be regenerated and the effort for this regeneration is one of the main selection criteria for the washing liquid.

Regeneration by microorganisms is a low cost possibility. The H$_2$S which is dissolved in the washing liquid will be transformed microbiologically to sulphur which is easily eliminated from the system. Humic substances are difficult to degrade biologically thus their use in a biological regeneration is attainable.

2.2.1 Hydrosulphide oxidation

The objective in the biological regeneration is on one hand the regeneration of the washing liquid and on the other hand the production of elemental sulphur. This elemental sulphur can be used as fertiliser in agriculture. The production of elemental sulphur by the species Thiobazilli was analysed in two laboratory bioreactors (2 l volume). Thereby the influences of the parameters pH value and oxygen concentration, as well as the kinetics of the Thiobazilli activity were determined.

The microbial basis is the multi-staged oxidation of hydrogen sulphide via sulphide to sulphite and finally sulphate. Firstly the Thiobazilli transform the hydrogen sulphide to elemental, polymeric sulphur, which is embedded in the cell wall. Afterwards the oxidation of sulphide via sulphite to sulphate occurs. This sub-reaction runs slower than the oxidation of hydrogen sulphide to sulphur. The following two reactions occur:

\[
(3) \quad 2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \\
(4) \quad 2S^0 + 3O_2 \rightarrow 2SO_4^{2-} + 2H^+ 
\]

(DAMMAN 2004)

In the bioscrubber-system only the partial oxidation to elemental sulphur is required. The elemental sulphur is hardly water-soluble and therefore easy to separate from the system.

The two bioreactors were inoculated with a mixture of hydrogen sulphide oxidising bacteria from a bioscrubber which operates under acidic conditions. They were fed with hydrogen sulphide and thiosulphate and aerated continuously.

Firstly it was determined if these bacteria, living in acidic conditions, could adapt to a neutral pH value. A pH value from 6 to 8 is the optimum for the sulphide producing Thiobazilli (SCHNEIDER 2001). This adaptation test was successful.

According to the reaction equations, the production of elemental sulphur should proceed at low oxygen concentrations. The accumulation of elemental sulphur at low oxygen supply could be verified. In addition, elemental sulphur accumulates at saturation concentrations of oxygen with sufficient substrate supply. This means that the production of elemental sulphide is not dependent on the oxygen supply at high feed rates of hydrogen sulphide or thiosulphate. This is in accordance with Buisman (BUISMAN 1990).

2.2.2 Biological compatibility of humic substances

The compatibility of the humic substances with the Thiobazilli is an important factor in the bioscrubber-system. Only with compatibility can this system operate effectively. The influence of the humic substances on the microorganisms was analysed in the laboratory.

Therefore comparison tests of two laboratory bioreactors were arranged. In one bioreactor humates were added (compare figure 5), apart from that they operated similarly. In these
bioreactors the following parameters (amongst others) were analysed and compared: pH, O₂, SO₄²⁻, S⁰, conductivity, turbidity, dry residue and dry matter. The only great difference in the two reactors was a large foam formation in the bioreactor with humic substances.

Furthermore the activity of the sulphide bacteria was measured and compared. This was carried out by the measurement of the oxygen consumption. The higher the oxygen removal rate, the higher the activity of the microorganisms. No markable difference was noted upon addition of humates.

These first entire laboratory tests showed that the humate Humin-P does not inhibit the bacteria and the microbiological production of elemental sulphur. The humate Humin-P seems to be inert in the bioreactor. In addition, humic substances ameliorate the soil activity and can be used in combination with the obtained elemental sulphur as agricultural fertiliser.

2.2.3 Biological regeneration

The regeneration of the washing liquid containing humates as solubiliser by microorganisms was tested in several laboratorial experiments. Thereby the reduction effectiveness of the humate solution was analysed as before in the steady state experiments. This time the washing liquid was put in a laboratorial bioreactor before using it repeatedly as washing liquid for the reduction of H₂S in steady state experiments. Table 2 presents the first results of the reduction of H₂S in equilibrium. In this experiment 30 ml of humate solution per litre biogas were used in a sample bag. The results show that the reduction of H₂S does not diminish.

<table>
<thead>
<tr>
<th>Date</th>
<th>21.7.09</th>
<th>6.8.09</th>
<th>1.9.09</th>
<th>11.9.09</th>
<th>21.9.09</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S in biogas [ppm]</td>
<td>1520</td>
<td>1400</td>
<td>948</td>
<td>2072</td>
<td></td>
</tr>
<tr>
<td>H₂S in equilibrium [ppm]</td>
<td>190</td>
<td>1</td>
<td>2</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

The series of regeneration experiments has just started, and so other experiments will follow. The complete capacity of the regeneration will be tested practically in the pilot plant.
2.3 Pilot plant

The results of the laboratorial experiments will be verified practically in a bioscrubber system at a biogas power station site. In this system the humates are added into the stream of washing liquid in a counter-current bioscrubber. The bioscrubber system contains a bioscrubber and a downstream biological regeneration. Due to the aeration of a separately connected bioreactor, a dilution of the biogas is avoided and therefore also a reduction of the calorific value of the biogas. The optimisation of this system will be carried out on the one hand by adding solubilisers (humic substances) and on the other hand by the variation of pH, oxygen concentration and air to water flow ratio. The pilot plant is demonstrated in figure 6. A schematic flow diagram is pictured in figure 7.

Fig. 6: Pilot plant in Albersdorf, Schleswig-Holstein
3 Results

In summary the results of the laboratory experiments show that the use of humates in the biogas treatment is effective. A bioscrubber system can be improved effectively by the addition of humic substances. The desulphurisation is simplified by the increased solubility of H₂S in a humate solution. Furthermore, it produces elemental sulphur as a by-product which can be used as an agricultural fertiliser.

The experiences of the laboratory experiments will be proven in the pilot plant. In addition, further experiments in the laboratory are necessary to determine the reactions between the hydrogen sulphide and the humic substances, as well as the characteristics of their regeneration and the kinetics of the sulphur bacteria. Another objective is the modelling of the whole process.
References


Thermophilic digestion of cellulose – Investigation of the inhibitory state

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Summary

The aim of the study was to investigate the effect of organic load (OL) change on control parameter performance for thermophilic cellulose digestion. With increase of OLs and exceeding the recommended volatile solids (VS) ratio of 0.5 VS Cellulose/VS inoculum an inhibitory state was targeted. Batch series with microcrystalline cellulose at six OLs were performed. Beginning with 5.7 kg VS/m$^3$ and increasing in each series by 5.7 kg VS/m$^3$ the extremely high final OL of 34.3 kg VS/m$^3$ was obtained. The pH, redox potential, volatile fatty acids, biogas production and composition were analyzed. Although huge OLs had been applied neither inhibitory state in terms of rapid or extreme parameters change nor biogas production decrease were detected. For the investigated batches simultaneous response changes of pH, redox and volatile fatty acids were observed. The elevated values of volatile fatty acids did not automatically lead to fermentation break and influenced neither the total gas production nor the total biogas composition even though the inhibitory concentrations of 50 mg/l for branched fatty acids were exceeded. The only explicit inhibitory sign observed was the gradually increasing total degradation time and the extended period of higher biogas production rate noted with every increase of OL.

Key words:

Anaerobic digestion; Inhibition; Cellulose, Thermophilic
1 Introduction

Biogas is regarded nowadays as a renewable energy carrier which can not only help countries to produce CO₂-neutral energy but also to alter their hitherto existing strong dependence on the fossil fuels (KARPENSTEIN-MACHAN, 2005). Maximal efficiency of the biogas plants can be accomplished by: (1) cofermentation of slurry with energy crops or wastes, (2) fermentation of energy crops only and (3) optimization of the fermenting process. The highest biogas yields per kg of dry solids (DS) can be obtained by dry fermentation of energy crops. This process though requires a constant control and understanding of the process parameters to early recognize the inhibition signs (FNR, 2005).

Native cellulose is a significant component of the energy crops and therefore an important substrate in dry fermentation. The aim of the experiment was to investigate the answer of a bacterial biocenosis to the increasing OL and to induce the OL-conditioned inhibition state in a set of batch tests with microcrystalline cellulose (as model substance) under thermophilic conditions.

2 Materials and methods

2.1 Inoculum and substrate

The original slurry for the batch tests was obtained from a 50 l quasi-continuously fed research fermenter, operated in a dry fermentation mode (fed with maize-grass silage-mix), under thermophilic (55°C) regime. The subsequent batches were performed with the same inoculum to achieve the optimal substrate and load adaptation. The inoculum was thermostated for 2-6 weeks to remove the residues of the previous trials. Guidelines for the fermentation of organic material were followed (VDI, 2004). The biomass was filtered through a kitchen strainer prior to the test to accomplish homogenous reproducible conditions for each batch. The DS content of the inoculum was 1.0-4.5% and the VS ranged between 45 and 60% of DS.

The pharmaceutical microcrystalline cellulose powder (98% DS = VS) was used as a model substrate in the test (VDI, 2004).

2.2 Experimental design and incubation

For each test a set of 12-18 fermenters filled with 700g of inoculum was run at 55°C. A reactor representing different stage of fermentation process was daily dismantled. An additional reactor was run with the slurry only to quantify the background production (VDI, 2004).

2.3 Analytical methods

Gas volume was measured daily with gas meters and calculated into STP-conditions. The gas composition (CH₄, CO₂, O₂ and H₂S) was analyzed respectively with an IR and electro chemical gas monitor (Ansyco, Biogasmonitor BM2000). At high gas production rates the analysis were performed daily, at lower rates depending on the collected gas volume. The pH and redox during the tests were controlled continuously with the WTW on-line sensors SensoLyt SEA and PtA. Additional pH control of every reactor was performed directly after being dismantled (WTW, PH3210 with SenTix 41). The dissolved inorganic carbon (DIC) and the sum of volatile acids (VA) were obtained titrimetrically with TiroLine easy (Schott) following the Nordmann procedure (NORDMANN, 1985). Complementary to the
sum parameter VS the volatile fatty acids (VFA) were measured by gas chromatograph (Focus GC-FID, Interscience) equipped with Econo-CapTM-1000 (Grace) capillary column. For the VFA analysis a method similar to PECHER (1989) and BARLAZ et al. (1989) was developed.

3 Results and discussion

Batch series with six OLs were performed. Starting from 5.7 kg VS/ m³ and increasing in each following test by 5.7 kg VS/ m³ the final OL of 34.3 kg VS/ m³ was achieved (s. Tab. 1). Tab. 1 presents the cellulose/inoculum VS ratio, which is an important start parameter. The VDI standard procedures recommend keeping the ratio under 0.5 to ensure the non inhibitory digestion (VDI, 2004). Thus the suggested VS ratio was deliberately exceeded in 4 of 6 experimental sets to produce the controlled inhibitory state.

3.1 Biogas production and quality

Stable biogas production of 605-667 lN/kg VS was observed in all conducted experimental series independent of the OL level. This corresponds to 81-89% of theoretical biogas production from the substrate, which confirms sufficient activity of the microbial biocenosis (VDI, 2004). Methane concentration in the produced biogas in all tests varied between 51-55%. The summarized data are presented in Tab. 1.

Tab. 1: Test parameters and summarized biogas results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td>organic load kg VS/m³</td>
<td>5.7</td>
<td>11.4</td>
</tr>
<tr>
<td>VS cellulose/VS inoculum</td>
<td></td>
<td>0.22</td>
</tr>
<tr>
<td>test duration time d</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>total biogas production lN/kg VS</td>
<td>605</td>
<td>656</td>
</tr>
<tr>
<td>methane in total biogas %</td>
<td></td>
<td>55</td>
</tr>
<tr>
<td>percent of max. possible gas production %</td>
<td>81%</td>
<td>87%</td>
</tr>
</tbody>
</table>

A considerable extension of total degradation time depending on the OL was observed (s. Fig. 1). In tests with 5.7-22.9 kg VS/m³ total degradation time of 9-16 days was obtained whereas in batches with 28.6-34.3 VS/m³ the decomposition time doubled in comparison to the lower OLs. Although the OL was increased sixfold, both the time needed in test to produce 50% (t₅₀) and 90% (t₉₀) of the total biogas have tripled between the lowest and the highest OL (s. Tab. 2) The different OLs can be divided into 3 groups concerning their degradation times: (1) 5.7-11.4 VS/m³, (2) 17.1-22.9 VS/m³ and (3) 28.6-34.3 VS/m³. t₅₀ and t₉₀ increased proportionally for the subsequent groups with the respective OLs, though t₉₀ rose slower than expected for group (2). This relation is good illustrated by the t₅₀/t₉₀ ratio change in Tab. 2.

The decrease in final CH₄ concentration with increasing OL, perceivable especially for the higher OLs, was observed (s. Fig. 2). The period of lower (but constantly increasing) CH₄ concentrations associated with hydrolysis and acetogenesis was observed in the first 7 days of digestion for all batches of the experimental study. In the tests with 5.7-22.9 VS/m³ at least 60% of biogas was already produced in this degradation phase. This
implies that the biogas production rate was mainly determined by the hydrolysis and acetogenesis for the lower OLs.

For higher OLs almost 65% of biogas was produced after the final stable CH$_4$ concentration of 52% (very low in comparison to the other batches) was accomplished. The observed delay in biogas production could be a consequence of slower acetic acid (AA) production or uptake. In this case acetogenesis or methanogenesis would be the rate-limiting process. Another explanation for the degradation time extension could be the decrease of hydrolysis rate due to the poor bioavailability of the cellulose (the surface access limits for higher cellulose amount). Both ways of interpretation could explain the high CO$_2$ concentrations in the end phase of degradation for higher OLs and both are not contradictory to the literature. There is a general agreement on considering hydrolysis as rate-limiting step (NOIKE et al., 1985; TOMEI et al., 2007, VAVILIN et al. 1996). Nevertheless VAVILIN et al. (2007) emphasizes that the rate-limiting step may alter for higher OLs depending on the bioavailability of the substrate. Also ATV (1994) refers of cellulose degradation at higher OLs being limited by acetogenesis.

![Fig. 1](image1.png)

**Fig. 1** Summary biogas production over the total degradation time for batches with different organic loads

![Fig. 2](image2.png)

**Fig. 2** Changes of CH$_4$ concentration in biogas

<table>
<thead>
<tr>
<th>organic load [kg VS/m$^3$]</th>
<th>degradation time [d]</th>
<th>ratio $t_{50}/t_{90}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.7</td>
<td>3.0</td>
<td>7.0</td>
</tr>
<tr>
<td>11.4</td>
<td>3.8</td>
<td>7.5</td>
</tr>
<tr>
<td>17.1</td>
<td>5.3</td>
<td>9.5</td>
</tr>
<tr>
<td>22.9</td>
<td>6.0</td>
<td>11.5</td>
</tr>
<tr>
<td>28.6</td>
<td>9.0</td>
<td>20.5</td>
</tr>
<tr>
<td>34.3</td>
<td>9.3</td>
<td>21.0</td>
</tr>
</tbody>
</table>

**Tab. 2** Degradation time ($t_{50}$ and $t_{90}$) for the different organic loads
In the first step of decomposition (days 2-3), the elevated values of 300-400 ppm H₂S occurred. Only for 34.3 VS/m³ a higher concentration of 1700 ppm was observed. In the subsequent decomposition step H₂S concentrations of 100-200 ppm were measured. Since the substrate (cellulose) consists of C, O and H solely, the only possible source of H₂S emissions was dissolved H₂S from the inoculum. Thus the higher concentrations of H₂S noticed in the first few degradation days resulted from the decrease of pH only, which caused the chemical equilibrium shift in the inoculum (s. DEUBLEIN & STEINHAUSER, 2008; FNR, 2006). Therefore an increase of H₂S in biogas of reactor fermenting carbohydrates and fats only (which do not contain S), suggests a decrease of pH in the fermenter. This correlation could be applied to detect the pH changes in the reactor with the help of biogas sampling only. The method though cannot be introduced for digestion of protein rich substrates.

3.2 VFA spectrum

Fig. 3 presents the maximal concentrations of acetic (AA), propionic (PA), iso-butryric (iso-BA), n-butyric (n-BA) and iso-valeric (iso-VA) acid measured for the different OLs. The concentration of n-valeric acid (n-VA) was negligible (max. 5 mg/l) and did not vary considerably during the time of experiment

![Graph](image)

The 5.7-VS/m³-test indicated typical acid pattern for not inhibitory decomposition. The AA and PA concentrations stayed increased for maximal 5 days¹ with the values of 1.7 and 0.3 g/l respectively as presented in Fig. 3. The other short chain fatty acids remained at the low concentration level with not more than 20 mg/l (s. Fig. 3). The increased concentration of AA was observed for days 1 to 6 for the tests with 5.7, 11.4, 22.9 and 34.3 VS/m³. For 17.1 and 28.6 kg VS/m³ longer uptake time of 10 days was neccesary¹.

The literature mentions that short chain fatty acids with more than 3 carbons in a chain (VFA-3) and particularly their branched forms e.g. iso-BA are inhibitory for the biomass degradation process already at the concentration of 50 mg/l (Hill & Holmberg, 1988; Fisher et al. 1983; Chen & Day, 1986). Such low concentrations were only observed for 5.7 kg VS/m³. However also with the higher concentrations of VFA-3 (for 11.4-34.3 kg VS/m³) no permanent acidosis was observed. The VFA-3 concentration in tests with 28.6-34.3 kg VS/m³ was surprisingly lower and the uptake time shorter in comparison to 17.1-22.9 kg VS/m³. These results are contradictory to the literature mentioned and sup-

¹ Results not shown in the article
port the conclusion of Ahring et al. (1995) that different anaerobic systems are incomparable and find their own acid balance. Furthermore the results show that a methanogenic biocenosis is capable of achieving an enormous adapting level if fed with the unchanged substrate.

### 3.3 Variations of pH, redox potential, VFA and VA

The on-line registered changes of pH and redox potential were supported with daily measured VA as well as VFA. The signal changes for all controlled parameters synchronized with each other (s. Fig. 4). The most rapid changes in the response were revealed directly in the first two days of degradation. The vast biogas production was accompanied by elevated or diminished values of VA, VFA, redox and pH respectively. In Fig. 4 this step can be observed between day 1 and 6. Redox potential measured for all tests independent of the OL oscillated between -330 and -400 mV.

The synchronized changes of pH, redox, VFA and VA are contradictory to the conclusions of RIEGER & WEILAND (2006), who claim that on-line measured redox potential reacts quicker to the system changes and disorder than the pH or VA. No such correlation was observed. The on-line pH electrode reacted to the system changes at the same rate as the redox electrode. Also daily measured VFA and VA confirm these trends. As also noticed by RIEGER & WEILAND (2006), particularly for VFA and VA the sampling frequency is an important aspect since the parameters cannot be measured on-line.

![Fig. 4](image-url) The response changes for redox potential (on line), pH (on line) and VA (daily sampled) measured for 5.7 VS/m³ of cellulose. Changes of redox between day 0 and 1 are regarded as the effect of oxygen still present in the system.

![Fig. 5](image-url) Volatile acids (VA), acetic acid (AA) and the gas production rate (GPR) observed for 34.3 kg VS/m³.

Effects of initial oxygen on the redox electrode signal and the process itself were observed in the fermenters during the studies. Batches with cellulose were opened only once for feeding at the test start. About 3 hours after electrode was submerged and reactor closed the redox values obtained a level typical for anaerobic digestion. Oxygen though was still influencing the system even 24 hours after feeding (s. Fig. 4). Difficulties with redox electrode sensitivity to oxygen were already mentioned by PLOOG et al. (1996) and UTEC (2003). It is important that the electrode has no contact with oxygen, which dramatically increases the values measured. This could be particularly difficult for a continuously fed stirred digester, in which every feed introduces oxygen to the system.

Although extreme OLs were applied no inhibitory state in terms of rapid or extreme parameters change were detected. Even at highest OLs the revealed changes of redox potential were in the range mentioned in the literature as typical for the methane production (DEUB-
3.4 Inhibition

Neither the highest acid peaks nor other parameter changes indicating an inhibited degradation (e.g. noticed as pH or redox pattern changes) were revealed in the trial with the highest OL (34.3 kg VS/m\(^3\)). Both the maximal concentrations and the complete time evolution of VFA-3 were similar to the batch with 11.4 kg VS/m\(^3\), which is assumed as a not inhibitory degradation. Nevertheless the high gas production rate (GPR) of 0.8 -1.6 l\(_N\)/d, remaining for 10 days, as well as the atypical zig-zag-pattern of the VA in the second degradation phase (after day 5) and the discrepancy between VA and AA were observed (s. Fig. 5).

4 Conclusions

pH, redox, VA and VFA changed simultaneously during fermentation. Therefore any of these parameters, if measured frequently enough, can be applied to control fermentation state. Although high inhibitory VS Cellulose/VS inoculum ratios were applied, the only explicit sign of system stress was the increasing total degradation time and the extended period of higher biogas production rate with every increase of OL. This confirms the biogas production rate as the first and most important control parameter for the fermentation supervision. In the investigated batches the elevated VFA (also VFA-3) did not automatically lead to fermentation break and had influence neither on the total gas production nor on the total methane production even though the inhibition limit of 50 mg/l for VFA-3 was exceeded. These results show that it is not possible to define the VFA-3 concentration, which would directly cause the inhibition in any digesting system. With adapted cultures a non-inhibitory degradation of cellulose at extremely high OLs and with higher VFA-3 concentrations is possible.

A further study to compare the model substrate (cellulose) with a natural one - maize (containing native cellulose) in batch as well as quasi continuous mode is being conducted and will be complemented by the corresponding mesophilic trials.

References


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In-situ methane enhancement system using differential solubility of biogas

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A simple in-situ technique to enhance digester offgas was developed by using the differential solubilities of biogas which normally contains 40–50% carbon dioxide (CO₂) and 50–60% methane (CH₄) by volume.

The methane enhancement system was low solids plug-flow sorghum digester coupled by a leachate recycle loop to an external stripper. The stripper removed dissolved CO₂, resulting in an enhanced CH₄ contents in digester offgas as shown in Fig. 1. Plug-flow type reactor with internal recycle of leachate was operated under parallel condition as the control reactor to provide baseline digestion kinetics. All experiments were conducted at 35 using nitrogen as a sweep gas.

Fig. 1: A Schematic Diagram of Methane Enhancement System
As shown in Table 1, quantitative evaluation of system variables defined the effects of leachate recycle rate (LRR) and reactor alkalinity on the resulting offgas CH₄ contents. Offgas CH₄ contents and CH₄ productivity correlated well with LRR as illustrated in Fig. 2, Fig. 3 and Fig. 4. However excessively high recycle rates led to digester pH levels above 8.7, resulting in inhibition of methanogenesis and lowered CH₄ production. Fig. 5 explains that the total volatile solids (TVS) removal efficiency was decreased as LRR increased.

**Tab. 1: A summary of experimental conditions**

<table>
<thead>
<tr>
<th>Reactor</th>
<th>OLR (gVS/L-d)</th>
<th>SRT (days)</th>
<th>T.Alk (g/L as CaCO₃)</th>
<th>Leachate Recycle Rate(v/v-d)</th>
<th>Sweep Gas</th>
<th>Stripper Gas Flow Rate(ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Reactor</td>
<td>2.0</td>
<td>52</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Methane Enrichment Reactor</td>
<td>2.0</td>
<td>52</td>
<td>2.0</td>
<td>1.0</td>
<td>N₂</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.0</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.0</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
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<td></td>
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<td>3.0</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 2:** Effect of reactor alkalinity on biogas methane contents of mesophilic methane enhancement system at LRR 3v/v-d with N₂ sweep gas
Fig. 3: Effect of reactor alkalinity on biogas methane contents of mesophilic methane enhancement system at different leachate recycle rates with N₂ sweep gas

Fig. 4: Effect of leachate recycle rate on methane productivity of mesophilic methane enhancement system at different alkalinity with N₂ sweep gas
It is likely that the optimum recycle rate was 3 volume of leachate recycle per volume of reactor per day (3 v/v-d) at the reactor alkalinity of 4 g/l as CaCO₃, which resulted in offgas CH₄ contents of over 94% and TVS removal efficiency of 82%.

Due to leachate flow limitation, CH₄ production rates of the methane enhancement system were limited to the range of 0.7~0.8 v/v-d under all paralleled conditions. However this CH₄ production rates showed 97%~128% of the control reactor. For practical purposes, the application for Semi-Continuously Fed and Mixed Reactor (SCFMR) or Plug-flow digesters is limited to relatively low solid systems, with solids that are easily separated from the leachate stream. Hence, the leachate moves through the solid mass at a relatively slow rate and the solids must separate in the methane enhancement system. The maximum digester solids concentration is approximately 7 to 9% dry matter for the methane enhancement system.

References


Entwicklung eines neuen Biogasverfahrens zur effizienten Verwertung von NawaRo auf thermophiler Basis

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Zusammenfassung


Schlüsselwörter:
Zweistufig, einphasig, zweiphasig, anaerobe Vergärung

Summary

The evaluation and optimization of a biphasic concept for biogas production from renewable resources (RR) on a microbiological and process engineering level was the aim of this investigation. This concept should improve the degradation of a given silage mixture within a shorter time than a conventional monophasic system and concomitantly increase methane production. For this aim, methane productivity and process stability of a lab-scale two phase fermenter run at thermophilic condition in the first stage was compared with the performance of a monophasic system run at different temperatures.

According to the results of this lab-scale study, the one phase anaerobic digestion system provided an increased degradation and better process stability for the given substrate mix when compared to the two-phase system. We conclude that research aiming for process optimization of the hydrolysis stage in RR digestion is still needed.

Keywords:
two stage, hydrolysis, one phase, two phase, anaerobic degradation
1 Einleitung

Die Vergärung Lignocellulose-reicher Biomasse (LCB) ist ein zentrales Thema für Biogasanlagen, die am Rande der Wirtschaftlichkeitsgrenze arbeiten. Hier besteht ein hoher Optimierungsbedarf. Um die Effizienz zu erhöhen, spielt die Hydrolyse von Cellulose-Lignin Komplexen eine Schlüsselrolle, da diese Gerüstsubstanzen nur langsam und unvollständig abgebaut werden (Lynd et al., 2002). Eine Intensivierung dieses Teils des Biogasprozesses könnte die Methanisierung von LCB wesentlich verbessern.


2 Material und Methoden

Die Untersuchungen wurden in 2-stufigen Durchflussfermentern mit einer Beschickung von 31% Mais, 31% Gras und einer Mischung aus 38% Roggen und Gerste durchgeführt (Abb. 1: für zweiphasiges Konzept 35 L Hydrolysereaktor (IF); 70 L Methanreaktor (stF). Für einphasiges Konzept 35L Hauptfermenter (IF); 70L Nachgärer (stF). Stündliche Analysen des produzierten Biogases und eine regelmäßige Bestimmung der flüchtigen Fett säuren (FOS), des FOS/TAC- und des pH-Werts ergänzten das Prozessmonitoring der IF und stF.

Abb. 1: 2-stufige Fermentersysteme am Institut für Landtechnik der LfL

2.1 Zweiphasiges Konzept

2.2 Einphasiges Konzept

Untersuchungen für einen einphasigen Betrieb wurden in den gleichen 2-stufigen Durchflussfermentern durchgeführt. Der Hauptgärer (IF) wurde bei 45, 50, 55 sowie 60°C betrieben, der Nachgärer (2. Stufe, stF) bei 38°C. Parallele Versuche bei denselben Temperaturen wurden durchgeführt, um die Wiederholbarkeit des Prozesses nachzuweisen. Die Raumbelastung wurde jeden zehnten Tag um 1,5 bis auf 12 kg oTS * (m³ * d)⁻¹ erhöht. Durch Rezirkulation eines Teils des Nachgärerinhalts in den Hauptreaktor wurden kürzere Verweilzeiten im Hauptgärer (10 Tage) eingestellt.

3 Ergebnisse

Abb. 2 zeigt die Ergebnisse der Versuche mit separierter Hydrolyse. Aufgrund von Instabilitäten in der Hydrolysestufe kam es immer wieder zu kurzen Einbrüchen der Methanproduktion. Diese Instabilitäten sind auf eine schwierige Prozesssteuerung zurückzuführen.


Abb. 3: Zusammensetzung des produzierten Biogases im liegenden Fermenter (lF) und stehenden Fermenter (stF) bei unterschiedlichen Temperaturen im liegenden Fermenter

Abb. 4: Methanausbeute des 2-stufigen Gesamtsystems bei unterschiedlichen Temperaturen im Hauptgärer (IF)

Weiterhin war bei hohen Raumbelastungen trotz kürzerer Verweilzeit im Hauptgärer ein hoher Substrataufschlussgrad festzustellen.

Bei der Betrachtung der Methanausbeuten (Mittelwert der Ergebnisse der Versuchs wiederholungen) für die vier Temperaturen zeigte sich für alle Temperaturen im Verlauf des Versuches eine gute Substrat-Verwertungseffizienz. Selbst bei einer höheren Raumbelastung von 10,5 kg oTS * (m³ * d)⁻¹ im IF war noch eine Methanausbeute von 307,3 Lₙ CH₄ * (kg oTS)⁻¹ bei 60°C zu erzielen. Dabei wurden die höchsten Ausbeuten durchwegs bei 45°C und 60°C erzielt (Abb. 4). Auffällig ist, dass die Versuche bei 50°C und 55°C besser
reproduzierbar waren als jene bei 45°C und 60°C (höhere Standarabweichungen in \textit{Abb. 4}).

4 Schlussfolgerung

Bei einer Raumbelastung von 10 kg oTS \( \cdot (m^3 \cdot d)^{-1} \) in der Hydrolyse wurde eine Methanasubeute von 188 L\( _{CH_4} \cdot (kg \text{ oTS})^{-1} \) für die ganze Anlage erzielt, während bei 1-phasigem Betrieb ein Wert von 307,3 L\( _{CH_4} \cdot (kg \text{ oTS})^{-1} \) bei 60°C erreicht wurde. Die Stabilität des einphasigen Prozesses war deutlich besser als bei Trennung der Phasen. Der Methangehalt in der Methanstufe war bei 2-phasigem Betrieb mit 70-72 [Vol.- %] vergleichsweise hoch, während bei einem einphasigen Betrieb 52-60 [Vol.- %] erzielt wurde.


Literaturverzeichnis


Ermittlung der maximalen Raumbelastung einer Maismono-Vergärung im ein- bzw. zweistufigen System bei 40°C und bei 50°C im Technikummaßstab

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Zusammenfassung

Im Rahmen des von der FNR geförderten Verbund-Projektes mit TUM-SWW, TUM-BÖ, LfL-ILT, TUM-MB (FKZ22011605) werden die optimalen Betriebsparameter für die anaerobe Vergärung von Maissilage als einzigem Substrat vorgestellt.

Es zeigt sich bei reproduzierten Technikumsversuchen im 150 und 400l-Maßstab, dass unter thermophilen Bedingungen bis zu 12% mehr Gasertrag mit vergleichbaren Methangehalten erzielt werden kann.

Die Raumbelastung kann jedoch unter thermophilen Bedingungen nicht über 4 kg oTS/m³*d unter Erhalt stabiler Gasproduktionsraten gesteigert werden, wohingegen der mesophile Betrieb eine Steigerung auf bis zu 5,5 kg oTS/m³*d zulässt.

Des Weiteren kann gezeigt werden, dass sowohl eine schnelle Umstellung von 40°C auf 50°C in einem Schritt, als auch eine Umstellung mit 1°C pro Woche von den Systemen verkraftet wird. Es zeigt sich allerdings in den Laborversuchen, dass bei langsamer Temperaturadaption eine höhere Effizienz erzielt werden kann.

Summary

Within the following project, which is funded by the FNR (FKZ22011605), the optimal running parameters for anaerobic digestion of corn-silage as sole substrate are presented.

In reproduceable lab-scale fermentations (150l and 400l volume) it is demonstrated that running a process at 50°C results in an increase of gasproduction up to 12% at comparable gasquality.

The spatial loading-rate in a thermophil process can not be raised above 4 kg oDM/m³*d at stable gasproduction rates, whereas at a mesophilic operation temperature it can be heightend up to 5,5 kg oDM/m³*d. Additionally it can be shown that a running biogas process at 40°C can be shifted to 50°C in two ways: it can be carried out quickly in one step and slowly with a rate of 1°C per week.

Both methods result in an ongoing biogasproduction, whereas the slow transposition from 40°C to 50°C results in higher efficiency.
1 Einleitung/Introduction


2 Ergebnisse der Maismono-Vergärung im einstufigen und zweistufigen System bei 40°C und 50°C

Die Ergebnisse der redundanten Maismonovergärungsversuche im Technikum weisen eine nur sehr geringe Abweichung auf (im Mesophilen <3%, im Thermophilen <5%). Interessant ist, dass der erzielte spezifische Gasertrag im untersuchten Bereich (1 bis 8 kg\textsubscript{GTS}/m\textsuperscript{3}*d) unabhängig von der Raumbelastung ist. Eine Abnahme des Abbaugrades und damit ein Sinken der Gasausbeute kann entgegen der gängigen Expertenmeinung nicht beobachtet werden. Dieses Ergebnis ist aufgrund der hohen Reproduzierbarkeit und der sehr geringen Abweichung der Einzelergebnisse untereinander qualitativ belastbar.

Die dargestellten Tabellen und die Abbildungen geben die in den Langzeitversuchen erzielten Gaserträge und Methangehalte bei Maismonofermentation wieder.

3 Abbaugrade unterschiedlicher Vergärungen

Die Abbaugrade der in 2. angesprochenen Maismonovergärungen sind dargestellt. Dabei zeigt sich, dass die mesophilen, zweistufigen Fermentationen im Unterschied zu den einstufigen Systemen eine um bis zu 10% höhere Effizienz aufweisen. Bei den thermophilen Systemen kann beim Vergleich von zweistufigen mit einstufigen Systemen eine um bis zu 12%ige Effizienzsteigerung nachgewiesen werden.

4 Energieausbeuten beim unterschiedlichen Umstellen der Betriebsparameter von mesophil auf thermophil

Es kann gezeigt werden, dass sowohl schnelles Umstellen von 40°C auf 50°C innerhalb eines Tages als auch langsames Umstellen mit 1°C pro Woche von den Systemen verkraftet wird, wobei ein langsames Umstellen in einer bis zu 12% höheren Energieeffizienz resultiert.

5 Danksagung

Der Fachagentur für Nachwachsende Rohstoffe danken wir für die finanzielle Förderung des Projektes (FKZ22011605).
Anaerobic digestion of rye silage in a two-phase process

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Summary

In the course of the joint research project “Biogas-Crops-Network” (BCN) we were able to come to new conclusions regarding the gastight or non-gastight operation mode of the first reactor system (hydrolysis) of a two-phase solid state fermentation of whole rye plant silage using a bio leaching method. The results with respect to the operation mode show that the non-gastight system only achieves 36% of the methane yield of the gastight system. Because of passive aeration the open hydrolysis reactor system was found to support the growth of fungi on the silage which results in an aerobic digestion process. The non-gastight operation mode of the hydrolysis reactor within the thermophile temperature range is not recommended.

Keywords:

biogas, solid state anaerobic digestion, leach bed, two-phase

Zusammenfassung


Schlüsselwörter:

Biogas, Feststoffvergärung, Bioleaching, zweiphasig
1 Introduction

Current agricultural facilities for biogas production usually base on a continuous mode of operation and a complete mixing of the reactor content. The increasing use of stackable, organic solid matter raises the energy input necessary for mixing and also the danger of a biological process-overload. As a consequence, float- and sink layers can be formed in the reactor in which intermediates accumulate and can inhibit the digestion processes.

For these reasons there is an increasing interest in the methods specifically developed for the digestion of solid matter, originally coming from the domain of biological waste treatment (THOME-KOZMIENSKY 1995). The discontinuous digestion of solid matter belongs to those methods. The advantage of it is the simple construction of the reactor system and the resulting low energy consumption (WEILAND 2006). The mass transfer inside the fermenter bases exclusively on the recirculation of the process liquid. The disadvantage of this method is the refeeding of up to 70 percent of digestate (KUSCH at al. 2005) as inoculum. This leads to the fact that the fermenter has to be much larger in its dimensions but doesn’t contribute to a significantly higher production of biogas.

An alternative to the single-phase of solid matter is the two-phase process. Due to the integration of a separate methane reactor into the circulation of the process liquid the solid matter reactor primarily used for hydrolysis and acidification. Together with immobilized micro biocoenosis the formed intermediates are transformed to biogas inside the methane reactor. This method of the process doesn’t require inoculation with digestate. Currently, only limited knowledge on the operability and efficiency of this procedure is available. Therefore further research and development is necessary (LINKE 2004).

The ATB was founded by the German Federal Ministry of Education and Research (BMBF) to examine a subproject of the Biogas-Crops-Network (BCN) within the joint research project “Basics research of biogas production from crops biomass: System analysis of microbiological substance conversion under special consideration of the influence of the type of crops provision, formation of intermediates and process control”. Ten research facilities from all over Germany participated in this research project. The aim was to analyze the use of rye silage of whole plants in a bioleaching process combined with a downstream methane reactor. Especially the kinetics analysis of the hydrolysis/acidification of rye silage and the optimization of the mode of operation were evaluated and its operability and efficiency were shown.

2 Laboratory scale plant of the two-stage process control with bioleaching

The in the scope of this study used laboratory scale plant consists of three reactor systems which are identical in construction. Each one contains a hydrolysis reactor and a fixed film methane reactor as a separate methane stage.

By technology developed at the BTU Cottbus (professorship of waste management) the process water (60 l/h) is leak back into the hydrolysis reactor (Fig. 1, 4). This serves tempering and maintenance of the optimal moisture content of the organic solid matter. Furthermore, the microorganisms which are involved in the degradation were feed back. A continuous volume flow (1 l/h) gets from the reservoir of the process liquid into the fixed film methane reactor (material: acryl glass, packing bulk Bioflow 40, 30 liters usable volume) (Fig. 1, 3). The liquid which is released by organic compounds to a large extend is
put back into the hydrolysis reactor (1 l/h) (Fig. 1, 5). The laboratory scale plant is individually controllable with regard to hydrolysis underflow rate and percolation rate.

The generated biogas is collected in separate gas tanks (100 liter bag, company TECOBAG (Fig. 1, 6). Once a day an automatic gas analysis and entry of quantities is executed (Fig. 1, 7). Therefore an activation of a magnet valve is done by a control unit. The gas is extracted from the gas analysis device (SSM 6000, company Pronova) and pumped through the gas meter (Trommelgaszähler, company Ritter) for gas composition analysis. Depending on the amount of gas the gas meter sends impulses to the control unit. At the same time the pressure sensor examines the difference between system pressure and ambient pressure. With an empty gas tank the pressure difference drops resulting in a voltage drop. The pump is turned off and the magnet valve is closing. The incoming data are converted with a computer and logged.

3 Characterization of the used rye silage

The rye silage was provided by the Lehr- und Versuchsanstalt für Tierzucht und Tierhaltung Groß Kreutz (Germany). The chaff length of the rye silage was two centimeter (cm). The rye straw was coming from the “Leibniz-Institut für Agrartechnik Potsdam-
The analytic parameters of rye silage and rye straw are listed in Table 1.

**Tab. 1: Analytic parameters of the substrate rye silage and rye straw**

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>pH</th>
<th>DM %</th>
<th>oDM %</th>
<th>TKN %</th>
<th>XL %</th>
<th>XF %</th>
<th>COD g/kg FM⁻¹</th>
<th>C/N ratio</th>
<th>C/S ratio</th>
<th>lactic acid g/kg FM⁻¹</th>
<th>VFA g/kg FM⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>RYE SILAGE</td>
<td>4.19</td>
<td>24.47</td>
<td>22.21</td>
<td>3.95</td>
<td>3.62</td>
<td>38.15</td>
<td>258.20</td>
<td>29.89</td>
<td>244.56</td>
<td>2.6</td>
<td>2.89</td>
</tr>
<tr>
<td>RYE STRAW</td>
<td>7.51</td>
<td>89.31</td>
<td>85.48</td>
<td>8.42</td>
<td>0.54</td>
<td>46.31</td>
<td>926.50</td>
<td>59.67</td>
<td>231.55</td>
<td>0.0</td>
<td>0.55</td>
</tr>
</tbody>
</table>

The substance specific decomposition according to van Soest (LENGERKEN 1991) in Figure 2 shows that the fraction of inorganic substance is 9.1 Ma.-% (mass percent) in the rye silage and 4.3 Ma.-% in the rye straw. The fraction of persistent materials (cellulose and lignin) is about one third in the rye silage (38.1 Ma.-%) and more than the half in the rye straw (57.8 Ma.-%) of the whole organic substance. The fraction of readily biodegradable materials (hemicellulose and cell compounds) is 51.6 Ma.-% in the rye silage and 37.9 Ma.-% in the rye straw. The volatile organic acids (fatty acids C2-C6, alcohols C2 and C3) are in both substrates only marginally present with 1.2 Ma.-% in the rye silage and 0.1 Ma.-% in the rye straw.

**Fig. 2: Composition of element groups of the used rye silage and rye straw**
4 Analyses on non-gastight, gastight and mixed hydrolysis phases

The non-gastight, gastight or mixed operation mode of the first reaction system (hydrolysis) was examined in tests lasting each for 21 days. Moreover, the gas formation in both parts of the facility was examined. For the hydrolysis reactor the thermophile temperature range (55°C) was chosen. The fixed film methane reactors were run under the mesophile temperature range (37°C). The three hydrolysis reactors were loaded in parallel each with 10 kg of rye silage fresh mass and with 0.5 kg of rye straw as structure material. Regarding the gastight system the hydrolysis phase was closed airtight. Regarding the non-gastight system, the lid of the hydrolysis reactor was closed but not locked. The gas bag was separated from the system. Thus, the ambient air was able to enter the system through openings, each with a diameter of 10 mm. The mixing of the third hydrolysis system was done once a week. The percolation of all three variations was done by an alternating sprinkling of the particulate material with process liquid out of the hydrolyzate reservoir at a rate of 60 l/h. After one minute of percolation a break of 29 minutes followed. This process was repeated in cycles.

Tab. 2: Biogas and methane yield of the examination of the operation modes: Comparison of non-gastight, gastight and mixed hydrolysis phase at thermophile temperature conditions

<table>
<thead>
<tr>
<th>reactor</th>
<th>Ω degradation COD [Ma.-%]</th>
<th>Ω degradation oDM [Ma.-%]</th>
<th>Ω biogas yield [NL/kg oDM]</th>
<th>Ω methane yield [NL/kg oDM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HR 1</td>
<td>69 ± 3</td>
<td>68 ± 6</td>
<td>495 ± 43</td>
<td>266 ± 22</td>
</tr>
<tr>
<td>HR 2</td>
<td>65 ± 3</td>
<td>65 ± 6</td>
<td>455 ± 10</td>
<td>247 ± 4</td>
</tr>
<tr>
<td>HR 3</td>
<td>73 ± 1</td>
<td>73 ± 2</td>
<td>108 ± 9</td>
<td>95 ± 8</td>
</tr>
</tbody>
</table>

The digestates of the gastight and mixed hydrolysis system showed a similar content of organic dry substance with approx 10.5 Ma.-%. The average degradation of organic dry substance of the rye silage was for all three approaches between 65 Ma.-% and 73 Ma.-%. The hydrolysis reactor system showed the highest degree of digestion (Table 2).

Figure 3 shows the organic components of the substrates and the digestate. The three different approaches showed the following results: 70 Ma.-% of the cell ingredients were digested during the gastight operation mode, 72 Ma.-% were digested during the mixed operation mode and 78 Ma.-% were digested during the use of the non-gastight operation mode. The hemicelluloses were nearly completely digested: more than 96 Ma.-% of the plant components were dissolved. Also there were minor differences regarding the digestion of the cellulose. The gastight operation mode dissolved 68 Ma.-% whereas the mixed operation mode reached 71 Ma.-%. However, the non-gastight operation mode was able to dissolve 78 Ma.-% of the cellulose ingredients. However, lignin was hardly dissolved.
The results of the analysis regarding the different operation modes of the hydrolysis systems and their impacts on the methane yield are shown in Figure 4. The results of the solid matter degradation cannot be reconfirmed with the results of the gas formation (Table 2). The mixed system version yielded $266\text{NI}_{\text{CH}_4}/\text{kgOS}$ – the highest yield. However, here we also found the greatest deviations. The gastight variant was a little less with $247\text{NI}_{\text{CH}_4}/\text{kgOS}$. The non-gastight system variation yielded only $95\text{NI}_{\text{CH}_4}/\text{kgOS}$. That equals 36% of the methane yield of the mixed system. Moreover the gas composition of the gas compartment of the non-gastight hydrolysis reactor was measured. In spite of the non-
gastight operation mode, methane was formed at the beginning of the analysis. Moreover, the oxygen content augmented during the course of the test and reached 15 Vol % towards the end. This supported mold formation on the lid and on the side walls of the reactor system. Also there was mold on the whole silage. We may assume that the non-gastight operation mode system fostered an aerobic digestion process. Furthermore the metabolites of the mold maybe had a toxic impact on the digestion process which caused the stop of the methane production in this reactor.

5 Conclusions

The results of the operation mode of the hydrolysis phase lead to the conclusion that the use of a non-gastight system in the thermophile temperature range cannot be recommended. The costs of a gastight hydrolysis phase are indeed remarkably higher; however this system forms 64% more methane than the non-gastight operation mode. In the non-gastight system of the hydrolysis phase, percolation caused swirls in the reactor, so that the volatile organic compounds were able to escape and up to 15 Vol.-% oxygen was able to enter the system. In consequence, the organic material oxidizes to CO₂, and was not still available for the formation of methane. Moreover formed mold at the walls of the reactor and on the silage might have a toxic impact on the methane forming process and it could pose a risk to health of the staff, respectively.

In general, the hydrolysis process by the gastight two-phase operation mode formed mainly carbon dioxide and hydrogen. However during the methanogenesis in the fixed film methane reactor, a methane concentration of about 80 Vol.-% was achieved. This high methane concentration is of advantage for feed-in into the gas pipe network. That is because of costs of processing biogas which are lower in comparison to the one-phase treatment. Additionally there is a need for further research regarding the use of the high hydrogen concentration in the hydrolysis gas.

Literature


Digestion of grass silage by a two-phase biogas process

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Zusammenfassung


Summary

In the frame of the cooperative project „Biogas-Crops-Network“ ten German institutes are studying the fundamentals of biogas production from energy crops. The University of Hohenheim is dealing with the digestion of grass silage in a two stage biogas process based on the bioleaching principle.

To serve better the different needs of the several bacteria which take part at the four steps process of the methane production the process is divided into two stages. A batch bioleaching stage where the percolate is produced and a fixed bed digester where the organic fraction of the percolate is digested.

Considering the results of the experiments conducted up to now, the two phase digestion of grass silage showed stable digestion behaviour. Neither in the hydrolysis nor in the fixed bed digesters could a biological disturbance of the process, e.g. due to an increased loading rate or a sudden change of substrate, be detected. In the first trials a degree of degradation of 75 to 85 % of the VS was reached. The biogas generated in the fixed bed digesters had an average methane content of 70 %. The fixed bed digesters yielded in the average of all experiments 63 % of the total methane production of the two phases. Digested grass silage of an intensively used grassland average biogas yields of 665 lN / kg VS and average methane yields of 335 lN / kg VS were reached with a retention time of 25 to 30 days. With the highest tested hydrolysis temperature of 55 °C, the largest biogas yield and the highest degree of degradation was achieved. Also a different suitability for two-phase fermentation with a batch percolation hydrolysis is observed for various substrates. Because the different substrates have the different influences on the course of the pH-value, the acid formation and concentration there is also an effect on the distribution of the biogas and methane yield to the two process phases.
1 Introduction

A reduction in pasture utilization has been observed in the German state of Baden-Württemberg. This has been attributed to the increasing efficiency in milk production. Given the fact that 26% of existing grassland is not in use for feed production by 2015 (RÖSCH 2007), the possibility of using grass for renewable energy production is of great interest. Until now, the high fibre content of grass technically borders its use in biogas plants for energy production.

The cooperative project "Biogas Crops Network" offers ten German institutes the framework for a study on the basics of biogas production from energy crops. The University of Hohenheim investigated the digestion of grass silage in a two-phase biogas process on the principle of a batch percolation hydrolysis digester.

2 Literature review

The degradation of an organic substrate to methane is a four-step process, and each of these steps is performed by several different bacteria. These bacteria have very special demands on their living conditions, and they each require different pH and temperature values for their optimal performance (WELLINGER et al. 1991). In a single-phase biogas process the four steps take place in the same fermenter at the same pH and temperature value, which are tailored to the needs of the methanogenic bacteria. These are the most sensitive organisms in the chain, while the hydrolysis bacteria are more flexible in terms of living conditions and adapt more easily to the living conditions of the methanogenic bacteria.

The pH range for hydrolysis is between 4.5 and 8.5. The metabolic optimum is at a pH of about 6.5. The methanogenic bacteria, however, achieve their optimum stability and activity in the mesophilic range at about 38 °C at pH value of 6.5 to 8 (WELLINGER et al. 1991). Therefore, the conditions under which the hydrolysis takes place in a single stage process are suboptimal.

3 Objectives

This suboptimal environment of the bacterial hydrolysis limits its performance. This results in an improvable conversion rate for the digestion of grass. The purpose of this project is to investigate whether the optimization of environmental conditions for the hydrolysis could improve the efficiency of bacterial fermentation of organic material. Considering the above mentioned facts, the use of a two-phase process could optimize the growth requirements of the various microorganisms. Therefore the State Institute of Agricultural Engineering and Bio energy develops a process which divides the biogas production in a hydrolysis phase and methanogenesis phase.

4 Material and methods

The experiments were conducted in the biogas laboratory of the State Institute of agricultural engineering and bio energy of the University of Hohenheim (Fig. 1). The lab facilities consist of five pairs of vertical solid phase digesters with a useable volume of 50 l per digester.
The substrate has been analysed in terms to its
- dry matter and organic dry matter (VS) content,
- organic and mineral nitrogen,
- chemical composition,
- biogas and methane yield potentials.

The following parameters have been analysed in the digesters:
- pH,
- electrical conductivity (salinity),
- COD,
- volatile fatty acids,
- Dry matter and VS and
- temperature.

The biogas yield was measured and the gas was analysed in terms to its content in CH₄, CO₂, H₂, H₂S and O₂.
The hydrolysis and acidogenesis phases of the biomass digestion take place in the so-called hydrolysis digester (the first stage digester), wherein the biomass is digested to organic acids which accumulate in the fluid fraction (the percolate). The percolate is then pumped into the fixed bed methane digester where its organic fraction (organic acids) are mineralised (digested).

For each trial the hydrolysis digesters are filled with 1 kg VS of grass silage (first cut of intensively used grassland) and 10 kg of tap water. The fixed bed digesters are filled with poly-ethylene filling bodies as a settling bed for microorganisms and 45 l of percolate. The pH of the percolate in the fixed bed digesters is around 7.5.

After filling the hydrolysis digester with grass silage a starting phase which lasts several days begins. During this starting phase the percolate is recirculated, but not exchanged between the stages. In the percolate of the hydrolysis digesters the organic matter is concentrated. In this phase the pH remains stable at a value of around 5. After this starting phase 3.25 kg of percolate (rich in organic acids, pH 5) are exchanged between the hydrolysis and methanogenesis stage daily. This exchange causes rapid digestion of the organic matter dissolved in the percolate. The percolate out of the methanogenesis stage is poor in organic acids and organic dry matter and has a pH of about 7.5. The exchange of the percolate with different pH values causes an increase in the hydrolysis pH. If the pH reaches 6.5 the methane production starts. After around 25 days retention time the gas production decreases markedly and the experiment is concluded.

5 Preliminary results

Taking into consideration the results of the experiments conducted so far, the two phase digestion of grass silage showed stable digestion behaviour. Neither in the hydrolysis nor in the fixed bed digesters could a biological disturbance of the process be detected. A degree of degradation of 75 % to 85 % was achieved in the first trials. Around 60 % of the biogas was produced during the hydrolysis and 40 % of the biogas in the fixed bed digesters. The biogas generated in the fixed bed digesters had an average methane content of 69 %. The fixed bed digesters yielded 63 % of the total methane production of the two stages.

The variation of the hydrolysis temperature showed that the thermophilic (55°C) variant has the fastest and highest biogas yield and the highest degree of degradation compared to a mesophilic (38°C) and psychrophilic (25°C) variant.

Comparison of the suitability of different substrates for the two-phase fermentation using batch hydrolysis

The substrates used - maize silage, rye silage and grass silage - showed an individual behaviour during the fermentation. In Figure 1 the pH of the percolate over the period of experiments are shown measured at the drains of the hydrolysis digesters and methane reactors. At the start all substrates had pH values between 4.5 and 5. Until the percolate was exchanged for the first time between the phases the pH values remained relatively stable. After the first exchange of process fluid between the phases on day four of the experiment a sudden increase in pH was observed caused by the mixing of liquids with different pH values. While the pH values of maize silage quickly fell below 5 again, the values of grass and rye silage only reach a pH of 5.6. Then the pH value of grass silage in the hydrolysis fermenters increases much faster than the ones of the other substrates, so that the pH value of 7.5 is reached four test days earlier (Figure 1).
The pH curve of maize silage shows an interim increase in pH between the sixth and tenth day of the experiment. This is in connection with the formation of acetic acid from maize silage. This reaches its maximum only on test day ten, while the maximum of other variants was observed on test day seven (Figure 2). Although all of the tested substrates reached a maximum of acetic acid equivalent of nine g/kg in the hydrolysis fermenters, the values of grass silage raise significantly faster than the value of maize and rye silage.

![pH vs. acetic acid of maize silage](image)

The slower increase in pH of maize and rye silage in the hydrolysis fermenters prevents the formation of methane in the fermenters, forming a higher proportion of methane in the methane reactors (Figure 2).

The maize silage provides the highest biogas and methane yields with 779 and 362 lN/kg VS followed by rye silage with 665 and 347 lN/kg VS and grass silage with 334 to 645 lN/kg VS (Table 1). While the average methane content of biogas from the hydrolysis fermenters varies greatly depending on the used substrates, the average methane content of the biogas from the methane reactors is in all variants relatively stable at 72 or 76%.
The high methane yield of maize silage in the methane reactors seems to not affect the quality of the gas.

The experiments showed stable substrate fermentation, despite the sudden substrate change, which followed a long-term mono fermentation of grass silage. The longer acid formation from maize and rye silage compared to grass silage let the pH value be in a more favourable area for the hydrolysis. Thus, the methane production can be prevented in the hydrolysis digesters, so that a better separation of the phases is achieved. So a different suitability for two-stage fermentation with a batch percolation hydrolysis is observed for the investigated substrates.

6 Conclusions and prospect

The two phase digestion of grass silage showed stable digestion behaviour. Neither in the hydrolysis nor in the fixed bed digesters could a biological disturbance of the process be detected, although there was a sudden substrate change. Every tested substrate showed its own characteristic digestion behaviour. The maize silage and rye silage compared to the grass silage showed a longer acid formation which kept the pH on a level good for the hydrolysis. This leads to a better distribution of the methane yield to the phases.

Considering the results of experiments conducted up to now a degree of degradation of 75 to 85 % of the VS was reached. The biogas generated in the fixed bed digesters had an average methane content of 70 %. The fixed bed digesters yielded 63 % of the total methane production of the two stages.Digesting grass silage of an intensively used grass land average biogas yields of 665 lN / kg VS and average methane yields of 335 lN / kg VS were reached with a retention time of 25 to 30 days. With the highest tested hydrolysis temperature of 55 °C, the largest biogas yield and the highest degree of degradation was achieved. And a different suitability for two-stage fermentation with a batch percolation hydrolysis is observed for the various substrates.

Literature


Session 3

Effizienz von Verfahren/Prozessen in der Praxis
Improvement of the efficiency of agricultural biogas plants by mashing the co-ferments

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Zusammenfassung


Als Partner des EU-AGRO-BIOGAS-Projektes entwickelt und analysiert die Firma Vogelsang innovative Einbringtechnologien, um Gasertrag und Energieausbeute in Biogasanlagen kostengünstig zu steigern.

Zu diesem Zweck ist eine Fermenterbeschickungsanlage entwickelt worden, die die Arbeitsschritte Zerkleinern, Mischen und Einbringen von Kofermenten und Gülle kombiniert.


Derzeit wird eine mobile Fermenterbeschickungsanlage europaweit unter den unterschiedlichsten Bedingungen eingesetzt und getestet.

The project EU-AGRO-BIOGAS (http://eu-agrobiogas.net/) is a European biogas initiative to improve the yield of agricultural biogas plants.

One of the main technologies which are currently not optimised is the feeding technology to bring in the substrates into the digester. The disadvantages of the hitherto existing methods of feeding the digesters of biogas plants are high energy consumption conditional on frequent mixing, high labour costs due to the use of mixing pits and slow decomposition of biomass because of dry-feeding of co-ferments.

Being a participant of the European project EU-AGRO-BIOGAS, Vogelsang develops and analyses innovative feeding technologies to improve biogas yield and energy output at more competitive costs.

For this purpose a mixing/feeding unit has been developed, which combines the operations of disintegrating, mixing and feeding of co-ferments and liquid manure. The organic dry matter is supplied into a double-toothed screw conveyor, e.g. by a vertical mixer. At the same time the liquid manure is supplied by a separate manure pump. The mixing screw disintegrates the coarse material and feeds a rotary lobe pump after transforming the dry matter and the liquid into a homogenized, high viscous suspension. A cutting process can be added. So several digesters in biogas systems can be supplied continuously with well prepared co-ferments.

A mobile mixing/feeding unit is presently being tested throughout Europe under the most different conditions.

Two stationary mixing/feeding units are being tested intensively at two biogas plants in Lower Saxony at present. At one biogas plant, the labour and energy consumption is ana-
lysed by comparing the results of the mixing/feeding system with the results of a conventional mixing tank. At the second biogas plant, the energy consumption of the stirring units and the gas yields of two identical digester arrangements are being measured. One arrangement is conventionally dry-fed; the other one is fed by a mixing/feeding unit, the QuickMix. The first test results at both biogas plants are very promising. So the labour and energy consumption could considerably be reduced and the gas yield could be increased.

Both, existing and new-built biogas plants can be equipped with this new mixing/feeding technology. Due to the improved feeding technology the economical and ecological benefit increases.

Keywords:
Biogas, gas yield, co-ferments, feeding of digester

1 Introduction

The efficiency of biogas production is not only depending on the amount and kind of high-energy organic material fed into the digester. The biogas production can be increased if the dry high-energy substances are fed into the digester in a well disintegrated condition. This ensures a high gas output.

The conventional solutions of the feeding problem are the following:

A mixing pit filled with liquid manure is fed with solids e.g. by a front-end loader, where the substrates are mixed by a propeller mixer. Then the suspension is pumped into the digester. This method requires always a separate mixing pit, where an unwanted fermentation may start. Besides, a high energy input is necessary for the mixing process. Further disadvantages are the high emission of bad odour, high labour costs and the impossibility of mixing several co-ferments, as e.g. swimming material like potatoes or big hard particles like starch bags.

Lately, fully automatic mixing tanks have been developed. This was labour-saving and odour-reducing, but the mixing process still consumes much energy and time. Also these improved mixing tanks cannot cope with all co-ferments.

Another method is to feed the solids directly into the digester by means of a screw conveyor or a hydraulically driven piston, which presses the matter into the digester. This saves a mixing pit, but requires high energy input for the mixing devices inside the digester. Further disadvantages are the formation of swimming and sinking layers in the digester and the impossibility of feeding several co-ferments like very liquid, dry, fibrous or sticky material.

2 Development of a new mixing-feeding system

The Vogelsang Company has developed an innovative mixing/feeding system (QuickMix), which combines the operations of disintegrating, mixing and feeding of co-ferments and liquid manure (see Fig. 1). The organic dry matter is supplied into a double-toothed screw conveyor, e.g. by a vertical mixer. The mixing screws disintegrate the coarse material and feed a rotary lobe pump after transforming the dry matter and the liquid into a homogenized high-viscosity suspension. A supplementary cutting device can be added. Completely new software and a control unit were developed for this new feeding method.
2.1 Mobile mixing/feeding unit

A mobile mixing/feeding unit (see Fig. 2) has been developed, which can be rapidly taken into operation at any biogas plant. This unit consists of a QuickMix, a vertical mixer for pre-mixing the co-ferments and supplying, a rotary lobe pump and wet cutter for supplying and cutting the manure, a complete control unit including frequency converter and a transporting and lifting frame. Arrived at the biogas plant, only one hose for manure supply, one hose for pumping the substrate into the digester and an electric cable must be connected. With the mobile mixing/feeding unit different tests have been conducted at six biogas plants throughout Europe.

2.2 Stationary mixing/feeding units

Within the scope of the project EU-AGRO-BIOGAS, two stationary mixing/feeding units are implemented at two biogas plants in Lower Saxony for test and research application.
2.2.1 Biogas plant Lamping GbR
At this biogas plant, two identical digester systems are arranged. One system is conventionally dry-fed by a screw conveyor (system I); the other system is fed by a special mixing/feeding unit (QuickMix, system II). On the one hand, the energy consumption of the complete systems is compared; on the other hand, the gas yield of the systems will be measured. Additionally, the maximum throughput of each system is determined.

2.2.2 Biogas plant Scherbring Biogas GmbH
This biogas plant is not only operated with regenerating raw material, but mainly with organic waste as e.g. pig manure, potatoes, apples, vegetables, starch, bleaching earth (waste from rape oil production). In the past, the co-ferments were fed in by a mixing pit (~350 m³). The weak points are a very high mixing power required in the mixing pit and a very labour-intensive mixing (partly with a high-pressure cleaner). Further disadvantages are high emission of bad odour and the impossibility of handling all types of co-ferments. Fully automatic feeding is impossible as well.

In addition to the mixing pit, a QuickMix has been installed. A wide range of co-ferments is being tested to compare the two feeding systems with regard to capability of processing these materials, energy consumption and labour costs. For this purpose an operation journal is kept.

3 Results

3.1 Mobile mixing/feeding unit
At different biogas plants (see Fig. 3) and sewage treatment plants in Europe the following co-ferments have been tested successfully: maize silage, green rye, bruised grain, whole plant silage, grass silage (30 mm), bleaching earth, poultry dung, craw contents, compost, fruit and vegetable waste, dog food, gelatine, filter cake and sludge. Merely tear-resistant, long-fibred screenings from raw sewage are still problematic because they wrap around the screws.

Fig 3: Mobile mixing/feeding unit in Sweden
The mixing/feeding unit can handle a wide range of co-ferments, manure and substrates in a great variety of physical conditions, as well as under different operating conditions. According to the owners and workers, the emission of bad odour and the labour costs are reduced significantly compared to the use of a mixing pit.

### 3.2 Biogas plant Lamping GbR

At present, the two digester systems are operated with the two different feeding devices. The contents of the digesters are pumped in a circuit to get interchanged and equalized. Due to problems with one CHP station and the gas pipe work, the measuring of the current output could not be realized. It is intended to install a gas measuring device. Nevertheless, the first results are promising. The substrate in the digester fed by the new feeding unit was mixed more intensively with the same mixing effort. In the meantime, at system I it was necessary to mix with higher power capacity, because sinking layers have built up. Grass silage can be handled with the new system, but not with the existing screw feeder. Repairing the damages at the screw conveyors caused by foreign bodies was more cost- and labour-intensive than at the new system and caused expensive idle time.

Due to the operator, system I was at its limitation at a throughput of 24 t of maize silage per day. System II could treat a throughput of 27 t per day completely without problems.

### 3.3 Biogas plant Scherbring Biogas GmbH

At present, both feeding systems are in operation. Bleaching earth is much easier to be handled by the new system compared to the mixing pit. In this case, the labour time is reduced by approximately 50%. According to the owner and the workers the emission of bad odour is reduced significantly.

Further improvement was achieved with the start of fully automatic operation. Therefore, the hopper between the QuickMix and the vertical mixer was rebuilt to handle sticky materials like bleaching earth.

Several other co-ferments like e.g. potatoes, hardened starch bags and cardboard boxes containing fruit, which up to now could not be coped with, are handled successfully by the new feeding system (see Fig. 4).

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**Fig. 4:** Examples of co-ferments at Scherbring Biogas GmbH
4 Conclusions

The method of feeding the digester by a combined mixing/feeding system shows lots of advantages. To obtain long-term results, the operating journals will be continued and analyzed, and the energy consumption and gas output will be measured and documented.

A wide range of co-ferments can be handled, which becomes more and more interesting because constantly new kinds of waste are found suitable for the production of biogas.

Additional treatment of the co-ferments like cutting, ultrasonic treatment, hydrolysis or mixing in additives like enzymes, which may increase the gas yield, can easily be applied if the co-ferments are mixed with the fluid before entering the digester.

In total, this means that a biogas plant equipped with the new mixing/feeding system is well prepared for the future.
Abluftreinigung nach einer Biogas-Druckwasserwäsche
- Verfahren und erste Praxiserfahrungen -

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Zusammenfassung


Schlüsselwörter:
Abluftreinigung, Druckwasserwäsche, Nachverbrennung, RNV-Anlage

Summary

When processing biogas in order to achieve the quality of natural gas for feeding it into the natural gas network exhaust air is emitted from the stripper contaminated with methane and hydrogen sulphide. The concentrations of these pollutants exceed the limits of the legal limits as fixed in the German Technical Instructions on Air Quality Control (TA Luft). The exhaust air is treated by a Regenerative Thermal Oxidiser (RTO) to comply with the regulations. The RTO is operating autothermically, i. e. without additional fuel.
1 Einleitung

Im Zuge der wirtschaftlichen Verwertung von Biogas gewinnt die Aufbereitung dieses CO₂-neutra len Energieträgers zur Einspeisung in Erdgasnetze immer größere Bedeutung. Bei der gängigen Praxis, Biogas in einem Gasmotor zur Energieerzeugung in einem Blockheizkraftwerk zu nutzen, fehlt zur vollen Ausnutzung der Wirtschaftlichkeit gerade im ländlichen Umfeld häufig die gesicherte und kontinuierliche Abnahme der dabei anfallenden Wärmeenergie. Im Gegensatz dazu ist die Einspeisung von entsprechend aufbereitetem Biogas überall dort dauerhaft gesichert, wo sich Erdgasnetze befinden.


2 Gesetzliche Richtlinien und Grundlagen

Emissionen luftfremder Stoffe sind in Deutschland durch die Technische Anleitung zur Reinhaltung der Luft (TA LUFT 2002) begrenzt und müssen gegebenenfalls durch geeignete Maßnahmen gemindert werden. Die für die Biogasaufbereitung zutreffenden Anforderungen an die Emissionsbegrenzungen sind dort wie folgt beschrieben:

- Gemäß „5.2.4 Gasförmige anorganische Stoffe“ darf Schwefelwasserstoff, der zu den Stoffen der Klasse II zählt, im Abgas einen Massenstrom von 15 g/h oder eine Massenkonzentration von 3 mg/m³ nicht überschreiten.
- Gemäß „5.2.5 Organische Stoffe“, zu denen Methan zählt, darf im Abgas dessen Massenstrom 0,50 kg/h oder dessen Massenkonzentration 50 mg/m³ nicht überschreiten. Diese Werte beziehen sich auf den Gesamtkohlenstoff der Emissionen.

Da bei der nachfolgend beschriebenen Technik der thermischen Nachverbrennung Schwefelwasserstoff zu Schwefeldioxid oxidiert wird, ist darüber hinaus auch dessen Grenzwert zu berücksichtigen:

- Gemäß „5.2.4 Gasförmige anorganische Stoffe“ dürfen Schwefeloxide, die zu den Stoffen der Klasse IV zählen, im Abgas einen Massenstrom von 1,8 kg/h oder eine Massenkonzentration von 350 mg/m³ nicht überschreiten. Diese Werte sind angegeben als Schwefeldioxid.

Wird die Abluft gemäß TA LUFT behandelt, enthält die gereinigte Abluft weniger als 0,5 % der Gesamtmethanfracht. Aufgrund des „Erneuerbare-Energien-Gesetzes“ (EEG, 2008, Anlage 1) wird dann ein Technologiebonus gewährt, der in Abhängigkeit der aufbereiteten Gasmenge 1 oder 2 Cent pro Kilowattstunde beträgt, sofern das aufbereitete Biogas zur Stromerzeugung genutzt wird.
3 Technik der Abluftreinigung

3.1 Thermische Oxidation

Da es sich sowohl bei Methan als auch bei Schwefelwasserstoff um brennbare Gase handelt, bietet sich als Entsorgungstechnik die Verbrennung in einer Nachverbrennungsanlage an. Dabei wird die Stripperabluft in einer Brennkammer bei einer Verweilzeit von ca. 0,7 Sekunden auf eine Temperatur von mindestens 750 °C erhitzt. Mit dem Luftsaurestoff werden so einerseits Methan zu Kohlendioxid und Wasser (1) und andererseits Schwefelwasserstoff zu Schwefeldioxid und Wasser (2) verbrannt bzw. oxidiert:

\[(1) \quad \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}\]

\[(2) \quad \text{H}_2\text{S} + 1,5 \text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O}\]


Bei der wirtschaftlichsten Technik, der regenerativen Nachverbrennung (RNV) (vergl. Abb. 1), wird diese Wärmerückgewinnung durch keramische Wärmespeicher erzielt, die in Zyklen von ca. 1 bis 3 Minuten wechselseitig von Roh- und Reinluft durchströmt werden. Dadurch wird soviel Wärme in der Nachverbrennungsanlage gehalten, dass thermische Wirkungsgrade von bis zu 96 % erzielt werden. Dies bedeutet, dass der regenerative Nachverbrennungsprozess bereits mit weniger als 1300 mg Methan pro m³ (entspricht 1900 ppm) autotherm abläuft. Aus der hohen Effizienz dieser Anlagentechnik resultiert eine sehr geringe Temperaturerhöhung der Abluft um nur ca. 40 K.

Abb. 1: Schema einer regenerativen Nachverbrennungsanlage
Der in der Abluft enthaltene Schwefelwasserstoff wird gemäß (2) zu Schwefeldioxid oxidiert, wovon gemäß (3) ein geringer Anteil – unter anderem in Abhängigkeit der Konzentration – zu Schwefeltrioxid oxidiert wird.

\[
(3) \quad \text{SO}_2 + 0,5 \text{O}_2 \rightarrow \text{SO}_3
\]

Vor allem dessen Korrosionspotential muss bei der Ausführung der Nachverbrennungsanlage besondere Beachtung geschenkt werden. Der Säuretaupunkt der Schwefelsäure in der Reinluft errechnet sich nach (4) (VERHOFF und BANCHERO, 1974):

\[
(4) \quad T_{TP} = \frac{1000}{(2,276 - 0,0294 \ln P_{\text{H}_2\text{O}} - 0,0858 \ln P_{\text{H}_3\text{SO}_4} + 0,0062 \ln P_{\text{H}_2\text{O}} \ln P_{\text{H}_3\text{SO}_4}}
\]


Abb. 2: Regenerative Nachverbrennungsanlage nach einer Biogasaufbereitung
3.2 Biologische Abluftreinigung und Neutralisation

Gemäß TA LUFT (siehe Kapitel 2) ist die maximal zulässige Fracht von Schwefeldioxid in der Reinluft auf 1,8 kg/h begrenzt. Dadurch errechnet sich ein maximaler Eintrag von Schwefelwasserstoff von ca. 1 kg/h, bis zu dem eine gesetzeskonforme Abluftreinigung allein durch eine regenerative Nachverbrennung sichergestellt werden kann. Bei größeren Schwefelwasserstofffrachten ist eine Nachverbrennung um eine zusätzliche Anlagentechnik zu ergänzen, durch die eine entsprechende Reduzierung der Schwefelemissionen erreicht wird.

Neben chemischen Maßnahmen zur Fällung des Schwefels bereits in der Biogasaufbereitungsanlage kann dies entweder mit einer der Nachverbrennung vorgeschalteten, biologischen Abluftreinigungsanlage oder mit einem nachgeschalteten Wäscherv erfahren werden. Im ersten Fall wird der Schwefelwasserstoff, meist in einem Rieselbettreaktor (Biotrickling-Anlage), zu Schwefelsäure oxidiert, die in entsprechend verdünnter Form ausgeschleust und neutralisiert werden muss. Durch die zweite Verfahrensweise wird das in der Nachverbrennungsanlage entstandene Schwefeldioxid in einem Wäscher durch den Einsatz einer basischen Waschflüssigkeit neutralisiert.


4 Praxiserfahrungen


Literaturverzeichnis


Fischzucht-Kreislaufanlagen in Kombination mit Biogaserzeugung – Möglichkeiten und Probleme

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Zusammenfassung

Seit einigen Jahren verzeichnen wir ein verstärktes Interesse von Seiten landwirtschaftlicher Biogasanlagenbetreiber an der Warmwasserfischproduktion. Insbesondere Afrikanische Welse sind aus rein biologischer Sicht für die Erzeugung in sog. geschlossenen Kreislaufanlagen geeignet, die sich mittels Wärmetauscher mit der Biogaserzeugung koppeln lässt.

Die Kombination mit der Energieerzeugung bietet aus produktionstechnologischer Sicht verschiedene Vorteile, wie z. B. kostenlose Abwärme, die Möglichkeit zur Schlamm- und Abwasserentsorgung sowie unter Umständen die Entsorgung von Schlachtabfällen.

Langjährige Erfahrungen dieser Fischproduktion zeigen jedoch, dass die Erzeugung Afrikanischer Welse unter den derzeitigen Marktbedingungen nur wirtschaftlich ist, wenn es durch intensives Marketing gelingt neue Absatzwege zu etablieren.

Summary

Since a couple of years, agricultural biogas producers show an increasing interest in fish culture in warmwater recirculation technology. From their biological characteristics, African catfish is a very suitable aquaculture species for production in closed systems that can be connected with biogas production by heat-exchange.

From a technological point of view, this combination is advantageous due to the reduction of heating-costs and the possibility to discharge excess water, sludge and possibly slaughter waste.

However, long-term experiences demonstrate, under current market situations, that African catfish production is only economically feasible, if new distribution channels can be established by intensive marketing activities.
1 Einleitung


2 Kombination von Kreislaufanlagen mit der Biogaserzeugung


Eine relativ neue Entwicklung stellt die Kreislaufanlagentechnologie zur Fischzucht in Verbindung mit landwirtschaftlichen Biogasanlagen dar. Bei dieser Integration der Aquakultur in die Energieerzeugung besteht der Vorteil, dass die aus der Biogasproduktion als Abwärme zur Verfügung stehende Wärmeenergie für die Fischproduktion genutzt werden kann. Mittels Wärmetauscher lässt sich das Produktionswasser der Fischhaltung und auch die Luft in der Produktionshalle beheizen. Damit entfällt ein wesentlicher Kostenfaktor für Heizenergie.
3 Welsproduktion in Kombination mit Biogasanlagen

Die kostenlose Abwärmenutzung aus Biogasanlagen in der Fischzucht ist grundsätzlich ökologisch sinnvoll und hat betriebswirtschaftliche Vorteile, die sich insbesondere bei der Erzeugung tropischer Fischarten auswirken. Im Gegensatz zu herkömmlichen Kreislaufanlagen, die in bisheriger Verfahrensauslegung zumeist mit fossilen Brennstoffen beheizt werden, bietet die preiswerte Erwärmung einerseits die Möglichkeit besonders hohe Wassertemperaturen (> 27 °C) einzustellen, und andererseits eine optimale Luftführung in der Anlage zu gewährleisten. Letzteres ist insbesondere bei luftatmenden Fischen wie Afrikanischen Welsen (*Clarias gariepinus* und Hybriden) bedeutsam. Aus der Sicht der Warmwasseraquakultur stellt die preiswerte Heizenergie aus Biogasanlagen demnach eine ideale Produktionsvoraussetzung dar. Darüber hinaus können die anfallenden Prozessabwässer und Schlamm in den Biogasanlagen oder auf betriebseigenen landwirtschaftlichen Nutzflächen verwertet werden.

Während JÄGER (1992) noch etwa 20 % der Produktionskosten für die Heizkosten (Gas) berechnete, stellen SCHEERBOOM und DOOREN (2005) unter heutigen Bedingungen (isolierte Gebäude, verringerter Wasserverbrauch) fest, dass die Ausgaben für Heizung nur noch etwa 10 % der Produktionskosten ausmachen (Tab. 1).

*Tab. 1: Produktionskosten pro kg Afrikanischer Wels in Warmwasser-Kreislaufanlagen (SCHEERBOOM und DOOREN 2005)*

<table>
<thead>
<tr>
<th>Kostenart</th>
<th>Euro / kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Satzfische</td>
<td>0,12</td>
</tr>
<tr>
<td>Futter</td>
<td>0,61</td>
</tr>
<tr>
<td>Gas, Wasser, Strom</td>
<td>0,15</td>
</tr>
<tr>
<td>Abwasser</td>
<td>0,05</td>
</tr>
<tr>
<td>Allgemeine Kosten</td>
<td>0,13</td>
</tr>
<tr>
<td>Arbeit</td>
<td>0,15</td>
</tr>
<tr>
<td>Abschreibungen</td>
<td>0,11</td>
</tr>
<tr>
<td>Zinsen</td>
<td>0,036</td>
</tr>
<tr>
<td><strong>Summe</strong></td>
<td><strong>1,356</strong></td>
</tr>
</tbody>
</table>
Wird die durch die Anbindung einer Warmwasser-Kreislaufanlage an die Biogasproduktion entstehende Kostenersparnis (Heizkostenanteil, günstige Wasser- und Entsorgungskosten) berücksichtigt, verringern sich die Produktionskosten für Afrikanische Welse auf rund 1,20 €/kg.


Bei der Betrachtung des landwirtschaftlichen Gesamtbetriebes kann sich ergebnisunabhängig ein betriebswirtschaftlicher Vorteil durch die mögliche Gewährung des KWK-Bonus für die Wärmenutzung durch die Fischzucht ergeben (lt. EEG), der zurzeit 0,03 €/kWh beträgt. Gegebenenfalls kann außerdem ein Güllebonus für den Einsatz des Gülleanteils der Fischabwässer in der Biogasanlage genutzt werden. Aktuell ist Fischzucht allerdings nicht in die sogenannte Positivliste des EEG (Anhang 3 Ziffer III) eingetragen, so dass zum Erhalt des KWK-Bonus ein Nachweis der Einsparung fossiler Energieträger erforderlich ist.

### 4 Aktuelle Entwicklungen/Ausblick

In den neuen Bundesländern (z.B. in Mecklenburg-Vorpommern) wurden in den vergangenen Jahren im Anschluss an Biogasanlagen Kreislaufanlagen zur Produktion Afrikanischer Welse errichtet. Diese wurden in Erzeugergenossenschaften integriert, die sich zentral um den Absatz der Fische bemühen. Mit einer zentralen Fischverarbeitung und -vermarktung, neuen Wels-Produkten und Marketingaktivitäten wird versucht gewinnbringende Preise zu erzielen.

Für interessierte Einzelerzeuger besteht – wie auch in anderen Bereichen der Fischerei – die Möglichkeit (und Notwendigkeit) den Fischverkauf direkt ab Hof aufzubauen. Hier gelten die Voraussetzungen, die auch in anderen landwirtschaftlichen Direktvermarktungen gelten: Es müssen Möglichkeiten zur betriebseigenen Fischbe- und -verarbeitung geschaffen werden: Es sollte ein möglichst hoher Anteil des Fischabsatzes an Gaststätten, Einzelhändler und Endverbraucher realisiert werden.

Die in Warmwasser-Kreislaufanlagen zu produzierenden Fische und das produktive Verfahren bieten grundsätzlich eine gute Voraussetzung dazu, allerdings stellt die Wirtschaftlichkeit dieser Art der Aquakultur ein grundsätzlich bestehendes Problem dar. Die erzeugten Produkte besitzen bisher nur einen Nischenmarkt und sind nur sehr begrenzt absetzbar.
5 Schlussfolgerungen

Für Betreiber von Biogasanlagen ist die Verwendung überschüssiger Wärmeenergie in Warmwasser-Fischzuchtanlagen eine interessante Anwendung, zumal dadurch u.U. der KWK-Bonus zu erhalten ist. Zudem ergeben sich technologische Vorteile im Biogasprozess dadurch, dass kostenfreie Heizenergie zur Verfügung steht und das Ablaufwasser der Fischzuchtanlage als Flüssigkeit zur Verwässerung der Fließfähigkeit landwirtschaftlicher Einsatzstoffe verbessert werden kann.

Für den Betrieb einer Warmwasser-Kreislaufanlage zur Welsproduktion ist die Anbindung an eine Biogasanlage prinzipiell von Vorteil, weil dadurch Kosten für die Heizung eingespart werden. Zudem können ggf. anfallende Reststoffe (Schlamm, Schlachtabfälle) kostenfrei in der Biogasanlage entsorgt werden.


Literatur


Session 4

Mikro- und Molekularbiologie
Der Einfluss von Antibiotika auf laufende Prozesse in der Biogasproduktion

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Zusammenfassung


Summary

Nowadays it has been common for agricultural biological gas facilities to mix vegetable materials and renewable biomass with liquid manure, sludge from farm animal operations or food wastes. In this way the manure from veterinary indicated applications of antibiotics or other health and environmental relevant chemicals from the sludge or wastes can be involved in the fermentation process of the facilities. These chemicals get to the fermentor where they could influence the gas production or the biological process. And still there is a lack of information about the decomposition and the metabolic processes of antibiotics or other chemicals during and after the fermentation process.
1 Einleitung


Die in der Landwirtschaft verwendeten Antibiotika und die prozentuale Verteilung auf die einzelnen Wirkstoffgruppen stellt sich dabei aus der Sicht des Jahres 2005 etwa wie folgt dar:

![Diagramm der Verteilung der Antibiotikaarten in der Tiermedizin](image)

Abb. 1: Verkaufszahlen für Antibiotika in der Tiermedizin in Deutschland 2005

2 Untersuchungen zur Wirkung und zum Abbau von Antibiotika

Die häufigsten antibiotisch wirksamen Stoffgruppen waren daher die Teracykline, Beta-Lactame und die Sulfonamide. Dies wird auch unterstützt durch ein anonymisiertes Güllemonitoring im Rahmen des Forschungsprojektes „Fachliche Überprüfung und Neubewertung von Wirtschaftsdüngern“. Dieses wurde am Lehrstuhls für Tierhygiene der Technischen Universität München (K. Harms, K. Meyer, J. Bauer) in Zusammenarbeit mit der Bayerischen Landesanstalt für Landwirtschaft durchgeführt. Dort wurden...

**Tetrazykline**

*Abb. 2: Im Versuch eingesetzte Tetrazykline*

**Beta-Lactame**

Die β-Lactam-Antibiotika sind eine Gruppe von Antibiotika/antibakteriellen Antiinfektiva, die alle in ihrer Strukturformel einen viergliedrigen Lactam-Ring aufweisen.

*Abb. 3: Beta-Lactam-Antibiotika mit unterschiedlichen Resten R für Penicillin, Benzylpenicillin, Amoxicillin*

**Sulfonamide**

*Abb. 4: Grundgerüst der Sulfonamide, eingesetzt wurden Sulfadiazin (R=C4H3N2), Sulfamethazin (= Sulfadimidin) und Trimethoprim*
3 Ergebnisse

In mehrwöchigen Batchversuchen wurden die Gasemissionen von Gärresten unter Zugabe unterschiedlicher Antibiotika getestet. Je Antibiotikum wurden vier bis fünf unterschiedliche Konzentrationen des gleichen Wirkstoffs und ein Blindwert (BW) eingesetzt.


Dabei stieg die Gasproduktion des unbehandelten Blindwertes, die sich im Wesentlichen aus den Gasen CH₄, CO₂, und O₂ zusammensetzte über die ersten 24 Stunden steil an. Die Kurven der mit Antibiotika behandelten Gärreste stiegen zwar auch, jedoch langsamer an.

Nach Beendigung dieser Versuchsanstellung waren bei den höheren Konzentrationen (100 mg Penicillin und 500 mg Penicillin) nur etwa 50 % der Gasmenge der unbeinflussten Probe entstanden. Die Gasausbeuten der einzelnen Versuchsansätze lagen zwischen 480 ml und 1080 ml.

Die Gaszusammensetzung nach 100 Stunden ergab:  
55 % Methangas  
30 % Kohlendioxid  
0,1 % Sauerstoff  
0,0 % Schwefelwasserstoff

Die folgende Abbildung zeigt die Gasemissionskurven der einzelnen Versuchsansätze.

*Abb. 5: Zeit-Druck-Diagramm (Gasentwicklung) von Penicillin G während 140 Stunden*

Literatur


LfL Schriftenreihe 12/08 (ISSN 1611-4159): „Neue Perspektiven für Biogas!?“
Selection and analysis of microbial cultures for efficient biomass conversion to methane

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Summary

The project investigated the composition of hydrolytic bacterial cultures in biogas plants run with pure plant material. Optimally hydrolyzing bacterial cultures were selected under laboratory conditions at thermophilic temperatures (65°C). The phylogenetic diversity in these cultures was determined with molecular microbiological methods. Quantitative and semi-quantitative screening methods for the major hydrolytic bacteria were developed. This was an RFLP-based screening method to sort out groups of 16S rDNA clones from metagenomic libraries. Only single members of each group had to be sequenced. Furthermore oligonucleotide primers for a quantitative PCR method to determine selectively the major hydrolytic members in the bacterial community. In addition a FISH method for the microscopical in-situ quantification of bacteria in biogas fermenter samples was established and developed esp. for the detection of the major hydrolytic bacteria. Examples for the application of these methods will be shown in the poster.
1 Introduction

One or the rate limiting steps in biogas production from plant biomass through a chain of events catalysed by bacteria is the hydrolysis of the biomass (LEBUHN ET AL. 2008). Incomplete hydrolysis would result in insufficient, suboptimal yield. It is therefore of great importance for the economy of the overall process. There has been until now relatively little research on the hydrolytic microorganisms in predominantly plant fibre-fed biogas fermenters. These are exclusively bacteria, most of them obligately anaerobic and belonging to the bacterial domain Firmicutes.

The hydrolysis of hydrated polysaccharides such as pectin, hemicellulose, β-1,3- or mixed linkage glucan and gums is relatively easily performed by single enzymes. Although due to the heterogeneity of the substrate a great number of different enzymes work together in hydrolysis, the local concentration and the order or complexity of the enzymes is not a decisive factor. With crystalline cellulose, however, the enzymes work only in locally very high concentration of different activities (synergism); the most successful and efficient cellulases are those organized in a cell bound particle, the cellulosome. Few bacteria have developed such a complex, such as the most successful of them, Clostridium thermocellum. Its cellulosome is well investigated and the single enzymes are characterized. 

C. thermocellum has been found in a wide range of diverse biotopes, all containing rotting plant biomass, although the first isolates have been made from hot springs.

C. thermocellum seems to dwell best in close vicinity with other anaerobic bacterial which seem to stimulate its growth as is to be assumed from the majority of bacteria in a natural environment. Consequently only a low percentage of all bacteria for instance in soil can be grown in pure culture on agar plates with synthetic media. This lead to the development of culture independent analytic technologies such as the population methodology by marker molecules (such as 16S rDNA) or microscopic techniques which exploit the differences in DNA sequences (FISH). As soon as a bacterial species is identified in a culture, a quantitative analysis method can be applied such as qPCR which is based on differences in the DNA sequences.

Such techniques have been applied here to investigate the hydrolytic bacteria in biogas plants and to develop monitoring technologies.

2 Results

2.1 Enrichment

Enrichment for hydrolytic bacterial cultures was done with 24 samples from around Freising (southern Germany) collected from compost, sludge from a pond, soil et cetera. Each sample was inoculated to a flask under anaerobic conditions in a sterilized phosphate buffered, pre-reduced medium with silage as carbon source. The flasks were pasteurized to select for spore-forming bacteria and incubated at 65°C for 5 days to a week. From bottles with visible substrate degradation and gas formation, cultures were transferred to identical flasks for sub-culturing and further enrichment. The efficiency of substrate degradation was assayed by measuring the loss of dry weight. The best silage-degrading culture was selected and subsequently subjected to van-Soest analysis of the silage residues for determination of the residual hemicellulose, cellulose and lignin+ash fraction.
The silage substrate was an air-dry mixture of whole plant silage from grass (30 % dry weight), maize (30 %), rye (20 %) and barley (20%). This mixture was ground in a disk-mill (Retsch, Germany), 2 mm sieve width. After incubation with bacteria, the residual substrate was washed through a nylon fabric (FOSS Fiber Cap 2023) and dried (Fig. 1). The van Soest analysis of this substrate revealed it consists of 10 % neutral detergent fibers, 35 % acid detergent fibers, 47 % acid detergent lignin and 9 % ash and lignin (Table 1). The reproducibility of the determinations was excellent at least for the undigested probe (Fig. 2).

**Tab. 1: Composition of the substrates used in this study**

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>g/kg TS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral detergent fibers</td>
<td>95</td>
</tr>
<tr>
<td>Acid detergent fibers</td>
<td>351</td>
</tr>
<tr>
<td>Acid detergent lignin</td>
<td>466</td>
</tr>
<tr>
<td>Ash and Lignin content</td>
<td>89</td>
</tr>
</tbody>
</table>

**Fig. 1:** Removal of soluble- (NDF), hemicellulose- (ADF), and cellulose- (ADL) fractions from the sample by heat, enzymatic and acid treatment, and filtration through Fiber Caps (FOSS, Germany)

**Fig. 2:** Composition of the used substrate; van Soest analysis was performed with four independent samples of the substrate; striped bars: soluble, white bars: neutral detergent fibre, black bars: acid detergent fibre, spotted bars: acid detergent lignin
To select the best hydrolytic culture at thermophilic conditions (65°C), the loss of dry weight after 3 days was determined. Inoculation with culture #10 led to the biggest loss of dry weight (10 % loss) in comparison to the control as shown in figure 3. This culture was selected for further investigations.

![Figure 3: Loss of dry weight by inoculation with the 4 best hydrolytic enrichment cultures within 3 days at 65°C. Control: medium (water with 25 % liquid plant-extract) without inoculation](image)

2.2 Influence of temperature on hydrolytic activity

The selected culture #10 was used to degrade the substrate for 1 and 3 days at 55, 60 and 65°C (Fig. 4). The determination of the fiber fractions revealed that the optimal temperature was 60°C. 60°C was the temperature for the further experiments.

![Figure 4: Van Soest analysis of rest fraction after inoculation with selected culture #10 and one or three days of incubation at temperatures 55, 60 and 65°C](image)
2.3 Comparison of enrichment with fermenter culture

The degradation property of the selected culture #10 was compared to a hydrolytic culture ("fermenter-culture") from a “best performance” thermophilic biogas fermenter run at 60°C with identical substrate (gratitude LfL-ILT, Freising). Especially after incubation times of more than 7 days (Fig. 5) a tendency of a better degradation with the selected culture can be recognized.

Fig. 5: Loss of dry weight by inoculation of selected mixed culture with culture from a thermophilic biogas fermenter at 60 °C. White bar: LfL-culture; black bar: selected culture #10. Error margins (standard deviation) are indicated.

Fig 6: End products of the 2 hydrolytic cultures (in mM, background subtracted) after 11 days of incubation at 60°C; black bars: culture #10; white bars: LfL-fermenter-culture; lactate was not determined.
2.4 Fermentation products

The fermentation products of the hydrolytic culture #10 and the LFL-culture were determined by GC analysis. Culture #10 produces mainly ethanol (22.1 mM) and acetate (26.9 mM), while after inoculation with the fermenter-culture no ethanol and a lower amount of acetate (9.6 mM) were produced. Additionally, the fermenter-culture produces small amounts of butanol (17.4 mM) and butyrate (4.1 mM) (Fig. 6). These products are good substrates for the downstream fermentation by syntrophic and acetogenic bacteria as well as partially for the methanogenic archaea. Gas was not analyzed. However, from other investigations the hydrolysis gas consisted of H₂ and CO₂.

2.5 Phylogenetic analysis of the hydrolytic culture

Culture #10 grown on silage and on cellulose as well as the fermenter-culture were investigated by molecular methods for its composition and taxonomic distribution. For this purpose the bacterial 16S rRNA genes were PCR-amplified from the metagenomic DNA with bacteria-specific oligonucleotide primers. The amplificate was cloned in E. coli. DNA from single clones was subjected to RFLP analysis to avoid sequencing of multiple copies of identical DNAs (Fig. 7). At least two clones from each RFLP group were sequenced (if possible) and aligned with the ARB software program (LUDWIG ET AL., 2004). The result is shown in Tab. B. Sequencing shows that line 1 and 2 displays C. thermocellum and C. stercorarium, respectively.

Fig. 7: RFLP analysis of 16S rDNA clones from a metagenomic library of thermophilic culture #10. The third lane is a molecular mass marker. Each lane represents DNA from one clone

Operational taxonomic units (OTUs) for each sequenced clone DNA were determined by 16S rDNA sequence similarity to known bacteria in the BLAST database. Clones with identical RFLP pattern were added to the numbers shown in table 2. All bacteria were members of the phylum Firmicutes which is not surprising given the initial pasteurization step which excluded non-spore forming bacteria.

The clone libraries from culture #10 were made from cultures grown on two different substrates (cellulose and silage) to investigate the bacterial composition dependent on the substrate. The composition differs with different substrate as was expected. Grown on Cellulose, 36% C. thermocellum, 12% Thermoanaerobacter pseudoethanolicus and 2% Ther-
moanaerobacter mathranii were found. On silage 28% C. thermocellum, 35% C. stercorarium and 2% Thermoanaerobacter mathranii were identified.

The bacteria in the LfL culture were: Clostridium stercorarium, Clostridium thermopalmarium, Thermoanaerobacter thermosaccharolyticum, and Thermobrachium celere.

Tab. 2: Operational taxonomic units by 16S rDNA sequence similarity to known bacteria in the ARB database. The sequence identity (in %) and the number of clones falling into this group are indicated

<table>
<thead>
<tr>
<th>Closest relative</th>
<th>Similarity [%]</th>
<th>cellulose</th>
<th>silage</th>
<th>LfL-culture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clostridium thermocellum ATCC 27405</td>
<td>98</td>
<td>36</td>
<td>28</td>
<td>0</td>
</tr>
<tr>
<td>Clostridium stercorarium DSM 8532T</td>
<td>98</td>
<td>0</td>
<td>35</td>
<td>2</td>
</tr>
<tr>
<td>Clostridium thermopalmarium</td>
<td>98</td>
<td>0</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Thermoanaerobacter pseudethanolicus ATCC 33223 ClusterV</td>
<td>97</td>
<td>12</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Thermoanaerobacter mathranii subsp. alimentarius ClusterV</td>
<td>99</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Thermoanaerobacter thermosaccharolyticum ClusterV</td>
<td>94</td>
<td>0</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Thermobrachium celere</td>
<td>98</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Clostridiaceae bacterium Aso3-CS325</td>
<td>96</td>
<td>20</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>Symbiobacterium thermophilum IAM 14863</td>
<td>92</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Uncultured bacterium clone: OTU5</td>
<td>95</td>
<td>12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Uncultured bacterium clone: CFB-4</td>
<td>100</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Uncultured Clostridium sp. clone: 6-2-K</td>
<td>100</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Uncultured bacterium clone: HTB1-B5</td>
<td>98</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>uncultured Bacillus sp. Clone 57</td>
<td>95</td>
<td>0</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>Anaerobic bacterium JW/HY-331</td>
<td>95</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

The only cellulytic bacteria related to the sequences obtained are C. stercorarium and C. thermocellum. Both species are described as thermophilic anaerobic degraders of cellulose (He et al., 1991). It is not sure if the two OTU’s belonging to the Clostridiaceae bacteria are cellulytic or not. The other sequences belong to surely not cellulytic bacterial groups (ZVERLOV & SCHWARZ, 2008).

The type strain of C. thermopalmarium was isolated from palm wine. It is an anaerobic, spore-forming rod with an optimal growth temperature of 55 °C. Sugars are mainly fermented to butyric acid, in addition H2, CO2, acetate, lactate, ethanol (LAWSON ET AL., 1991). Thermoanaerobacter spec. are closely related thermophilic, anaerobic species which ferment sugars to mainly butyrate. The OTU’s belonging to the Bacillus group are
most probably also saccharolytic, but non-cellulolytic bacteria. *Thermobrachium celere*
has a temperature range for growth from 43 ° to 75 °C (optimum temperature 66 °C), and
a pH range for growth from 5.4 to 9.5 (optimum pH, 8.2); the shortest doubling time is
around 10 min. Yeast extract is required for growth, and (depending on the strain) glucose,
sucrose, fructose, galactose, and ribose are utilized. The fermentation products from glu-
cose in the presence of yeast extract are CO₂, H₂, acetate, formate, and ethanol (ENGLE ET
AL., 1996). *Symbiobacterium thermophilum* is an uncultivable bacterium isolated from
compost that depends on microbial commensalism. The 16S ribosomal DNA-based phy-
logy suggests that this bacterium belongs to an unknown taxon in the Gram-positive
bacterial cluster (Ueda et al., 2004). *Bacterium Aso3 and Clostridiaceae bacterium Aso3-C
S349* were isolated from compost. Strain Aso3 is thermophilic and has 92 % similarity
with *Tepidimicrobium* sp. HUT8118, order clostridiales (Sekiguchi et al., 2006, Slobodkin
et al., 2006).

3 Discussion

The mixed substrate was that used in an actual biogas plant in southern Germany. The
hydrolytic culture selected as best hydrolyzing culture on that substrate was degrading the
polysaccharides at least as well as a “best performance” culture from a selected biogas
plant. Since diversification of the fermentation products by commensale bacteria and es-
pecially the mineralization of the fermentation products to methane and CO₂ play an im-
portant role in avoiding product inhibition, the slightly better degradation of the substrate
by the selected mixed culture in comparison to a fermenter culture (containing methano-
genic archaea and a complete acetogenic syntrophic bacterial mix) is a very good result
and points to the superior hydrolytic capacity of those bacteria (BAUER ET AL. 2008).

The composition of the hydrolytic bacterial consortium points to two cellulolytic bacterial
species which have been known to be important in biomass degradation, *C. thermocellum*
and *C. stercorarium*. The predominance of *C. thermocellum* in the culture grown on pure
cellulose as carbon source is not surprising, given the specialization of this species for the
degradation of cellulose. In addition *C. stercorarium* was found in great numbers if the
culture was grown on the silage mix. This is corroborating the earlier findings that *C. ster-
corarium* is primarily a hemicellulose utilising bacterium – hemicellulose and other solu-
ble polysaccharides are abundant in silage. The other bacterial OTUs identified in the cul-
ture can be attributed other roles in fiber utilization, the fermentation of the sugars re-
leased from the hydrolytic enzymes produced by the hydrolytic bacteria; partially the
complete degradation of oligosaccharides release by the cellulases and hemicellulases by
additional glycanases and glycosidases; or the conversion of the fermentation products
from the sugar metabolism by the saccharolytic bacteria. All these reactions together pro-
vide the methanogenic archaea with the acetate and the CO₂ and H₂ needed as substrates
for methane production.

*C. thermocellum* and *C. stercorarium* seem to be in this culture as in others (see accompa-
nying paper) the major hydrolysing bacteria for plant biomass in purely plant fed, thermo-
philic reactors. Presently a qPCR method as well as a FISH technology is developed for
quantifying the hydrolytic bacteria in biogas plants. Preliminary results of the status quo
of these developments are shown on the poster.
References


4 Acknowledgments

The authors were supported by grant N/07/45 from the bavarian state ministry Bayerisches Staatsministerium für Ernährung, Landwirtschaft und Forsten (StMELF). The cooperation, mutual discussion and support with samples from Landesanstalt für Landwirtschaft, Institut für Landtechnik, esp. of Dr. Lebuhn and C. Marin-Perez is acknowledged. Part of the results were produced in a students project performed by F. Kirschner. The technical assistance by Sabine Dummert is gratefully acknowledged.
Hydrolytische Enzyme zur Erhöhung des Gasertrages in der Biogasproduktion

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Zusammenfassung


Schlagwörter:
Hydrolytische Enzyme, Spurenelemente, Biogasproduktion, Biogasanlage, Elementare Massenbilanz, Gasertrag

Abstract

Besides improving the plant hardware, the largest reserves in the operation of a biogas plant are in maintaining a biologically stable process and in the effective use of the energy potential of the available feedstocks. The elaboration of mass balances at the elementary level is an applicable method to estimate the unused gas production potential in a biogas plant. This potential can be tapped using process enhancing additives. In practice, sustainable increases in biogas production up to 30% were achieved by application of hydrolytic enzymes and trace mineral preparations.
1 Einleitung


Im Folgenden wird die Erstellung von Massenbilanzen in Biogasanlagen auf elementar niveau Ebene dargestellt. Insbesondere ungenutzte Substratpotentiale können damit identifiziert werden. Durch die Anwendung von Spurenelementen zur Stabilisierung des Prozesses sowie den Einsatz hydrolytischer Enzyme zur Erhöhung der Substratumwandlung zu Biogas und zur Verbesserung der Fermenterrührfähigkeit werden diese Potentiale nutzbar gemacht.

2 Methoden und Ergebnisse

Massenbilanzen

Tab. 1: Massenströme einer Nawaro-Biogasanlage (Anlage El) mit 700 kW Leistung, ohne Enzymeinsatz. Die elementare Massenerhaltung wurde dabei berücksichtigt. (Farben: Grün = Produktion / Rot = Verbrauch)

<table>
<thead>
<tr>
<th></th>
<th>Input</th>
<th>Reaktion</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>mikrobielle Biomasse</td>
<td>0 kg/d</td>
<td>949 kg/d</td>
<td>949 kg/d</td>
</tr>
<tr>
<td>Rohasche</td>
<td>405 kg/d</td>
<td>0 kg/d</td>
<td>405 kg/d</td>
</tr>
<tr>
<td>Lignin</td>
<td>693 kg/d</td>
<td>0 kg/d</td>
<td>693 kg/d</td>
</tr>
<tr>
<td>Rohfett</td>
<td>410 kg/d</td>
<td>-410 kg/d</td>
<td>0 kg/d</td>
</tr>
<tr>
<td>Rohprotein</td>
<td>956 kg/d</td>
<td>-956 kg/d</td>
<td>0 kg/d</td>
</tr>
<tr>
<td>Cellulose</td>
<td>2.175 kg/d</td>
<td>-1.325 kg/d</td>
<td>850 kg/d</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>1.264 kg/d</td>
<td>-814 kg/d</td>
<td>450 kg/d</td>
</tr>
<tr>
<td>Stärke</td>
<td>4.196 kg/d</td>
<td>-4.196 kg/d</td>
<td>0 kg/d</td>
</tr>
<tr>
<td>weitere NFE</td>
<td>1.961 kg/d</td>
<td>-1.961 kg/d</td>
<td>0 kg/d</td>
</tr>
<tr>
<td>H₂O flüssige Phase</td>
<td>23.735 kg/d</td>
<td>-1.656 kg/d</td>
<td>22.079 kg/d</td>
</tr>
<tr>
<td>CO₂ flüssige Phase</td>
<td>0 kg/d</td>
<td>17 kg/d</td>
<td>17 kg/d</td>
</tr>
<tr>
<td>NH₃ flüssige Phase</td>
<td>0 kg/d</td>
<td>88 kg/d</td>
<td>88 kg/d</td>
</tr>
<tr>
<td>Summe flüssig</td>
<td>35.795 kg/d</td>
<td>-10.265 kg/d</td>
<td>25.530 kg/d</td>
</tr>
<tr>
<td>H₂O Verdampfung</td>
<td>0 kg/d</td>
<td>107 kg/d</td>
<td>107 kg/d</td>
</tr>
<tr>
<td>CH₄ gasförmig</td>
<td>0 kg/d</td>
<td>2.854 kg/d</td>
<td>2.854 kg/d</td>
</tr>
<tr>
<td>CO₂ gasförmig</td>
<td>0 kg/d</td>
<td>7.299 kg/d</td>
<td>7.299 kg/d</td>
</tr>
<tr>
<td>H₂S gasförmig</td>
<td>0 kg/d</td>
<td>4 kg/d</td>
<td>4 kg/d</td>
</tr>
<tr>
<td>Summe gasförmig</td>
<td>0 kg/d</td>
<td>10.265 kg/d</td>
<td>10.265 kg/d</td>
</tr>
</tbody>
</table>

Tabelle 1 macht sichtbar, dass die Substrate in der untersuchten Anlage unvollständig umgesetzt wurden. Insbesondere Cellulose und Hemicellulose verlassen die Anlage nicht verwertet (1.300 kg/d). Diese praktisch einsetzbare Methode zur Charakterisierung des anaeroben Abbaus in Biogasreaktoren, welche alle wesentlichen Stoffströme einer Biogasanlage berücksichtigt, ist zur Bewertung der Substratumsetzung in der Biogasanlage und zur Erkennung übrig bleibender Substratpotentiale einsetzbar.

Der Einsatz von Additiven

Zur Erschließung der ungenutzten Substratpotentiale steht der Einsatz hydrolytischer Enzympräparate zur Beschleunigung des Abbaus von Cellulose und Hemicellulose (Nicht-Stärke-Polysaccharide - NSP) in der Hydrolyse-Phase im Vordergrund (Beispiel siehe Tabelle 1). Nachwachsende Rohstoffe wie Maisilage, Grassilage, GPS u.a. Silagen bestehen etwa zur Hälfte aus NSP. In der Biogasanlage müssen diese polymeren Faserstoffe zu niedermolekularen Intermediaten gespaltet (hydrolysiert) werden, um für die weiteren Schritte des Gärprozesses verfügbar zu sein. Diese Hydrolyse ist aufgrund der molekularen Struktur der Faserstoffe besonders langsam und limitiert die Substratumsetzung zu Methan. Weiterhin sind NSP maßgeblich für die Viskosität des Fermenterinhaltes verantwortlich, erschweren die mechanische Homogenisierung und begrenzen die möglichen Trockensubstanzgehalte und damit die Faulraumbelastung im Fermenter. In Batch-Fermentern wurden die Gasproduktionen von Kulturen aus Biogasanlagen, Kläranlagen

### Tab. 2: Erhöhung des Gasertrages bei Anwendung von MethaPlus (100-1.000 ppm) in Batch-Fermentationen (25-35 Tagen, Mittelwerte)

<table>
<thead>
<tr>
<th>Substrat</th>
<th>ohne MethaPlus</th>
<th>mit MethaPlus</th>
<th>Absolut</th>
<th>Prozentual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maissilage</td>
<td>644 Nm³/t</td>
<td>719 Nm³/t</td>
<td>75 Nm³/t</td>
<td>11%</td>
</tr>
<tr>
<td>Grassilage</td>
<td>423 Nm³/t</td>
<td>490 Nm³/t</td>
<td>67 Nm³/t</td>
<td>18%</td>
</tr>
<tr>
<td>Getreidefaser (Gerste)</td>
<td>521 Nm³/t</td>
<td>651 Nm³/t</td>
<td>130 Nm³/t</td>
<td>25%</td>
</tr>
</tbody>
</table>


Ein zweiter limitierender Faktor im Biogasprozess ist die ausreichende Versorgung der Methanbakterien mit Spurenelementen. Bei intensiv betriebenen Prozessen (hohe Substratkonzentration, geringe Verweilzeit, Monovergärung von Pflanzensubstraten) ist die Zugabe von Spurenelementen zum Substratinput für eine stabile Fermentation erforderlich.

Die mesophile Monovergärung von Maissilage im gerührten Durchflussfermenter (Verweilzeit 33 d) wurde untersucht (Abbildung 1). In der Phase 1 ohne Zugabe von Spurenelementen bei Faulraumbelastung 1,5 kg oTS / m³.Tag versäuerete der Fermenter nach ca. 1,5 Verweilzeiten. Insbesondere an der Senkung des pH-Wertes, an der Anhäufung von Essigsäure im Fermenter und an dem Erliegen der Biogasproduktion wurde dieser Vorgang erkannt. Die Substratzufuhr wurde gestoppt, das Spurenelementpräparat MethaTrace® wurde dem Reaktor zugegeben. Durch diese Maßnahmen erholte sich die methanogene Fermentation; die Essigsäure wurde umgesetzt, der pH-Wert normalisierte sich in den Bereich 7,0-7,5. Anschließend wurde die Substratzugabe wieder vorgenommen. In der Phase 2 wurde der Reaktor weiter mit dem Spurenelementpräparat effizient...

---

1 MethaPlus ist ein Enzympräparat der DSM Biogas, hergestellt aus Kulturüberstand von Trichoderma reesei DSM 10683. MethaPlus® ist ein eingetragenes Warenzeichen der DSM New Business Development B.V.

2 MethaTrace ist eine Spurensalzmischung. MethaTrace® ist ein eingetragenes Warenzeichen der DSM New Business Development B.V.
stabilisiert. Über 3 Verweilzeiten mit Faulraumbelastung 1,5 kg oTS / m³.Tag und anschließend auch bei Faulraumbelastung 4,0 kg oTS / m³.Tag lief die Fermentation ohne Anzeichen von Versäuerung.

Abb. 1: Monovergärung von Maissilage im gerührten Durchflussfermenter – Phase 1: ohne Zugabe von Spurenelementen - Phase 2: bei Anwendung von Spurenelementen


Die Beobachtungen aus dem Labor stimmen mit den Ergebnissen in Biogasanlagen sehr gut überein. In der Praxis wurden nachhaltige Steigerungen in der Biogasproduktion um bis zu 30 % nachgewiesen [2, 3]. Weiter wurde damit bestätigt, dass der Einsatz extern produzierter Enzyme die Erschließung faserreicher, schwer zu verarbeitender, dafür kostengünstiger Substrate (Grassilage, Pflanzenreste aus der landwirtschaftlichen Produktion, Landschaftspflegeabfälle) ermöglicht bzw. vereinfacht. Es wurde in zahlreichen Anlagen festgestellt, dass beim Einsatz von NSP-hydrolysierenden Enzymen die Rührfähigkeit der Fermenterinhalte verbessert wird. Die Viskositätssenervierung beim Einsatz dieser Enzyme führt zum Abbau von Schwimmschichten und zu erheblichen Einsparungen an Prozessenergie und Reparaturkosten für Rührwerke und Pumpen. Durch den beschleunigten Abbau der Substrate im Fermenter verringert sich das Restgaspotenzial des Gärrückstandes, so dass die Methanemission im Endlager reduziert wird. Der Einsatz von hydrolytischen Enzymen und von Spurennährstoffen ist ohne zusätzliche Investitionen in jeder An-
lage sofort möglich und bietet dem Anlagenbetreiber zusätzliche, wertvollen Möglichkeiten zur wirtschaftlichen Optimierung seiner Anlage an.

**Literaturnachweise:**


Dynamics of microbial community for anaerobic digestion from a synthetic model substrate for maize silage under influence of trace elements

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Aim

Anaerobic digestion of plant biomass is an increasing future technology to provide energy in form of methane. In biogas plants working with plant biomass as only substrate repeatedly a decrease of biogas production is measured after a certain period after start-up which can be one year or later. A lack of specific trace elements, which acts as cofactors for enzymes in the metabolic pathway, could be one important reason for this effect. Further a pool of different eubacterial and archaeal microorganisms are involved in the process of methane formation. In the present study we investigated the influence of trace elements on the dynamic of bacterial community during anaerobic digestion of a defined model substrate (dS) mimicking the composition of the maize plant.

Methods

The defined substrate (dS) consisted of xylan and starch as the main carbon source, urea as nitrogen source and phosphorus from a 0.1 M potassium phosphate buffer. Anaerobic fermentations were carried out in batch reactors. Digester sludge from a full scale biogas plant fed with maize silage was applied for reactor start up. The sludge was filtered to eliminate particles larger 4 milimeters. The inoculum sludge was diluted with distilled water. The batch fermentations were started with a pH of 7.8 and carried out under mesophilic conditions (35°C) for 21 days. The trials where performed in 2 L batch reactors containing 1000 g fermentation medium. The medium included 1% organic dry matter (ODM) from the defined substrate and 1.5% ODM diluted digester sludge. Complete trace elements were added as trace element solution (SPL) and nickel (NiCl₂·6H₂O) were applied as single element. The microbial population was analysed with cultivation-independent molecular biological tools. 16S rDNA analysis with SSCP (single strand conformational polymorphism) and ARDRA (amplified rDNA restriction analysis) were utilized. Fluorescent microscopic analyses were also done for batch fermentation with complete trace elements and addition of nickel. Samples were taken on day 1, 7, 14 and 21 and examined immediately under the microscope Leitz Laborlux S equipped with epifluorescence. A 100 W high-pressure mercury lamp was used with a 460nm longpass filter for blue excitation.
Results

Batch-sequential tests were carried out for 21 days with a well defined trace element solution and varying nickel concentrations. 6 out of 8 bands were sequenced of the SSCP gel from the nickel batch fermentations. Two of them were analysed as uncultured bacterium, another two as *Clostridium spp.*, one as *Arcobacter sp.* and one as *Sedimentibacter sp* (Table 1). Furthermore variations of band pattern during the fermentation could be detected (Figure 1).

<table>
<thead>
<tr>
<th>Band</th>
<th>Sampling point</th>
<th>Species</th>
<th>Accession number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R17 day 21</td>
<td>Unc. Bacterium</td>
<td>AB249630.1</td>
</tr>
<tr>
<td>2</td>
<td>Blank day 21</td>
<td>Unc. Bacterium</td>
<td>FQ205850.1</td>
</tr>
<tr>
<td>3</td>
<td>R15 day 21</td>
<td><em>Clostridium sp.</em></td>
<td>DQ160250.1</td>
</tr>
<tr>
<td>4</td>
<td>R9 day 1</td>
<td><em>Arcobacter</em></td>
<td>EU403949.1</td>
</tr>
<tr>
<td>5</td>
<td>R18 day 21</td>
<td><em>Sedimentibacter</em></td>
<td>EF164626.1</td>
</tr>
<tr>
<td>6</td>
<td>R15 day 7</td>
<td><em>Clostridium sp.</em></td>
<td>AY330125.1</td>
</tr>
</tbody>
</table>

Fig. 1: SSCP gel of fragments of the 16S rDNA of the batch fermentation with different nickel concentrations. The framed bands were cut out and DNA was amplified for sequencing. R3: dS, R6: dS+SPL, R9: dS+SPL+1x Ni, R12: dS+SPL+1.5 x Ni, R15: dS+SPL+2.5 x Ni, R17+R18: dS+SPL+ 3 x Ni, Bl: blank

Fig. 2: agarose gels (1.5%) of archaeal and eubacterial inserts digested with HhaI. A digested archaeal inserts from R18 day 1 (with 3 x Nickel). Two different band patterns can be seen. Both represent the species Methanoculleus. The same result was achieved with the samples of day 21 B digested eubacterial inserts of R18 day 1 (with 3 x Nickel). The diversity of the OTUs was much higher than the archaeal. The band patterns were analysed manually and a member of one OTU was sequenced.
Molecular biological analyses indicated that the bacterial population changes clearly during the fermentation process. This result could be achieved with both molecular biological analyses techniques. The ARDRA as well as the SSCP method showed a dominance of hydrolytic bacteria. Nearly the half of the analysed bacteria was identified as Firmicutes. 70% in this phylum belonged to the class of Clostridiales and 30% to the class of Bacilli. Bacteroides and uncultured bacteria represented each a quarter of the analysed community (Figure 2 B).

Methanogenic archaea were analysed with ARDRA, too. Here it could be seen that the species Methanoculleus sp. was dominant. No other archaeal species could be detected (Figure 2 A). This means that under the experimental conditions methane is mainly produced by this hydrogenotrophic methanogen. These results are typical for anaerobic digestion of maize silage thus indicating that the new synthetic medium is a good model for maize silage.

A further activity analysis for methanogenic bacteria was done by means of fluorescence microscopy. The cells autofluorescent due to the unique co-factor F420 of methanogens. It can be seen that rod-shaped cells form clusters which got bigger and appeared more often with additional trace elements (Figure 3). The results from fluorescence microscopy complied with the measured methane formation (data not shown). An increase of fluorescent activity was also detected in enhancement of methane production.

![Fig. 3: Fluorescence micrographs of community samples of the batch fermentation. The samples were taken on day 21 from the blank (A), dS (B), dS+SPL (C) and dS+SPL+ 3 x Ni (D)](image-url)
Isolierung und Charakterisierung von Methanbakterien aus Biogasanlagen

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Zusammenfassung


Summary

Methanogens represent an important microbial group in the last step of anaerobic degradation of organic material in biogas plants. They produce methane and carbon dioxide as metabolic end products. Due to an immoderate acid production false fermentations during the anaerobic degradation of organic material could inhibit the methanogenic bacteria and so the methanogenesis. Therefore, a stabilization of the anaerobic microbial degradation of biomass and an optimization of the methane production should be the goal of microbial investigations. In order to minimize a financial loss for the operators it is necessary to avoid microbial disorders and to provide suitable starter cultures to facilitate a normal operation in a short time. Detailed knowledge about the composition and interactions of the microbial flora is required in order to take appropriate measures. Due to the importance for the methane production from organic material we have isolated and characterized the methanogenic flora from NawaRO biogas plants.

Schlüsselwörter:

Biogas, Methanbakterien, Methanobacterium, Methanosarcina
1 Einleitung


Deshalb ist eine Früherkennung und Vermeidung bzw. Verminderung einer Fehlgärung und damit eines wirtschaftlichen Schadens ein sehr wichtiger Aspekt. Dafür ist als erstes eine Analyse der an der Methanogenese maßgeblich beteiligten methanproduzierenden Archaea in Biogasanlagen nötig.

![Abb. 1. Schema des anaeroben mikrobiellen Polymerabbaus](image-url)
2 Hauptteil

2.1 Probennahme aus Biogasanlagen und Laborfermentern


Tab. 1: Anlagenparameter der untersuchten Biogasanlagen

<table>
<thead>
<tr>
<th></th>
<th>BGA 1</th>
<th>BGA 2</th>
<th>BGA 3</th>
</tr>
</thead>
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<tr>
<td>Fermenter</td>
<td>Rührkessel</td>
<td>Rührkessel</td>
<td>Rührkessel</td>
</tr>
<tr>
<td>Rühren</td>
<td>LARW/TMRW</td>
<td>Zentralrührwerk</td>
<td>LARW/TMRW</td>
</tr>
<tr>
<td>$V_{brutto}$ [m³]</td>
<td>1 x 1260</td>
<td>2 x 1.000</td>
<td>2 x 1260</td>
</tr>
<tr>
<td>Nachgärer</td>
<td>Rührkessel</td>
<td>Rührkessel</td>
<td>Rührkessel</td>
</tr>
<tr>
<td>Rühren</td>
<td>TMRW</td>
<td>LARW</td>
<td>TMRW</td>
</tr>
<tr>
<td>$V_{brutto}$ [m³]</td>
<td>1 x 1260</td>
<td>1.000</td>
<td>1 x 1260</td>
</tr>
<tr>
<td>Leistung</td>
<td>370 Pₐ [kW]</td>
<td>380 Pₐ [kW]</td>
<td>550 Pₐ [kW]</td>
</tr>
<tr>
<td>Inputstoffe</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fest [t/d]</td>
<td>MS [18]</td>
<td>MS/GPS² [20/2]</td>
<td>MS [33]</td>
</tr>
<tr>
<td>pH-Wert³</td>
<td>7,5 – 7,7</td>
<td>7,2 – 7,6</td>
<td>7,2 – 7,5</td>
</tr>
<tr>
<td>Temperatur</td>
<td>41 °C</td>
<td>39 °C</td>
<td>40 °C</td>
</tr>
<tr>
<td>NH₄-N³ [mg/kg]</td>
<td>1800 – 2000</td>
<td>2000 – 2500</td>
<td>1400 – 1500</td>
</tr>
<tr>
<td>Gesamtsäure [mg/kg]</td>
<td>500 – 2000</td>
<td>1000 – 4500</td>
<td>1000 – 2500</td>
</tr>
</tbody>
</table>

¹) LARW = Langachsrührwerk; TMRW = Tauchmotorrührwerk; ²) MS = Maissilage; GS = Grassilage; RG = Rindergülle; SG = Schweinegülle; GPS = Ganzpflanzensilage; ³) Spektrum im Betrachtungszeitraum

2.2 Anreicherung und Isolierung methanogener Archaea

2.3 Physiologische und phylogenetische Charakterisierung von methanogenen Reinkulturen

Eine physiologische und eine phylogenetische Charakterisierung der Reinkulturen wurden mit Hilfe von biochemischen Tests und molekularbiologischen Methoden vorgenommen.

2.3.1 Phänotypische Charakteristika

Zur morphologischen und physiologischen Charakterisierung gehörten die Mikroskopie von aus Fermentern isolierten methanogenen Species sowie Ermittlung des Substratspektrums.

Es wurden unterschiedliche Reinkulturen erhalten. So zum Beispiel ein methanogenes Bakterium (Stamm TAF1) aus dem Fermenter 1 der Biogasanlage 2 (BGA 2). Bei dem Isolat handelte es sich um gerade Stäbchen, die teilweise kurze Ketten bildeten. Die Stäbchen leuchteten im Fluoreszenzmikroskop bei einer Anregungswellenlänge von 420 nm aufgrund des Kofaktors F₄₂₀ grünlich (Abb. 2).

Abb. 2: Fluoreszenzmikroskopische Aufnahme einer Reinkultur (Stamm TAF1) in Vollmedium 287. Einzelne und paarweise zusammenhängende grün fluoreszierende Stäbchen sind sichtbar. (Maßstab = 5 μm)

Das Isolat TAF1 wuchs auf den Substraten H₂ und CO₂ oder Formiat und bildete Methan. Dagegen wurden Acetat, Ethanol, 2-Propanol und Essigsäure nicht verwertet.

2.3.2 Phylogenetische Zuordnung

Die phylogenetische Zuordnung der methanogenen Isolate erfolgte durch eine 16S rDNA-Analyse. Dazu wurde die genomische DNA isoliert, die 16S rDNA-Gene amplifiziert und sequenziert. Die molekularbiologische Analyse der Teilsequenz der 16S rDNA des Stamms TAF1 ergab, dass dieses Isolat 96% Sequenzhomologie mit einem Stamm der Gattung Methanobacterium besaß und eine gewisse Verwandtschaft mit Methanobacterium formicicum aufwies.
3 Schluss


4 Danksagung

Wir möchten uns beim Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz (BMELV), Berlin, für die finanzielle Unterstützung dieses Projektes bedanken.

Literaturverzeichnis


Enhancement of biogas production by addition of hemicellulolytic bacteria immobilised on activated zeolite IPUS meth-max®

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A new strategy for the enhancement of biogas production from hemicellulose containing substrates was demonstrated. Hydrolytic populations from a common biogas fermenter consortium were enriched in fed-batch-culture in a medium containing xylan as the only carbon source, semi-continuously fed under anaerobic mesophilic conditions. Xylanase activity increased continuously during the subsequent enrichment cycles. Concomitantly, enrichment of hemicellulolytic bacteria was demonstrated using SSCP analysis based on the unibacterial 16s rDNA fragment and sequencing of bands (figure 1 a and b).

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Fig. 1a and b: (s. next page)
Fig. 1a,b: Exemplary non-denaturating gels from the SSCP-analysis based on 16S rDNA fragments of bacterial communities cultured in L47 medium and second-stage sludge: (M) represents 1 kb DNA-ladder marker lanes; (C) represents the control, i.e. pure second-stage sludge (NF 01/02); (III), (IV), (V) represent corresponding cultivation periods in L47 medium on xylan as mono-substrate. Sample-Code: L47 = medium, 08/16/24 = replicate number, III/IV/V = cultivation period, 3/4/5 = day of current cultivation. Box [a], [b] and [c] show the intensification, box [d] and [e] the weakening of specific band patterns indicating shifts in bacterial community organisation during the cultivation in L47 medium. Box [2], [8], [9], [10], [11], [12] represent specific bands used for DNA extraction and sequencing analysis.

With direct sequencing of the DNA extracted from non-denaturing polyacrylamid gels Bacteroides sp., Azospira oryzae (Dechlorosoma sp.) as well as a wide spectrum of diverse species from the phylum Firmicutes within the order of Clostridiales were identified. Enriched hydrolytic bacteria were immobilised on activated zeolite IPUS meth-max® to ensure a stable storage and easy application.

Through addition of hemicellulolytic microorganisms the production of methane was increased by 53.3% compared to controls without additionally introduced microorganisms (figure 2). Using HPLC analysis a correlation between increased biogas productivity due to addition of hemicellulolytic bacteria and resulting increased concentrations of acetic acid, i.e. +88% in average was observed (data not shown here).

Fig. 2: Comparative discontinuous fermentation results. Cumulative biogas production (CH₄ at SATP = standard ambient temperature and pressure per kg TOS) in the presence of zeolite-immobilised hemicellulolytic microorganisms (black line ⚫) and the control zeolite but without immobilised microorganisms (grey line ■) at 35 °C over a total period of 34 days. From day 21 of the fermentation on differences in biogas amounts are significant. Significance differences are defined as P < 0.05 and marked with [*] in the diagram.
Session 5

Analytik, MSR-Technik und Prozessmodellierung
Visualisierung von Methanemissionen

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Zusammenfassung


Das Einsparpotential, welches sich aus den erkannten Leckagen ergibt, hängt grundlegend von der Qualität der Biogasanlage selbst ab, die gerade im Fokus steht. Selbst auf qualitativ hochwertigen Anlagen sind dennoch durch Wartungsfehler und/oder mangelhafte Bauausführung Verluste von ca. 5% der Einspeisevergütung entdeckt und beseitigt worden. Auf einigen Anlagen dürfte diese Zahl noch höher liegen.

Verschiedensten Bereiche der Branche können von der Entwicklung profitieren, wie zum Beispiel Anlagenhersteller zur Qualitätssicherung, Betreiber zur Effizienz- und Sicherheitsüberprüfung sowie Behörden zur Überprüfung der Regeln des Bundes-Immissionsschutzgesetzes.
Summary

The consequences of uncontrolled leakages at methane-tanks or -pipes are of environmental and economical importance. As a consequence scientists and engineers of the Technical University of Hamburg-Harburg, E.ON Ruhr Gas and the company Esders have developed a special camera to detect and visualize methane leakages in real-time and from larger distances. The camera helps to save resources by simplifying the inspection of defect or inaccessible parts or large-scale installations. While the camera had originally been developed for the fossil energy industry it has now been successfully proved by Esders and Ecofys Germany GmbH on biogas installations for leakage detection and quality assurance.

The estimated saving potential arising from the detected leakages basically depends on the quality of the biogas installation in focus. Even considering top-quality installations, mistakes in maintenance and/or deficient construction works that led to a loss of about 5% of the green electricity remuneration have been detected and corrected. This potential might be even higher for other installations.

Many different actors of the Biogas-industry can benefit from this development, e.g. constructors for quality assurance, operators for efficiency and security means as well as authorities for assuring the policies of the Federal Emission Control Law.
1 Einleitung

Die ökonomischen Folgen von Undichtigkeiten in Biogasanlagen sind von großer Bedeutung. Der unkontrollierte Gasaustritt aus Behältern oder Rohrleitungen bedeutet einen höheren Substratbedarf und, im schlimmsten Fall, eine Minderung der Leistung und somit der Erlöse.


2 Entwicklung eines neuen Verfahrens

Ingenieure und Wissenschaftler der Technischen Universität Hamburg-Harburg (TUHH), des Gasversorgers E.ON Ruhrgas und des Messgeräteherstellers Esders haben die Grundlagen für ein Werkzeug zur Visualisierung von Methanwolken erarbeitet. Das Ergebnis ist ein mobiler Infrarotdetektor, der in Echtzeit Undichtigkeiten in Gas führenden Anlagen erkennt und dem Anwender sofort ein farbiges, bewegtes Bild des austretenden Methans zur Verfügung stellt. Die Entfernung zwischen der GasCam, so der eingetragene Name der Kamera, und dem Gasaustritt kann dabei bis zu 200 m betragen.

3 Vorteile des Verfahrens


4 Anwendungsbeispiele

Obwohl ursprünglich mit dem Fokus auf die fossile Energieversorgung entwickelt, wurde die Bedeutung der GasCam sehr schnell auch für den Bereich Biogas deutlich, als im Zuge von Messungen mit dem Prototypen auf Biogasanlagen einige Leckagen entdeckt wurden. Es kamen noch einige Anwendungen auf ähnlichen Anlagen hinzu, die den Bedarf verdeutlicht haben, wie zum Beispiel die Leckage in einer Gasspeicherfolie in Abbildung 2.

Abb. 2: Standbild der Methanemissionen am Auslass eines Tragluftdaches
(Quelle: Fa. Esders, GasCam)

5 Nutzer

Unterschiedliche Nutzer profitieren von GasCam Messungen:

5.1 Betreiber von Biogasanlagen

Messungen können vor Gefahrenübergang oder Abnahme einer neu errichteten Anlage erfolgen, um eine umfassende Qualitätsüberprüfung und sicherheitsrelevante Untersuchung in Verbindung mit bekannten Verfahren vornehmen zu können.

Insbesondere bei großen Anlagen oder überdurchschnittlichem Besucheraufkommen bietet sich hier eine regelmäßige Überprüfung der Anlage an. Aber auch kleine Anlagen können sich keine Gasverluste oder Sicherheitsdefizite erlauben.

5.2 Biogasanlagenhersteller


Zusätzlich kann der Biogasanlagenhersteller auch kontinuierlich an der Verbesserung des Systems Biogasanlage arbeiten und planungsseitige oder konstruktive Schwachstellen seiner Systeme identifizieren und verbessern.

5.3 Klimaschutz/Gesetzgeber

Durch die GasCam ist es erstmals möglich, die Vorgaben der Dichtigkeit von Anlagen gemäß Bundes-Immissionsschutzgesetz bei der Abnahme zu überprüfen, oder sich vom Betreiber den Nachweis erbringen zu lassen, dass die Anlage auch im Betrieb ohne nennenswerten klimarelevanten Emissionen betrieben wird. Bei Verdachtsfällen von nicht genehmigungskonformen Anlagen, können durch die Behörden Messungen zur Verifizierung der Vermutungen aus der Distanz durchgeführt werden. So führen die Messungen zu effizienter Verringerung der klimarelevanten Emissionen und dienen der Sicherstellung dessen.

6 Vorteile des Verfahrens

Aufgrund der erheblichen Zeiteinsparung bei Messungen mit der Kamera ist davon auszugehen, dass sowohl die Betreiber von Biogasanlagen als auch die Hersteller zunehmend auf dieses Verfahren zurückgreifen werden, um die geforderten Qualitätsmaßstäbe einzuhalten und nachzuweisen.

Auch die Behörden werden die jetzt gegebenen Möglichkeiten zur Überprüfung von BImSch- und Baurechtsgenehmigten Anlagen nutzen, um ihrem Grundsatz der Emissionsminderung nachzukommen.

Bei durch die Fa. Ecofys Germany GmbH durchgeführten Messungen wurden z.B. Mängel an Gasspeicherfolien entdeckt, die nach der Reparatur zu erheblichen Einsparungen führten.

Die Einsparungen an Inputmaterial und damit auch Substratkosten, die sich durch Behebung der Mängel ergeben, können durchaus bis zu 10% betragen, wie diese Messungen bereits gezeigt haben.

Für eine 500 kWel. NaWaRo Anlage bedeutet eine Substrateinsparung von 7,5% z.B. eine Ersparnis von ca. 15.000 € p.a. bei einem Preis von 26 € pro Tonne Maissilage.

7 Technische Grundlagen der Messung


Die erstellten Videosequenzen werden für die Dokumentation der Überprüfung abgespeichert und in einer Abschlusspräsentation vorgeführt.

Auch wenn sich die durchschnittliche Anlage in Deutschland gut ins Landschaftsbild einfügt und auf den ersten Blick einen sehr guten Eindruck macht, wie in Abbildung 3, gilt es doch, mit den nun gegebenen Mitteln, einen wirtschaftlichen und klimaschonenden Betrieb sicher zu stellen.

Abb. 3: 500 kW NaWaRo Anlage (Quelle: Marcus Brand)
Process control of an anaerobic hydrolysis-acidogenesis phase of a two-stage fermenter system treating maize silage

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Zusammenfassung

Ein zweiphasiges anaerobes Vergärungssystem wurde entwickelt, das Maissilage bei 55°C in der hydrolytisch/acidogenen Phase (HAP) zu nutzbaren Energieträgern umsetzt. Das System dient dazu, die Energieproduktion aus nachwachsenden Rohstoffen zu optimieren und soll Möglichkeiten bieten, die Unterprozesse verfahrenstechnisch besser zu steuern. Eine stabile HAP wurde etabliert, die ein konstantes Niveau an flüchtigen Fettsäuren (VFA) und HAP-Gas produziert. Die HAP konnte so stabilisiert werden, dass der Methangehalt unter 3% (typischerweise 1%) und die VFA im Bereich 8 and 11 g • L⁻¹ lagen (CSB 24,5 bis 29,6 mg • L⁻¹).

Der pH-Wert in der HAP hatte einen starken Einfluss auf die Konzentration vor allem von Essig-, Propion-, Butter und Capronsäure sowie auf die Gasatz VFA-Konzentration. Bei etwa pH 6,0 ergab sich ein Maximum an VFA-Produktion, während bei ca. pH 7,0 am meisten HAP-Gas produziert wurde. Bei steigendem pH-Wert stieg die Konzentration an Buttersäure unter den VFA an, während der prozentuale Anteil an Essigsäure sank. CO₂ und H₂ waren die Haupt-Gasprodukte der HAP. Bei pH 5,0 – 5,5 war das Verhältnis von H₂ zu CO₂ etwa 50% zu 50%, und bei pH 6,0 – 6,5 lag es bei etwa 20% zu 80%. Der Methangehalt im Biogas der methanogenen Phase lag durchwegs zwischen 70 bis 76%.

Summary

A two-phase anaerobic digestion system mono-digesting maize silage at 55°C in the hydrolytic/acidogenic phase (HAP) has been developed to optimize energy production from renewable resources and provide opportunities for process engineering. A steadily running HAP with constant volatile fatty acid (VFA) concentration and gas production was successfully achieved. The CH₄ content in HAP was controlled below 3% (typically 1%). VFA concentration was maintained between 8 and 11 g • L⁻¹ (COD from 24.5 mg • L⁻¹ to 29.6 mg • L⁻¹) throughout the experiments.

The pH value in the HAP had a strong effect on the concentration particularly of acetic acid, propionic acid, butyric acid, capronic acid and the total acid concentration. A maximum of VFA was produced at ca. pH 6.0, whereas maximum gas production was observed at ca. pH 7.0. By elevating the pH value, the percentage of butyric acid among the produced VFA increased and the portion of acetic acid decreased. CO₂ and H₂ were the main gas products in the HAP. At pH 5.0 – 5.5, the relation of H₂ to CO₂ was ca. 50 % to 50 %, and 20 % to 80 % at pH 6.0 – 6.5. The CH₄ content in methanogenic phase steadily ranged from 70 to 76 % throughout the experiments.

The findings provide an opportunity to manipulate the acid and gas composition by controlling the pH value in HAP in order to optimize the transformation efficiency to energy from renewable resources. Utilization of produced HAP gas is a question that is currently addressed to improve the ecobalance.
1 Introduction

A large energy potential lies in agricultural products or residues with dry matter contents around 35%, making the energy potential difficult to exploit directly. Conversion to a useful energy carrier must typically first be performed. Using anaerobic digestion (AD), substrates like maize silage can be converted into the energy carrier biogas (typically CH₄ and CO₂).

Most agricultural biogas plants are designed as monophasic systems in which all of the four AD phases (hydrolysis, acidogenesis, acetogenesis, methanogenesis) are running simultaneously. In biphasic systems, combined hydrolysis and acidogenesis is performed in a so called “hydrolysis” fermenter. During (hydrolysis and) acidogenesis, a large amount of volatile fatty acids (VFA) and biogas rich in CO₂ and H₂ are produced. VFA degradation to acetic acid and H₂/CO₂ is energy consuming and driven by the downstream methanogenesis (SCHINK, 1997). Because optimal conditions for hydrolysis/acidogenesis and methanogenesis are different (DEMIREL and ORHAN, 2002), physically separating these two phases could give us the opportunity to configure and optimize them specifically.

In order to provide more flexibility in controlling the complicated degradation subprocesses, we developed a two-stage two-phase AD system for biogas production from lignocellulose-rich material. We have carried out a series of experiments to determine the performance of the hydrolytic phase under different conditions in order to assess which combination of conditions in the hydrolytic/acidogenic phase (such as pH, HRT, acid concentrations) affect the quantity and quality of produced gases and acids aiming at designing products that are optimally suited as feed of the methanogenic phase and as energy carriers.

In this paper, we report on the optimization of a thermophilic hydrolysis/acidogenesis phase to produce high-quality input for the methane-forming phase using maize silage as the substrate.

2 Material and methods

The two-stage fermenter systems used for our experiments are shown in Figure 1.

Fig. 1: Two-stage fermenter systems of the Institute of Agricultural Engineering and Animal Husbandary
Fig. 2:  Design of the two-phase AD system

*Figure 2* illustrates setup and design of the two-stage/2-phase fermenter systems. Stirrers were installed separately for each phase (1: thermophilic hydrolytic phase run at 55°C; 2: methanogenic phase) and run by an automated time and interval program. Gas produced in each phase was led through the gas meter (numbers 4 in *Figure 2*) and the produced volume recorded. The gas was then collected in gas bags (numbers 5), and the gas composition was determined by device number 3. To compensate for the pressure drop when fermenter content was removed from each phase, gas balance bags (numbers 6) were installed. Device number 7 was a heating unit constantly circulating water to keep each stage at desired temperature.

2 L samples were taken from the HAP of the biphasic system and subjected to tests (1 d duration, i.e. the feeding interval) with different pH values (5 – 8) adjusted by the addition of NaHCO₃. VFA amount and composition and gas production were determined. The performance of the HAP served as the reference. Conditions in the tests were the same as in the lying HAP fermenter (*Figure 1*) which was run at pH 6.0 and an organic loading rate of 6.7 kg VS * m⁻³ * d⁻¹. The hydraulic retention time lay within 5.5 – 6 d (recirculation of liquid from the methanogenic fermenter).

Chemical and physical environmental parameters were determined as reported in *Lebuhn* et al. (2008).

3 Results and discussion

A steadily running HAP with constant VFA (volatile fatty acid) and gas production from maize silage was successfully achieved. The CH₄ content in the HAP biogas was less than 3% (typically 1 %). Only at conditions where the 2-phasic system began to shift towards a one-phase digestion, the CH₄ concentration in the biogas reached a higher value (around 15 – 25 %). The CO₂ content of the HAP gas was 60 – 62 %, and the H₂ % 37 – 39 %. VFA concentrations obtained in the hydrolytic phase ranged between 8.5 to 11.1 g * L⁻¹ during the experiment (COD 24.5 to 29.6 mg * L⁻¹).
Fig. 3: VFA and gas production in the hydrolytic/acidogenic phase at different pH values

Total VFA concentration showed a good relationship with the HAP pH value at the feeding time. *Figure 3* shows the production of individual and total VFA at different pH values, as well as total VFA production change (in comparison to the HAP fermenter) and HAP gas production (HAP-GP).

*Figure 3* shows that a maximum of VFA was produced at ca. pH 6, whereas maximum gas production was observed at ca. pH 7. By elevating the pH value, the percentage of butyric acid increased and the portion of acetic acid among the produced VFA decreased (*Figure 3*). These results are generally in agreement with findings for AD of other feedstocks (MATA-ALVAREZ et al., 2000).

At pH 5.0 – 5.5 the relation of H₂ to CO₂ was ca. 50 % to 50 %, and at pH 6.0 – 6.5 it was 20 % to 80 %.

The CH₄ content in the biogas of the methanogenic phase steadily ranged from 70 to 76 % throughout the experiment, and the VFA concentration in the methanogenic fermenter was maintained at a low level (*Figure 4*). This indicates the methane-forming phase had no sign of acid accumulation.
Conclusions and outlook

In the hydrolytic/acidogenic phase (HAP), VFA concentrations could be maintained in a range from 8 to 11 g L\(^{-1}\) throughout the experiments, and VFA composition differed with the pH value. VFA concentration and composition in the HAP are key parameters to optimize the performance of the methanogenic phase and the whole AD system. Our results suggest that it is e.g. possible to manipulate the HAP products either toward more HAP gas production (pH value near 7) or higher VFA concentration (pH value near 6) by controlling the operational conditions of the system.

In the methanogenic phase, a high methane content (70 – 76 %) was achieved in the two-phase AD system. The higher the methane content of the biogas, the easier can be a biogas purification if is intended to feed the biogas into the gas grid. This contributes to the overall efficiency of the system.

The overall efficiency also depends on losses arising from side products of the hydrolysis/acidogenesis phase such as H\(_2\) and CO\(_2\) if these are not further utilized. A possibility to use these products is to press in the H\(_2\)/CO\(_2\) into the methanogenic phase. Respective research is carried out actually in our institute.

Acknowledgement

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References


Labordienstleistungen und Qualitätssicherung im Bereich der Biogasproduktion

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Zusammenfassung

Es wird der Aufbau einer externen Qualitätssicherung für Anbieter analytischer Dienstleistungen im Bereich der Biogasproduktion beschrieben. Dabei wird besonders auf die Durchführung von Ringversuchen eingegangen.

Summary

The Installation of a quality control for analytical laboratories which are involved in the biogas analytics for biogas production is described. Especially the realization of interlaboratory comparison is focussed in detail.

1 Einleitung


Aber auch die Art der Anlage, ob es sich um eine reine NawaRo-Anlage, oder um eine Biogasanlage mit Gülle oder Zuschlägen anderer organischer Stoffe, wie z.B. Speisestoffen, Produkten aus der Landschaftspflege, Speiseölen und Fettten handelt, bestimmt den ökonomischen Nutzen einer Anlage. Zudem haben die eingesetzten Substrate unterschiedliche Gasausbeuten.

Werden die Substrate falsch dosiert oder fehlen wichtige Spurenelemente zur Ernährung der Bakterien oder steigt der Anteil unerwünschter Stoffe im Fermenter an, so kann es zu erheblichen Störungen im Biogasprozess kommen. Die Folge ist eine verminderte Gasausbeute, eine suboptimale Gasproduktionsleistung und im Extremfall der Zusammenbruch des Betriebs einer ganzen Anlage.

Dies kann zu erheblichen finanziellen Einbußen und immensen Folgekosten für den erneuten Anfahrbetrieb führen. Daher ist es sehr wichtig, eine optimale Betriebsführung im kontinuierlichen Betrieb zu gewährleisten und durch ständige Eigenkontrollen, Messungen und Laboranalysen die Substrate und die Prozessgülle zu überwachen. Wenn ausbringfähige Gärreste entsprechend den gesetzlichen Bestimmungen als Wirtschaftsdünger wieder
Die Laboranalytik spielt daher für den Betrieb einer Biogasanlage eine große Rolle.

2 Aufbau einer externen Qualitätssicherung für Biogaslabore

Eine im Jahr 2008 von der bayerischen Landesanstalt für Landwirtschaft (LfL) und der Arbeitsgemeinschaft Landtechnik und landwirtschaftliches Bauwesen in Bayern (ALB) bei Landtechnikberatern, Biogasfirmen und Anlagenbetreibern durchgeführte Bedarfsanalyse zeigte, dass es in Bayern einen erheblichen Bedarf zur Verbesserung der Qualität und Verbreitung von Beratungs-, Schulungs- und Labordienstleistungen für die Biogasproduktion gibt.


Die erzielten Ergebnisse des ersten Ringversuchs weisen vor allem bei den Parametern, die nicht nach einheitlichen Analysevorschriften untersucht werden, große Varianzen auf. Z.B. wurden für den Gehalt an Essigsäure Werte zwischen 500 mg/l und 2800 mg/l ermittelt. Ebenso lässt die erzielte Standartabweichung von knapp 20% den Schluss zu, dass durch die unterschiedlichen Untersuchungsmethoden keine zufriedenstellende Präzision der Ergebnisse erreicht wurde (siehe Abbildung 1).

Ziel dieser Ringversuche ist einerseits, die Qualität der angebotenen Dienstleistungen zu prüfen und den Laboratorien die Möglichkeit zu geben, ihre Analytik zu überprüfen und zu vergleichen, zum anderen zu einem späteren Zeitpunkt die Anbieter von Labordienstleistungen aufzulisten und zu veröffentlichen.

3 Ausblick

Alle Ergebnisse dieser Studie werden in verbesserte Beratungsunterlagen einmünden, die für alle Beteiligten, Betreiber und Berater von Biogasanlagen, Biomasseproduzenten und Gärrestverwerter gleichermaßen zu einem genaueren Verständnis der Zusammenhänge im Prozess, zur Erhöhung der Produktivität und zur besseren Interpretation von Analysenergebnissen führen sollen.

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SOFTWARE „PROLAB PLUS, Version 2.9.0.6“ der Fa. quo data, Dresden
Parameteridentifikation für ein nichtlineares Modell zur Biogasgewinnung

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Zusammenfassung

Ein Modell, welche den Biogasprozess beschreibt, erlaubt das Nachvollziehen verschiedener Prozesszustände, die Simulation von zukünftigen Ereignissen oder das Prozessverhalten unter anderen Anlagenkonfigurationen. Zukunftig kann das Modell ein wichtiges Werkzeug darstellen um den Biogasprozess zu optimieren und Regelungen zu entwerfen.


Mit diesen Erkenntnissen zur Identifikation wurde begonnen, ein Szenario für Praxisversuche zu entwickeln, welches den Prozess ausreichend genug anregt, um eine Identifikati-
on vorzunehmen. Dieses Szenario wird während eines Laborversuches erprobt. Verlaufen
diese ersten Versuche in der Praxis positiv, kann die Identifikation an großtechnischen
Biogasanlagen getestet werden. Die folgenden Kapitel dienen zur genaueren Beschreibung
dieser Lösung der Parameteridentifikation.

Summary

Ein Modell, das den Biogasprozess beschreibt, ermöglicht die Simulation von verschiedenen Prozesszuständen, die Simulation von zukünftigen Ereignissen oder Prozessverhalten, das unter verschiedenen Prozesskonfigurationen eintreten kann. Ein Modell ist ein wichtiges Werkzeug für die Optimierung des Biogasprozesses und die Entwicklung von Prozesssteuerungsalgorithmen.


Dieses Wissen ist der erste Schritt hin zu der Entwicklung eines Szenarios für Laboratoriumsexperimente, das die Identifikation unterstützt. Dieses Szenario wird in Laboratoriumsexperimenten validiert. Wenn sich diese ersten Experimente als erfolgreich erweisen, kann die Identifikation an vollskalierten Biogasanlagen getestet werden. Die folgenden Kapitel geben eine detaillierte Beschreibung des Lösungskonzepts für die Parameteridentifikation.
1 Einleitung


2 Prozessmodell

Das entwickelte dynamische Prozessmodell zur Berechnung der Biogasgewinnung ist eine mathematische Beschreibung der einzelnen Umwandlungsschritte: Hydrolyse, Acidogenese (Versäuerung), Acedogenese (Essigsäurebildung) und Methanogenese (Methanbildung aus Essigsäure).

Die Prozesse Hydrolyse und Versäuerung werden zusammengefasst und als Reaktion erster Ordnung beschrieben. Dies wird in der Gleichung (1) beschrieben.

\[
\frac{dS}{dt} = -k_1 \cdot S
\]

Dabei sind \(k_1\) die Abbaukonstante und \(S\) die Stoffkonzentration des abzubauenden Stoffes. Aus dem aus der Differentialgleichung bestimmten Konzentrationsabbau werden mittels Stöchiometrie die Endprodukte des Abbauschrittes berechnet.

Die Prozesse der Essigsäurebildung und die Methanbildung aus Essigsäure werden durch die Monod-Kinetik abgebildet. Diese beschreibt für eine Bakterienpopulation die spezifische Wachstumsrate, die unter anderem von der Konzentration \(S\) der limitierenden Säure abhängig ist. Auf der Basis des stöchiometrischen Ansatzes ergeben sich vier Bakteriengruppen für die abzubauenden Säuren Propion-, Valerian-, Butter-, und Essigsäure. Sie unterliegen unterschiedlichen kinetischen Bedingungen für das Biomassewachstum. Die Gleichung (2) beschreibt die Wachstumsgeschwindigkeit für die Propion-, Valerian- und Buttersäure abbauenden Bakteriengruppen.
Die Gleichung (3) beschreibt die Wachstumsgeschwindigkeit der Essigsäure abbauenden Bakteriengruppen.

\[
\mu = \mu_{\text{max}}(T) \cdot \left( \frac{1}{1 + \frac{K_s}{[S]}} \right) \cdot \left( \frac{1}{1 + \frac{K_{s,NH_3}}{[T - NH_3]}} \right) \cdot \left( \frac{1}{1 + \frac{[HAc]}{K_{i,HAc}}} \right) \cdot F(pH)
\]

Dabei wird die Abhängigkeit des Biomassewachstums vom pH-Wert mittels einer Michaelisfunktion beschrieben. Diese wird mit der Gleichung (4) beschrieben.

\[
F(pH) = \frac{1 + 2 \cdot 10^{0.5(pH - \mu) - pK_u}}{1 + 10^{(pH - \mu)} + 10^{(pK_i - pH)}}
\]

Die Parameter der Monod-Kinetik sind prozessspezifisch, das bedeutet, dass sie für jeden Prozess neu bestimmt werden müssen. Dabei ist \( \mu_{\text{max}} \) die maximale Wachstumsgeschwindigkeit, \( K_s \) die Wachstumskonstante der jeweiligen Säure, \( K_{s,NH_3} \) die Konstante für die Stickstoffverfügbarkeit und \( K_i \) die entsprechende Inhibierungskonstante. Diese Parameter sind für jede Bakteriengruppe zu bestimmen. [Fritsche, 2007]

3  Identifikation


Das Verfahren betrachtet den Fehler, welcher zwischen dem realen Prozess und dem berechneten Prozessmodell bei falschen Parametern existiert. Dieser Fehler ist durch das Korrigieren der Parameterstartwerte zu minimieren. Zunächst ist der betrachtete Fehler zu
bestimmen. Er ergibt sich aus dem Vektor der aufgenommenen Messwerte \( z(t_k) \) und dem Vektor der berechneten Modellwerte \( y(t_k) \). [Yin, 1994]

Das Fehlerminimierungsprinzip beruht auf der Dichtefunktion der Wahrscheinlichkeit für das Eintreten des gewünschten Ereignisses unter der Bedingung der gewählten Parameter. Diese Dichtefunktion wird als Funktion von \( \theta \) auch Likelihood-Funktion \( L(\theta|Z) \) genannt. Verallgemeinert wird das Likelihood-Verfahren beschrieben mit:

\[
p(Z_L|U_L, \hat{\theta}) = \max_{\theta} p(Z_L|U_L, \theta)
\]


\[
J(\theta) = -\ln(L(\theta|Z)) = \frac{1}{N} \sum_{k=1}^{N} (w^T(t_k)R^{-1}w(t_k))
\]


\[
\Delta\theta_h = -\left[ \frac{\partial^2 J(\theta)}{\partial \theta^2} \right]^{-1}_{\theta_h} \left[ \frac{\partial J(\theta)}{\partial \theta} \right]_{\theta_h}
\]

Mit Hilfe dieser Methode können die benötigten Parameter aus den Messwerten bestimmt werden. Voraussetzung hierfür ist jedoch, dass die gemessenen Prozessdaten genügend Information über den Prozess besitzen. [Yin, 1994].

4 Anwendung und Auswertung


Die Ergebnisse der Identifikation für die Parameter der Valeriansäure abbauenden Bakteriengruppen werden in der Abbildung 1 dargestellt. Zu sehen ist dabei, dass sich die Para-
Parameter nach einer gewissen Anzahl von Iterationen auf die gewünschten Parameterwerte einschwingen. Dabei wurde bei jeder Berechnung der Parameter zunächst eine Bakteriengruppe betrachtet.

*Abb. 1: Parameter der Valeriansäure abbauenden Bakteriengruppen*

Die Abbildung 1 zeigt die Konvergenz der Parameter beim dem gewählten Rechenbeispiel.


Abb. 2: Feststoffe Input
Unter der Voraussetzung, dass der Prozess in seiner Dynamik ein vergleichbares Verhalten wie das Modell mit der angenommenen Konfiguration aufweist, sind die Parameter bestimmbare.

Abb. 3: Identifikation der Vorberechnung des Versuchsszenarios

Literaturverzeichnis


YIN, XIUXIN (1994): Zur Identifikation zeitkontinuierlicher nichtlinearer Systeme. VDI-Verlag, Düsseldorf
FOS/TAC: Herleitung, Methodik, Anwendung und Aussagekraft

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¹ VE efficiency solutions GmbH, Wacholderweg 15, 31628 Landesbergen, Deutschland
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Zusammenfassung


Summary

One parameter which can be determined quite easily, but which still yields meaningful information to evaluate the conditions and development of the anaerobic degradation process in a biogas plant is the so-called FOS/TAC value, which relates two measuring variables to each other: the contents of Volatile Organic Acids (FOS) and the buffer capacity (TAC). Each individual analysis value will yield valuable insights into the status of the anaerobic process. The relation of the two values, however, to some extent allows for the evaluation of the process stability of the plant and for decisions for the further operation. In this paper, both the historical development of this analysis method and its applicability and significance will be discussed on the basis of operation experiences.
1 Einleitung


Abb. 1: Anaerober Abbau in vier Phasen [JUNGHANS, 1987]

2 Pufferkapazität und organische Säuren

Im anaeroben System kann der pH-Wert nur bei vorhandenem Puffersystem (Aufnahme von freien Protonen (H⁺-Ionen)) stabil gehalten werden. Die Pufferkapazität wird meist ausgedrückt als Carbonatpuffer (Kalkreserve) in mg CaCO₃/l. Neben dem Carbonatpuffersystem gibt es aber je nach pH Wert und Substratzusammensetzung noch weitere Puffersysteme. Im Falle der Biogasanlagen kann hier z. B. das Stickstoffpuffersystem genannt werden, in dem Ammoniak als Protonenakzeptor auftritt.

Die organischen Säuren spielen in dem anaeroben System eine wichtige Rolle, da die kurzkettilge Essigsäure (CH₃COOH) neben Kohlendioxid (CO₂) und Wasserstoff (H) als einzige Quelle für die Erzeugung von Biogas (Methan (CH₄) und CO₂) zur Verfügung
steht. Neben der Essigsäure produziert das System in der acidogenen Phase aber auch eine Vielzahl weiterer organischer Säuren, von denen hier lediglich die kurzkettigen und leichtflüchtigen Säuren wie Propionsäure (C2H5COOH), Milchsäure (C2H5COOOGH), Buttersäure (C3H7COOH) und Valeriansäure (C4H9COOH) zu nennen sind. Diese leichtflüchtigen Säuren müssen in ihrem Abbauweg hin zum Biogas zunächst in Essigsäure umgewandelt werden.

Aus Tabelle 1 lässt sich ersehen, dass die am häufigsten in diesen Systemen anzutreffen- den organischen Säuren ihre Säurekonstante im pH Bereich zwischen pH 5,0 und pH 4,4 haben und durch die Schwefelsäure mit einer Säurekonstante von pKₐ -3,9 verdrängt werden. Somit kann eine qualitative Aussage über den Gehalt an flüchtigen organischen Säu- ren FOS ausgedrückt als Essigsäureäquivalent getroffen werden.

Tab. 1: Säurekonstanten einiger flüchtiger organischer Säuren

<table>
<thead>
<tr>
<th>Name</th>
<th>Ion</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kohlensäure</td>
<td>HCO₃⁻</td>
<td>6,35</td>
</tr>
<tr>
<td>Essigsäure</td>
<td>CH₃COO⁻</td>
<td>4,76</td>
</tr>
<tr>
<td>Propionsäure</td>
<td>C₂H₅COO⁻</td>
<td>4,86</td>
</tr>
<tr>
<td>Valeriansäure</td>
<td>C₄H₉COO⁻</td>
<td>4,84</td>
</tr>
<tr>
<td>Buttersäure</td>
<td>C₃H₇COO⁻</td>
<td>4,82</td>
</tr>
</tbody>
</table>

Die Stabilität des anaeroben Prozesses kann sowohl durch Kenntnis der einzelnen Parameter (flüchtige organische Säuren und Pufferkapazität), als auch durch ihr Verhältnis beur- teilt werden. Ist z.B. der Anteil an organischen Säuren sehr hoch (z.B. > 10 g/L), weist dies auf einen unvollständigen Stoffwechsel hin und kann zur Hemmung führen. Dieser Effekt ist aber nicht so ausgeprägt, wenn gleichzeitig in der Anlage eine adäquate Puffer- kapazität gegeben ist.

3 Entwicklung des FOS/TAC


Der H₂SO₄-Verbrauch bis pH 5 spiegelt das Puffervermögen des Carbonatpuffersystems als Kalkreserve heute auch TAC genannt wieder. Zwischen pH 5 und pH 4,4 werden die Protonen von den organischen Säuren aufgenommen.

Tabelle 2 zeigt weitere Referenzen und Arbeiten, denen zum Teil unterschiedliche Probenvorbehandlungen und Titrationsendpunkte zu Grunde liegen, um die Genauigkeit der Methode zu erhöhen.

*Abb. 2: Titrationsverlauf bei der FOS/TAC Analyse [WEICHGREBE, 2007 erweitert nach NORDMANN, 1977]*

<table>
<thead>
<tr>
<th>Autoren</th>
<th>Jahr</th>
<th>pH₁</th>
<th>pH₂</th>
<th>pH₃</th>
<th>pH₄</th>
<th>Vorb.</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>DiLallo/Albertson</td>
<td>1961</td>
<td>3,30</td>
<td>erhitzen</td>
<td>4,00</td>
<td>7,00</td>
<td>zentr.</td>
<td>Faulwasser</td>
</tr>
<tr>
<td>McGhee</td>
<td>1968</td>
<td>5,00</td>
<td>4,40</td>
<td></td>
<td></td>
<td>FF</td>
<td>Faulwasser</td>
</tr>
<tr>
<td>Nordmann</td>
<td>1977</td>
<td>5,00</td>
<td>4,40</td>
<td></td>
<td></td>
<td>FF</td>
<td>Faulwasser</td>
</tr>
<tr>
<td>Jenkins</td>
<td>1983</td>
<td>5,75</td>
<td>4,30</td>
<td></td>
<td></td>
<td>n.a.</td>
<td>Faulwasser</td>
</tr>
<tr>
<td>Kapp</td>
<td>1984</td>
<td>5,00</td>
<td>4,30</td>
<td>4,00</td>
<td></td>
<td>0,45μm</td>
<td>Faulwasser</td>
</tr>
<tr>
<td>Anderson/Yang</td>
<td>1992</td>
<td>5,10</td>
<td>3,50</td>
<td></td>
<td></td>
<td>n.a.</td>
<td>Faulwasser</td>
</tr>
<tr>
<td>Moosbrugger</td>
<td>1993</td>
<td>6,70</td>
<td>5,90</td>
<td>5,20</td>
<td>4,30</td>
<td>FF</td>
<td>Faulwasser</td>
</tr>
</tbody>
</table>

Vorb. = Probenvorbehandlung, zentr. = zentrifugierte, 0,45 μm = filtriert mit 0,45μm, FF = Faltenfilter
Abbildung 3 zeigt McGHEE’s grafische Auswertung seiner Titrationsversuche mit filtrierten Schlammproben. Die lineare Regression der ermittelten Messpunkte ergab eine Ausgleichsfunktion mit einem Bestimmtheitsmaß von 0,985.

Durch Umstellung und Vereinfachung dieser Geradengleichung von

\[ Y = 0,15 + 2,06 \times 10^{-3} \times X \]

zu

\[ X = ((B \times 1,66) - 0,15) \times 485,44 \] oder

\[ FOS \approx ((B \times 1,66) - 0,15) \times 500 \left[ \text{mg/lHAc} \right] \]

entwickelte NORDMANN die Bestimmung der flüchtigen organischen Säuren (FOS) ebenfalls durch die Titration von pH 5,0 nach pH 4,4 einer 0,1n Schwefelsäure in ein Probenvolumen der filtrierten Schlammprobe von 20 ml, mit B als Säureverbrauch in [ml] [NORDMANN, 1977].

Das Puffervermögen des Systems wird bestimmt durch die Titration der 20 ml Probe von ihrem Ursprung pH Wert auf pH 5.

\[ TAC = A \times 250 \left[ \text{mgCaCO}_3 / l \right] \]

mit A als Säureverbrauch von 0,1 n H₂SO₄ in [ml] für diesen pH-Bereich.

Für was die Abkürzung TAC tatsächlich steht, konnte nicht abschließend ermittelt werden. Eine deutschsprachige Abkürzung -wie FOS- ist nicht ersichtlich; am besten passen: Total Alcalinity of Carbonates oder Titre Alcalimétrique Complet, wobei zu berücksichtigen ist,
dass hier nur bis pH 4,4 titriert wird und nicht wie bei der Bestimmung der Säurekapazität (DIN 38 409-H7) bis pH 4,3.


4 Anwendung des FOS/TAC

Die beschriebene Methode zur Bestimmung des Verhältnis FOS/TAC ist eine preisgünstige und schnelle Methode um vor Ort auf der Biogasanlage oder einer anaeroben Abwasserbehandlungsanlage eine qualitative und schnelle Aussage über die Stabilität des Abbauprozesses zu bekommen. Zu berücksichtigen ist, dass hier aufgrund der Titration bis pH 5,0 auch nur die Säure- oder Pufferkapazität bis pH 5,0 erfasst wird und nicht die gesamte Säurekapazität des Systems. Nach DIN 38 409-H7 wird die Säurekapazität durch Titration mit 0,1 n HCL bis pH 4,3 titriert.


Eine weitere mögliche Fehlerquelle ist die manuelle Titration verschiedener Personen, was durch den Einsatz von modernen Titratoren auf den Biogasanlagen eliminiert werden kann. Die Ungenauigkeiten bei der Titration von Hand sind von Bedeutung, was derzeit auch an der fehlende Referenzprobe für eine Kalibrierung und Validierung liegt. Es wird momentan am ISAH daran gearbeitet, geeignete Standards zu entwickeln, die die anlagen- spezifische Hintergrundmatrix ausblendet und somit eine zuverlässigere Aussage dieser Methode sowohl für FOS als auch für TAC ermöglicht.
5 Aussagekraft der ermittelten FOS/TAC Werte

Da die Titrationsmethode zur Bestimmung des FOS/TAC eine qualitative Aussage zur Pufferkapazität und zu den organischen Säuren zulässt, sollte sie auf der Biogasanlage täglich und immer mit der gleichen Prozedur durchgeführt werden. Ein Vergleich mit anderen Methoden zur Bestimmung der organischen Säuren und eine quantitative Bestimmung auf diesem Wege kann nur unter bestimmter Berücksichtigung der Randbedingungen angestellt werden. Abbildung 4 zeigt eigene Erfahrungen mit unterschiedlichen Analyseverfahren

![Vergleich FOS, org. Säure (Küvette) und externe Laborwerte](image)

Abb. 4: Vergleich verschiedener Analyseverfahren zur Bestimmung der organischen Säuren


Weitere Ursachen für Betriebstörungen können sein: Mangel an Spurenelementen, zu viel leicht abbaubares Inputmaterial (Kohlenhydrat) gefüttert, zu hohe Raumbelastung, ständig wechselndes Inputmaterial.
Die tägliche Analyse und Aufzeichnung der ermittelten Werte, so dass diese grafisch dargestellt werden können, ist unseres Erachtens für einen sicheren und stabilen Betrieb von Biogasanlagen unerlässlich. Aus der grafischen Auszeichnung lässt sich erst erkennen, ob man sich im normalen Schwankungsbereich befindet, oder ob es einen deutlichen Trend gibt, auf den man reagieren muss.

Literaturverzeichnis


Untersuchungen zur Vorhersage von Prozesskenngrößen des anaeroben Abbauprozesses in Biogasfermentern mittels NIR-Spektroskopie

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Zusammenfassung


Schlüsselwörter:

Nahinfrarotspektroskopie, Prozesskenngrößen, Modellierung
Summary

An efficient and stable system operation of a biogas plant requires information about the physico-chemical condition of the fermenter content on a regular basis. Useful process parameters for describing the fermenter condition include the amount of total dry material, the amount of organic material, the ammonium concentration as well as the concentration of volatile fatty acids. In the context of near-infrared spectroscopic measurements for the prediction of these parameters the present evaluation focuses on a global modeling approach. Samples from different fermenters (lab-scale and large-scale fermenters) that were fed with different substrates were taken for calibration and validation of the model. These fermenters mainly were fed with maize and grass silage as well as liquid manure. Spectroscopic measurements were taken offline.

For the total dry material and the organic dry material a correlation (r) of 0,94 and 0,95 was observed, respectively. The root mean square error of prediction (RMSEP) for the parameters was found to be 0,9 and 0,8. The RPD as the ratio of the standard deviation of the reference values to the standard error of prediction is 2,89 for the prediction of the total dry material and 3,13 for the organic dry material. By focusing on a robust calibration it can be stated that the prediction of these parameters via NIRS across different fermenter contents is principally possible. The calibration for ammonium led to a correlation of 0,89 a RMSEP of 450 and a corresponding RPD value of 2,16. The calibration for acetic and propionic acid as well as for the FOS/TAC value was found to be rather small. For improving prediction accuracy of the model future attempts will focus on a submodeling approach based on the structure of the data.

Keywords:

Near-infrared spectroscopy, process parameters, modeling
1 Einleitung


2 Material und Methoden

Probenahme und -material

Die für die Modellbildung erforderlichen Proben kamen sowohl aus Laborfermentern der Bayerischen Landesanstalt für Landwirtschaft in Freising als auch aus Praxisanlagen in Bayern. Mit dem Ziel eines substratübergreifenden Modellansatzes wurden bewusst Proben unterschiedlicher Substratzusammensetzung verwendet. Hierzu gehörten insbesondere folgende Substrate:

- Mais- und Grassilage
- Ganzpflanzensilage
- Grünroggen
- Rindermist und -gülle
- Puten- und Hähnchenmist

Die Probenziehung erfolgte parallel zu unterschiedlichen Prozesszuständen. Diese reichten von einem stabilen Betrieb bis hin zu kritischen Zuständen mit einsetzender bzw. bereits fortgeschrittener Übersäuerung. Ziel war es, den Modellraum für jeden Prozessparameter dadurch gleichmäßig abzubilden und eine möglichst breite Spreizung der Konzentrations-

Spektrale Messungen


Referenzanalytik


NIRS-Kalibration

S5 – Krapf, C. et al. – Vorhersage von BGA-Prozesskenngrößen mittels NIRS

zient (r), der mittlere Vorhersagefehler sowie der RPD-Wert verwendet. Letzter gibt das Verhältnis der Standardabweichung der Werte der Referenzanalytik zum mittleren Vorhersagefehler des Modells wieder.

3 Ergebnisse und Diskussion


Die Ergebnisse der globalen Kalibrierung, d.h. einer Kalibrierung mit unterschiedlichen Substratarten, zeigen, dass sich für die beiden Parameter TS und oTS Modelle mit einer Korrelation ≥ 0,9 erzielen lassen, hierbei werden mittlere Vorhersagefehler von 0,9 bzw. 0,8 erreicht. Der Temperatureinfluss auf das Modell ist dabei in einem Bereich von 23 bis 40 °C berücksichtigt. Für TS und oTS sind je 6 PLS-Faktoren im Modell abgebildet. Der Parameter TS war bereits nach den ersten drei Faktoren zu 80% erklärt. Mit insgesamt 6 Faktoren steigt der erklärte Anteil weiter auf 91%. Für oTS sind mit drei Faktoren 84% der y-Variante erklärt und die Erhöhung auf 6 Faktoren erklärt weitere 7%. Kritisch zu hinterfragen ist hierbei, inwieweit die höheren Hauptkomponenten tatsächlich noch Informationen für eine robuste Modellierung liefern. Weitere Spektrenvorbehandlungen führten bisher nicht zu einer Verbesserung der Modellgüte bzw. zu einer reduzierten Faktorenanzahl bei gleichbleibendem erklärndem Anteil der y-Variante.


<table>
<thead>
<tr>
<th>Parameter</th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>SD</th>
<th>n*</th>
<th>RMSEP</th>
<th>r</th>
<th>RPD</th>
<th>PLS-Faktoren</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS (%)</td>
<td>4.0</td>
<td>14.8</td>
<td>9.2</td>
<td>2.6</td>
<td>183</td>
<td>0.9</td>
<td>0.94</td>
<td>0.89</td>
<td>2.89</td>
</tr>
<tr>
<td>oTS (%)</td>
<td>3.3</td>
<td>13.5</td>
<td>7.5</td>
<td>2.5</td>
<td>180</td>
<td>0.8</td>
<td>0.95</td>
<td>0.91</td>
<td>3.13</td>
</tr>
<tr>
<td>NH4-N (mg/kg)</td>
<td>546</td>
<td>6230</td>
<td>2462</td>
<td>971</td>
<td>144</td>
<td>450</td>
<td>0.89</td>
<td>0.84</td>
<td>2.16</td>
</tr>
<tr>
<td>Essigsäure (mg/kg)</td>
<td>52</td>
<td>3562</td>
<td>456</td>
<td>679</td>
<td>147</td>
<td>567</td>
<td>0.56</td>
<td>0.37</td>
<td>1.19</td>
</tr>
<tr>
<td>Propionsäure (mg/kg)</td>
<td>50</td>
<td>4742</td>
<td>976</td>
<td>1202</td>
<td>59</td>
<td>990</td>
<td>0.63</td>
<td>0.58</td>
<td>1.21</td>
</tr>
<tr>
<td>FOS/TAC</td>
<td>0.2</td>
<td>1.77</td>
<td>0.39</td>
<td>0.23</td>
<td>172</td>
<td>0.18</td>
<td>0.63</td>
<td>0.48</td>
<td>1.28</td>
</tr>
<tr>
<td>Temperatur (°C)</td>
<td>22.2</td>
<td>40.6</td>
<td>29.9</td>
<td>2.8</td>
<td>183</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
4 Schlussfolgerungen und Ausblick


Literaturverzeichnis


Session 6

Ökonomie,
Ökologie und Bilanzierungen
Ökonomische Sensitivitätsanalyse des Biogasprozesses auf der Basis Neuronaler Netze

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Zusammenfassung


Summary

The artificial neural network is a suitable instrument for the simulation of biochemical processes in the biogas digester and for the calculation of methane yields during biogas production. The configuration of a three-layer-network-structure with 33 neurons was successful in enabling a simplified calculation of profits. Nevertheless, a higher precision can only be achieved by using a larger network of at least 500 neurons, which require computers of higher performance. The use of a standardized monitoring program by the biogas plants involved would also be of advantage.

Schlüsselwörter:

Künstliches Neuronales Netz, Biogas-Fermenter, Simulation, artificial neural network
1 Einleitung

Da derzeit nur etwa 5 % des technisch erschließbaren Biogaspotenzials in Deutschland genutzt werden, sind generell weitere Innovationen in der Biogaserzeugung und, damit verbunden, eine kritische ökonomische Gesamtauswertung der Vergärungsverfahren dringend notwendig. Es fehlen insbesondere Untersuchungen zur ökonomischen Bewertung des Gesamtverlaufs der mikrobiologischen Stoffumwandlung und hierbei der Analyse der spezifischen Kosten der einzelnen Prozessschritte. Geeignete ökonomische Modelle könnten dazu beitragen, nicht nur den Einfluss ausgewählter Parameter der Prozessschritte auf die Rentabilität einer Biogasanlage zu ermitteln, sondern darüber hinaus auch auf das wirtschaftliche Ergebnis Gasentzug.


2 Künstliche Neuronale Netze

Die KNNs sind in der Lage, auch ohne Kenntnis der inneren Kausalbeziehungen Zusammenhänge aufgrund von empirischem Datenmaterial zu „erlernen“. Als erfolgreiches Anwendungsbeispiel Neuronaler Netze sei die Wettervorsage genannt.


Im realisierten Projekt wurde der im Netz frei nutzbare Stuttgart Neural Network Simulator (SNNS) verwendet.

3 Netzerzeugung

Die Datenbasis der Simulation bildeten drei mesophil arbeitende Biogasanlagen im Land Brandenburg, die täglich ausgewählte Prozessdaten mit überwiegend hoher Priorität zur Verfügung stellten (Tabelle 1). Unter ihnen erschienen vor allem die Mengen der Futtersubstrate und des gebildeten Methans wichtig. Sie wurden als In- bzw. Outputneuronen festgelegt. Insgesamt konnten 855 Tagesdatensätze für das Training genutzt werden.
Tab. 1: Ausgewählte Parameter zur Erfassung der Biogaserzeugung

<table>
<thead>
<tr>
<th>Parameter/Messwerte</th>
<th>Maßeinheit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stoffspezifische Daten - Eingabedaten</strong></td>
<td></td>
</tr>
<tr>
<td>1  Maissilage</td>
<td>m³/Tag; %TS; kg oTS/Tag</td>
</tr>
<tr>
<td>2  Rindergülle</td>
<td>m³/Tag; %TS; kg oTS/Tag</td>
</tr>
<tr>
<td>3  Schweinegülle</td>
<td>m³/Tag; %TS; kg oTS/Tag</td>
</tr>
<tr>
<td>4  Sonstiges</td>
<td>m³/Tag; %TS; kg oTS/Tag</td>
</tr>
<tr>
<td><strong>Leistungsparameter - Ausgabedaten</strong></td>
<td></td>
</tr>
<tr>
<td>5  Gasertrag</td>
<td>m³/Tag</td>
</tr>
<tr>
<td>6  mittlerer Methangehalt (zusätzl. O₂, CO₂, H₂S)</td>
<td>% (%, ppm)</td>
</tr>
<tr>
<td>7  Methanausbeute</td>
<td>m³CH₄/Tag</td>
</tr>
<tr>
<td>8  Methanerzeugung</td>
<td>m³CH₄/t FM; m³CH₄/kg oTS</td>
</tr>
<tr>
<td><strong>Prozessdaten</strong></td>
<td></td>
</tr>
<tr>
<td>9  Fermentervolumen</td>
<td>m³ (Netto)</td>
</tr>
<tr>
<td>10 Hydraulische Verweilzeit</td>
<td>Tage</td>
</tr>
<tr>
<td>11 Raumbelastung</td>
<td>kg oTS/(m³ * Tag)</td>
</tr>
<tr>
<td>12 Fermentertemperatur</td>
<td>°C</td>
</tr>
<tr>
<td>13 Gärrestlagerkapazität</td>
<td>m³</td>
</tr>
</tbody>
</table>

Für die Ermittlung aussagekräftiger Werte war ein Beobachtungszeitraum von einem Jahr erforderlich. Die fortlauende Erfassung der benötigten Daten stützte sich im Wesentlichen auf die regelmäßigen Aufzeichnungen des Betreibers der Biogasanlage sowie auf die automatische Aufzeichnung von Messdaten.

Die Datenbank, die zur Speicherung der Werte konzipiert wurde, kann auch die für ein Neuronales Netz nötigen Trainingsdateien erstellen. In diesen müssen alle Werte normiert vorliegen, z.B. zwischen 0,1 und 0,9.

Abb. 1 zeigt die in Vorversuchen ermittelte Topologie des Neuronalen Netzes. Sie wurde mittels eines Delphi-Programms in die entsprechende Datei geschrieben. In Vorversuchen wurde eine dreischichtige Netzstruktur als günstig ermittelt. Die insgesamt vorhandenen 17 Eingangsparameter bilden die Neuronen der Inputschicht, während die vier Zielgrößen die Neuronen der Outputschicht belegen. Dazwischen wird zur breiteren Einflussverteilung eine Hiddenschicht eingefügt, für die sich eine Anzahl von 12 Neuronen als optimal herausgestellt hat. Die Topologie des Netzes ist also eine 17-12-4-Struktur.


Abb. 1: Untrainiertes Neuronales Netz mit 33 Neuronen
4 Gewinnberechnung


Da das neuronale Netz In- und Outputwerte nur innerhalb der Normierungsgrenzen verarbeiten bzw. liefern kann, ist die Simulation von Biogasanlagen nur innerhalb der Grenzen der Trainingsdatensätze möglich. Die Inputparameter können jeden Wert zwischen diesen Grenzen annehmen. Bei 17 Inputparametern ist die Anzahl der Kombinationsmöglichkeiten sehr groß. Letztendlich wurden sechs Parameter variert, bei vier Parametern ausschließlich der Mittelwert verwendet sowie sieben Parameter berechnet und anschließend normiert (Tab. 2).
Tab. 2: Varianten der Inputparameter in der Simulation

<table>
<thead>
<tr>
<th>Eingangsparameter</th>
<th>(Einheit)</th>
<th>Varianten bzw. Begründung</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fütterungsmengen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Maissilage</td>
<td>m³/d</td>
<td>Übernahme der oTS-Norm-Werte</td>
</tr>
<tr>
<td>2 Rindegülle</td>
<td>m³/d</td>
<td>Übernahme der oTS-Norm-Werte</td>
</tr>
<tr>
<td>3 Schweinegülle</td>
<td>m³/d</td>
<td>Übernahme der oTS-Norm-Werte</td>
</tr>
<tr>
<td>4 sonstige Biomasse</td>
<td>m³/d</td>
<td>Übernahme der oTS-Norm-Werte</td>
</tr>
<tr>
<td>organische Trockensubstanz der</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 Maissilage</td>
<td>kg oTS/d</td>
<td>0,1 - 0,3 - 0,5 - 0,7 - 0,9</td>
</tr>
<tr>
<td>6 Rindegülle</td>
<td>kg oTS/d</td>
<td>0,1 - 0,3 - 0,5 - 0,7 - 0,9</td>
</tr>
<tr>
<td>7 Schweinegülle</td>
<td>kg oTS/d</td>
<td>0,1 - 0,3 - 0,5 - 0,7 - 0,9</td>
</tr>
<tr>
<td>8 sonstige Biomasse</td>
<td>kg oTS/d</td>
<td>0,1 - 0,3 - 0,5 - 0,7 - 0,9</td>
</tr>
<tr>
<td>9 gesamte Biomasse</td>
<td>kg oTS/d</td>
<td>wird berechnet</td>
</tr>
<tr>
<td>Trockensubstanzgehalt der</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 Maissilage</td>
<td>%</td>
<td>nur 0,5 wurde von BGA kaum bestimmt</td>
</tr>
<tr>
<td>11 Rindegülle</td>
<td>%</td>
<td>nur 0,5 wurde von BGA kaum bestimmt</td>
</tr>
<tr>
<td>12 Schweinegülle</td>
<td>%</td>
<td>nur 0,5 wurde von BGA kaum bestimmt</td>
</tr>
<tr>
<td>13 sonstige Biomasse</td>
<td>%</td>
<td>nur 0,5 wurde von BGA kaum bestimmt</td>
</tr>
<tr>
<td>sonstige Parameter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14 Fermentervolumen</td>
<td>m³</td>
<td>0,1 - 0,3 - 0,5 - 0,7 - 0,9</td>
</tr>
<tr>
<td>15 Temperatur im Fermenter</td>
<td>ºC</td>
<td>0,1 - 0,3 - 0,5 - 0,7 - 0,9</td>
</tr>
<tr>
<td>16 Verweilzeit</td>
<td>d</td>
<td>wird berechnet</td>
</tr>
<tr>
<td>17 Raumbeastung</td>
<td>kg oTS/d</td>
<td>wird berechnet</td>
</tr>
</tbody>
</table>


Abb. 3: Ökonomisch bewertete m³CH₄/d-Outputrelativwerte des Neuronalen Netzes
Die übrigen variierten Parameter (z. B. Kosten der sonstigen Biomasse, Fermentervolumen und -temperatur) ließen sich in dieser Form nicht grafisch darstellen, weil sie während der Simulation zu oft wechselten.

Im Rahmen der Simulationsberechnung wurde das meiste Methan bei Datensatz 1.146 gebildet. Die nachgeschaltete Gewinnberechnung ermittelte ein Maximum von 801 € je Tag beim Datensatz 646. Die höchsten Gewinne innerhalb der Simulation konnten dann erreicht werden, wenn die Substratkosten nur geringe Werte aufwiesen.

5 Ergebnis

Im Projekt wurde erstmalig der Einsatz eines Neuronalen Netzes zur Simulation der Gaserzeugung in Biogas-Fermentern mit folgenden Ergebnissen getestet:

1. Der Einsatz eines Neuronalen Netzes für die Berechnung der Methanausbeute während der Biogaserzeugung ist prinziell möglich.
2. Die Simulation des Biogasprozesses war, wenn auch unter eingeschränkten Bedingungen, erfolgreich.
3. Es ist gelungen, eine dreischichtige Netzstruktur mit insgesamt 33 Input-, Hidden- und Output-Neuronen als Basis einer modellierten Gewinnberechnung aufzubauen.

6 Schlussfolgerung

Das positive Ergebnis der generellen Eignung wird durch Erfahrungen ergänzt, die Grundlage der weiteren wissenschaftlichen Arbeit sind:


- In zukünftigen Projekten sind regelmäßige und häufigere Messungen der Parameter TS oder besser oTS von Futtersubstraten Voraussetzung der Berechnungen.

**Zusammenfassung**


**Schlüsselwörter:**

Silierung, Biogas, Nacherwärmung, aerobe Stabilität, Effizienzsteigerung

**Summary**

The biogas potential of different silages is evaluated without consideration prior dry mass losses. Space efficiency of biogas plants is highly depending on prior dry mass losses which occur during silage making and during feed-out phase. Influence of ensiling and aerobic exposure is evaluated in lab-scale conditions. Exposure to air of untreated silages resulted in high dry mass and energy losses. Deteriorated silages showed a decline in methane yield, correlated with dry mass losses according to HONIG. Aerobic stability is improved by heterolactic fermentation.

**Keywords:**

Silage, biogas, aerobic stability, methane yield
1 Einleitung


2 Substratbereitstellung


Die Verfahrenskette der Biomassebereitstellung umfasst in der Praxis:

– Anbau & Ernte
– Lagerung & Konservierung (Silierung)
– Auslagerung aus dem Silo

Die einzelnen Verfahrensschritte sind dabei verlustbehaftet und wirken sich auf die Flächenproduktivität aus. Die Lagerung und Konservierung großer Erntemengen, wie sie in der Biogaserzeugung benötigt werden, stellen neue Anforderungen an Ernte- und Siliermanagement, Siloabmessungen sowie an die Silagequalität. Tab. 4 gibt einen Überblick über benötigte Silagemenge üblicher Biogasanlagengrößen.

Tab. 4: Substratmengen bei üblichen Biogasanlagengrößen (Energieausbeute nach KTBL 2006)

<table>
<thead>
<tr>
<th>Anlagengröße</th>
<th>250</th>
<th>500</th>
<th>700</th>
<th>1.000</th>
<th>2.000</th>
<th>20.000</th>
</tr>
</thead>
<tbody>
<tr>
<td>kW_{el} installiert</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tonnen Maissilage (380 kWh_{el} / t FM)</td>
<td>5763</td>
<td>11.526</td>
<td>16.137</td>
<td>23.053</td>
<td>46.105</td>
<td>461.053</td>
</tr>
<tr>
<td>Siloraum (750 kg FM/m³)</td>
<td>7.684</td>
<td>15.368</td>
<td>21.516</td>
<td>30.737</td>
<td>61.474</td>
<td>614.737</td>
</tr>
</tbody>
</table>

Die Konservierung großer Mengen an feuchtem Erntegut erfolgt als Silierung im Fahrsilo oder im Freigärhaufen. Prinzip der Silierung ist die Absenkung des pH-Wertes durch die Bildung organischer Säuren durch mikrobielle Fermentation unter anaeroben Bedingun-

Wesentliche Verlustgrößen bei der Silierung und Substratbereitstellung sind:

- Restatmungsverluste
- Sickersaftverluste
- Verluste durch aerobe Instabilität

Die bei Biogasanlagen benötigten Silagemengen stellen hierbei besondere Anforderungen an das Silagemanagement.

3 Aerobe Stabilität


4 Silierversuche

Im Rahmen von zwei Labor-Silierversuchen wurde der Einfluss der Silierung und einer anschließenden aeroben Exposition an Luftsauerstoff, auf den Methanertrag bestimmt. Als Varianten wurden bei zwei Erntematerialien eine unbehandelte und mit einem heterofermentativen Siliermittel behandelte Silage angelegt.
Tab. 5: Gärparameter und aerobe Stabilität nach 90 Tagen Silierdauer

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>K</td>
<td></td>
<td></td>
<td></td>
<td>35,3</td>
</tr>
<tr>
<td></td>
<td>Beh</td>
<td>35,3</td>
<td>5,8</td>
<td>3,9</td>
<td>22</td>
</tr>
<tr>
<td>II</td>
<td>K</td>
<td>33,8</td>
<td>9,6</td>
<td>4,4</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>Beh</td>
<td>27,5</td>
<td>8,6</td>
<td>4,0</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4,2</td>
<td>&gt; 280</td>
</tr>
</tbody>
</table>

Wie vielfach in der Literatur beschrieben neigen insbesondere energiereiche Silagen zur Nacherwärmung. Dies bestätigt sich auch in den hier untersuchten Maissilagen (Tab. 5). Unter Berücksichtigung der Trockenmasseverluste wirkt sich die Lagerung unter Luftsaugerstoff deutlich auf den Methanertrag der unbehandelten Silagen aus. Durch den Einsatz eines heterofermentativen Siliermittels konnten die Nacherwärmungsverluste verhindert werden.

5 Stoffstromanalyse

Der Flächenbedarf landwirtschaftlicher Biogasanlagen, die ausschließlich mit nawaRo’s betrieben werden, richtet sich im Wesentlichen nach dem energetischen Flächenertrag. Bei einem unterstellten Energieertrag von 1188 kWhel. / t TM ergeben sich für eine Biogasanlage mit 500 kWel. installierter Leistung der nach Tab. 6 berechnete Flächenbedarf in Abhängigkeit des Hektarertrages.

Tab. 6: Flächenbedarf einer 500 kWel. Biogasanlage (1188 kWhel. / t TM)

<table>
<thead>
<tr>
<th>Flächenertrag</th>
<th>t TM</th>
<th>14</th>
<th>17</th>
<th>21</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flächenbedarf</td>
<td>ha</td>
<td>263</td>
<td>217</td>
<td>176</td>
</tr>
</tbody>
</table>

Energieverluste durch unzureichende Silierbedingungen und aerob instabile Silagen haben erhebliche negative Auswirkungen auf die Wirtschaftlichkeit von Biogasanlagen. Dem Biogasprozess vorgelagerte Trockenmasseverluste müssen durch einen höheren Flächenbedarf ausgeglichen werden. In Abb. 1 sind für unterschiedliche Verlustgrößen der entsprechende Flächenmehrbedarf gegenübergestellt.
6 Fazit


Literatur


ECOLOGIC: Biogasnutzung im ländlichen Raum. Der Beitrag verschiedener Anlagenkonzepte zur regionalen Wertschöpfung und ihre Umweltleistung. Institut für internationale und Europäische Umweltpolitik gGmbH 2008


Assessing the overall efficiency of Bavarian pilot biogas plants

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Zusammenfassung


Schlüsselwörter:
Bewertung; Biogasanlage; Effizienz; AHP
Summary

For the assessment of the overall utility or efficiency of biogas plants, particular difficulties arise from the selection of relevant criteria and the assignment of weights to these criteria in an objective manner. In this paper, a methodology for the objective assessment of biogas plant performance is presented. It can be used to compare and rank different biogas plants. The method combines the Analytic Hierarchy Process (AHP) for deriving weights of selected criteria that are relevant to plant performance and Simple Additive Weighing (SAW) to apply these weights to a data set.

In this study, criteria weights were derived by a group of nine reputable experts in the field of biogas. The weights were applied to a data pool from the long-term monitoring of 10 agricultural biogas plants in Bavaria. Using the proposed methodology, a ranking order of the biogas plants could be determined based on technical, environmental and economical criteria. In addition, possible reasons for inefficiency of individual plants could be recognized.

Keywords:
Assessment; biogas plant; efficiency; AHP
1 Introduction

Since 2001, on the basis of incentives for “green” electricity defined in the Renewable Energy Law (EEG), the number of biogas plants has grown rapidly in Germany. Thereby the production of biogas from energy crops and animal manure has become an important branch of agricultural production. Consequently, assessing and comparing biogas plants with respect to their performance are of great interest, both for the individual plant owner and the overall economy of energy supply from biogas.

The complex process chain of biogas production and utilization consists of: 1) growing, harvesting and transporting energy crops or collecting manure; 2) digesting the input material to produce biogas; 3) utilizing the biogas to produce energy (electricity and heat); and 4) handling and utilizing the digested residue (EFFENBERGER et al., 2008). This process chain is defined by manifold parameters. The assessment of the performance of biogas plants is a multi-criteria problem for which multi-criteria decision making (MCDM) methods are suitable.

MCDM methods are used to solve problems of ranking several alternatives (in this case biogas plants) with respect to selected criteria. All methods require the assignment of criteria weights in order to obtain a measure of overall utility. The difficulty in this assignment is connected to the analyst’s personal tendencies, field of expertise, etc., which inevitably leads to a subjective assessment. Therefore, a larger number of experts from different fields should be involved, in order to achieve objectivity.

So far, few methodologies for the assessment of biogas plants performance have been proposed. MADLENER et al. (2009) compared MCDM and data envelopment analysis (DEA) for assessing the performance of biogas plants in terms of economic, environmental and social criteria. They proposed the complementary use of these two methods. MCDM was used to assign the evaluated biogas plants to categories (poor, fair, good or very good) and DEA served to identify performance inefficiencies as distances from efficiency frontiers. None of these two methods incorporates experts’ preferences concerning the relative importance of criteria.

The objectives of this research were: 1) To define and select performance figures that are most relevant for the assessment of biogas plant performance; 2) To propose a methodology for the assessment of biogas plant performance that facilitates the incorporation of experts’ preferences. The proposed methodology should overcome the problem of subjectivity and be applicable to any set of biogas plants. The goal was to derive a single measure of efficiency for ranking and comparing various biogas plants. The task was verified by the assessment of ten Bavarian pilot biogas plants.

2 Materials and methods

2.1 Biogas plants

Ten medium-sized agricultural biogas plants were to be assessed based on close monitoring over a period of two years. The plants reflect the diversity of geographical locations and technical concepts of biogas installations in Bavaria. Some of their technical characteristics are presented in Table 1. A detailed description of the ten biogas plants and their concepts can be found in EFFENBERGER et al. (2009).
Tab. 1: Technical characteristics of 10 Bavarian biogas plants

<table>
<thead>
<tr>
<th>Technical characteristics</th>
<th>Unit</th>
<th>Biogas plant ID</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Total digester volume*</td>
<td>m³</td>
<td>3,015</td>
</tr>
<tr>
<td>CHPU engine type</td>
<td>–</td>
<td>G</td>
</tr>
<tr>
<td>Rated electrical capacity</td>
<td>kW</td>
<td>329</td>
</tr>
<tr>
<td>Rated thermal capacity</td>
<td>kW</td>
<td>447</td>
</tr>
</tbody>
</table>

1) G: Gas engine; 2) PI: Pilot-injection engine; *) Sum of the usable volume of all process stages of the biogas plant excluding digested residue storage.

2.2 Analytic Hierarchy Process (AHP)

AHP was originally developed by Thomas Saaty (Saaty, 1980; Saaty, 1986). It structures a complex problem into hierarchy and thereby simplifies it. The goal of the procedure is placed at the top while the assessment of criteria and alternatives (e.g. biogas plants) are on the lower levels and sublevels of the hierarchy (Figure 1). After structuring the problem, an expert (decision maker) is making pair wise comparisons of elements on each level of the hierarchy with respect to the element on the next higher level. Elements are assessed by means of the proposed Saaty’s scale of relative importance. The outcome is a set of overall utilities for the alternatives, extracted by the technique of eigenvector. As an intermediate result, weights of relative importance of criteria are obtained.

The method is constrained by the effort and time that experts have to spend on the problem when the number of criteria and alternatives is large. Already in this study, with 10 alternatives to be assessed with respect to 8 criteria, the number of pair wise comparisons in AHP would be 360. This would have been impracticable for the decision makers (experts). Therefore, the AHP methodology was used only for obtaining criteria weights. The eight criteria described in section 2.4 were firstly divided into four categories (Figure 1): 1) biogas production; 2) biogas utilization; 3) environmental and 4) socio-economic impact. Secondly, biogas production and biogas utilization were subsumed in the category of biogas plant efficiency.

Fig. 1: Hierarchical structure of the problem in AHP: Derivation of weights of relative importance of criteria (C1-C8: selected criteria for assessment of biogas plants)
Criteria weights were derived by a group of nine reputable experts in the field of biogas: practitioners, biogas plant operators, agro-economists and government officials. Final weights were calculated as the arithmetic mean of individual experts’ ratings.

2.3 Simple Additive Weighting (SAW)

SAW (Hwang & Yoon, 1981), also known as the weighted sum method, is the simplest and most frequently used MCDM method. It directly applies criteria weights \( w_j \) to criteria values for each alternative \( x_{ij} \). After weighting, an overall utility value \( U_i \) is calculated for each alternative with respect to all criteria (Equation 1) and afterwards normalized \( (n \) is the number of alternatives to be assessed while \( m \) represents the number of criteria). The alternatives are ranked in descending order where the best alternative has the highest utility value. Hereinafter, the measure of utility is called overall efficiency as the result of the assessment of biogas plant performance.

\[
U_i = \sum_{j=1}^{m} w_j x_{ij} \quad i = 1...n
\]

In order to obtain criteria values for each alternative \( x_{ij} \), values of performance criteria are scaled in the non-dimensional range between 0 and 1. This is required for the calculation of an efficiency value by summation of weighted criteria values that have different dimensions and are expressed in different units (e.g. %, €*kWhel⁻¹, etc.). Additionally, some of the criteria are minimizing such as cost and some of them are maximizing such as profit. Therefore, value 0 was always assigned to the worst and value 1 to the best performance.

2.4 Criteria for assessment of biogas plant performance

During the monitoring, about 100 parameters were collected on each of the biogas plants. Numerous performance figures were derived from these parameters (see Effenberger et al., 2008; 2009; Bachmaier & Gronauer, 2007). Comprehensive overviews of performance figures in biogas production are given in Schöftner et al. (2006), Strobl & Keymer (2006), and Braun et al. (2007). Eight of these figures were chosen as criteria for the assessment with MCDM methods.

Prerequisites for the selection were:

- Data availability: Plant operators should be able to collect all necessary data with simple and affordable measurement devices;
- Accuracy of measurement and simplicity of calculation;
- Ability to compare biogas plants with different sizes, concepts, input materials, etc.;
- Coverage of all aspects of biogas production and utilization: technical, environmental and economic.

The decision matrix with standardized (scaled) criteria values for the ten biogas plants that were assessed in this study is presented in Table 2.
2.4.1 C1: Relative methane yield, %

An indicator of the degradation efficiency of the input materials is described by the relative methane yield \((Y_r)\). It is computed as the ratio of measured methane yield \((Y_m)\) and potential methane yield \((Y_p)\) based on animal feed value analysis:

\[
Y_r = \frac{Y_m}{Y_p}
\]

2.4.2 C2: Methane productivity, \(\text{Nm}^3*(\text{m}^3*\text{d})^{-1}\)

The methane productivity describes the efficiency of biogas production in the digester. It is the ratio of daily methane production rate \((M_p)\) and usable digester volume \((V_d)\):

\[
P = \frac{M_p}{V_d}
\]

2.4.3 C3: Utilization ratio of CHPU, %

The utilization ratio of the combined-heat-and-power unit \((UCHPU)\) is the ratio of realized total electricity production \((E_p)\) and theoretical electricity production given 100% availability \((E_t)\), over the same period of time.

\[
U_{UCHPU} = \frac{E_p}{E_t}
\]

2.4.4 C4: Degree of methane utilization, %

The degree of methane utilization is the sum of electricity production \((E_p)\) less the electricity demand of the biogas plant \((E_d)\) and the heat that is utilized outside the biogas plant \((Q_{ext})\), related to the lower heat value of the methane contained in the biogas \((H_m)\).

\[
U_M = \frac{E_p - E_d + Q_{ext}}{H_m}
\]

2.4.5 C5: Specific GHG emissions, \(\text{g CO}_2\text{eq}*\text{kWh}_{el}^{-1}\)

The specific greenhouse gas emissions \((E_{GHG})\) of electricity production from biogas are determined as the difference between emitted \((E_e)\) and avoided amounts of GHG \((E_a)\) from the entire cycle of biogas production and utilization, including the supply of the input materials and the treatment and disposal of the digested residue, specified to the amount of electricity produced from biogas \((E_p)\).

\[
E_{GHG} = \frac{E_p}{E_e} E_{GHG} = \frac{E_a - E_e}{E_p}
\]

2.4.6 C6: Cumulated energy demand, \(\text{kWh}*\text{kWh}_{el}^{-1}\)

The cumulated energy demand \((CED)\) is the sum of energy input from fossil resources for the construction \((ED_c)\), operation \((ED_o)\) and removal \((ED_r)\) of the biogas plant, specified to the amount of produced electricity \((E_p)\).

\[
CED = \frac{ED_c + ED_o + ED_r}{E_p}
\]
2.4.7 C7: Profit, €*kWh⁻¹

The profit is calculated as the difference between total yearly income (I) and cost (C) of agricultural biogas production, specified to the amount of produced electricity (E_p).

\[ P = \frac{I - C}{E_p} \]  

2.4.8 C8: Labor input, Lh*kWh⁻¹

The labor input (L) is the sum of labor hours spent for operation (L_o), maintenance (L_m) and repairs (L_r) of the biogas plant, specified to the amount of produced electricity (E_p).

\[ L = \frac{L_o + L_m + L_r}{E_p} \]

Tab. 2: Standardized criteria values for ten agricultural biogas plants

<table>
<thead>
<tr>
<th>Criterion</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.5464</td>
<td>0.7322</td>
<td>0.5758</td>
<td>0.6766</td>
<td>0.5065</td>
<td>0.0000</td>
<td>0.5612</td>
<td>0.7367</td>
<td>1.0000</td>
<td>0.6066</td>
</tr>
<tr>
<td>C2</td>
<td>0.2097</td>
<td>0.0608</td>
<td>0.2498</td>
<td>0.6559</td>
<td>0.6314</td>
<td>0.2222</td>
<td>0.6845</td>
<td>0.1787</td>
<td>1.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>C3</td>
<td>1.0000</td>
<td>0.6068</td>
<td>0.8940</td>
<td>0.5280</td>
<td>0.9818</td>
<td>0.8336</td>
<td>0.9566</td>
<td>0.8578</td>
<td>0.0000</td>
<td>0.7751</td>
</tr>
<tr>
<td>C4</td>
<td>0.0122</td>
<td>0.0000</td>
<td>1.0000</td>
<td>0.5508</td>
<td>0.5383</td>
<td>0.8000</td>
<td>0.3466</td>
<td>0.5923</td>
<td>0.3625</td>
<td>0.3519</td>
</tr>
<tr>
<td>C5</td>
<td>0.0079</td>
<td>0.2283</td>
<td>0.8189</td>
<td>0.2795</td>
<td>1.0000</td>
<td>0.5866</td>
<td>0.2756</td>
<td>0.0000</td>
<td>0.4291</td>
<td>0.4488</td>
</tr>
<tr>
<td>C6</td>
<td>0.0606</td>
<td>0.0000</td>
<td>0.9091</td>
<td>0.3333</td>
<td>1.0000</td>
<td>0.9697</td>
<td>0.0000</td>
<td>0.0303</td>
<td>0.2879</td>
<td>0.6515</td>
</tr>
<tr>
<td>C7</td>
<td>0.5500</td>
<td>0.0000</td>
<td>0.8300</td>
<td>1.0000</td>
<td>0.9400</td>
<td>0.9200</td>
<td>0.7200</td>
<td>0.5000</td>
<td>0.4300</td>
<td>0.8300</td>
</tr>
<tr>
<td>C8</td>
<td>0.4000</td>
<td>0.8500</td>
<td>0.7800</td>
<td>1.0000</td>
<td>0.9400</td>
<td>0.9200</td>
<td>0.7200</td>
<td>0.5000</td>
<td>0.4300</td>
<td>0.8300</td>
</tr>
</tbody>
</table>

3 Results

The criteria weights from 9 individual experts and assessments with AHP are presented in Table 3. The set of overall criteria weights for the entire group of experts is presented in Figure 2. After applying criteria weights with SAW to the criteria values, the ten biogas plants were ranked according to their overall efficiencies (Figure 3).

Tab. 3: Criteria weights from 9 individual experts

<table>
<thead>
<tr>
<th>Criteria weights from individual experts</th>
<th>Statistical data</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>C1</td>
<td>0.001</td>
</tr>
<tr>
<td>C2</td>
<td>0.012</td>
</tr>
<tr>
<td>C3</td>
<td>0.017</td>
</tr>
<tr>
<td>C4</td>
<td>0.050</td>
</tr>
<tr>
<td>C5</td>
<td>0.107</td>
</tr>
<tr>
<td>C6</td>
<td>0.015</td>
</tr>
<tr>
<td>C7</td>
<td>0.718</td>
</tr>
<tr>
<td>C8</td>
<td>0.080</td>
</tr>
</tbody>
</table>

*σ: Standard deviation; †CV: Coefficient of variation.
Fig. 2: Overall criteria weights derived with nine experts

Fig. 3: Ranking order of ten Bavarian pilot biogas plants
4 Discussion

The ten biogas plants assessed in this study were thoroughly monitored over a longer time period. Compared to similar studies, less biogas plants were investigated, while the parameters were collected exhaustively and continually. Possible measurement errors were minimized and removed timely. Therefore, the quality of the data pool that was used for this assessment is considered a particular strength of the study.

The criteria weights presented in Table 3 show that profit was the most important criterion for all experts. Nevertheless, the weights for all criteria varied between individual experts. By averaging these subjective decisions, the result presented in Figure 2 becomes objective and partly satisfies all experts. By structuring the problem in AHP (Figure 1), full consistency was assured, since only two and, in one case three comparisons had to be made. Derived weights may be applied to the assessment of any other set of biogas plants. If necessary, it is possible to derive new criteria weights. Furthermore, another set of criteria could be selected according to changing trends of environmental and economic impacts. An alternative group of biogas experts could participate as well.

Due to the fact that profit was assigned by far the highest weight, the biogas plants with good economic performance received the highest ranks for overall efficiency (D, C, F and E), while the biogas plant with the worst economics (B) clearly lost (Figure 3). In some cases, the connectivity between good (C, F and E) or poor (A and B) economic performance with other aspects of performance was obvious. By analyzing only fragments of overall efficiency, it is possible to get an insight into which aspect of the assessment determined overall efficiency of the individual biogas plants. For example, in comparison of plants D and I, their efficiency was similar except for the profit, which placed plant D on the first and plant I on the seventh rank.

By calculating cardinal numbers for overall efficiency, a ranking order for the biogas plants was obtained. Beyond that, the biogas plants could be assigned to particular groups of efficiency. For example, plants D, C, F, E and J may be assigned to the group with “good”, plants G and I to the group with “average”, and plants H, A and B to the group of biogas plants with “poor” efficiency (Figure 3). The measures of overall efficiency are relative indexes of performance and are not comparable with the efficiency measures from another set of biogas plants. For example, an overall efficiency value of 1 for plant D states that this plant is ranked first (best) among all of the ten biogas plants, but not that it is 100 % efficient or two times more efficient than biogas plant A with an overall efficiency value of 0.5.

5 Conclusions

Based on thorough monitoring of ten Bavarian biogas plants, eight characteristic figures were derived and selected as criteria that are relevant to the assessment of biogas plant performance. These eight criteria explicitly describe technical, socio-economic and environmental aspects of performance.

The proposed methodology for the assessment of biogas plant performance comprises the AHP method for deriving criteria weights and applying these weights to the data set using SAW. For the derivation of objective criteria weights, a group of experts is involved. A single number of biogas plant performance (overall efficiency) can be computed and a ranking order can be determined. Besides the ranking of different biogas plants, the pro-
posed methodology gives an insight into possible reasons for efficient or inefficient performance.

Future investigations should focus on the improvement of the methodology, particularly by incorporating more criteria into the assessment and achieving absolute comparisons.

6 Acknowledgements

This research was supported by the German Academic Exchange Service (DAAD) and the Bavarian State Ministry for Food, Agriculture and Forestry.

References


EFFENBERGER, M., H. BACHMAIER, E. KRÄNSEL, A. LEHNER and A. GRONAUER (2009): Wissenschaftliche Begleitung der Pilotbetriebe zur Biogasproduktion in Bayern (in German); Abschlussbericht, Projekt im Auftrag des Bayerisches Staatsministerium für Ernährung, Landwirtschaft und Forsten, Bayerische Landesanstalt für Landwirtschaft (LfL), Freising, August/2009


Die Zielsetzung der vorliegenden Studie ist es, die Energieeffizienz von Silomais für die Stromproduktion unter Berücksichtigung der vollständigen Produktionskette zu bestimmen. Bei der Betrachtung der CO₂-Emissionen wurden nicht nur die energiebedingten Emissionen berücksichtigt, sondern z.B. auch der Humusabbau unter Mais, der das Ergebnis deutlich beeinflusst.

Tab. 1: Kennzahlen der Energiebilanz von Silomais zur Stromerzeugung aus Biogas in Abhängigkeit der Düngerart

<table>
<thead>
<tr>
<th>Kennzahl</th>
<th>ME</th>
<th>Null</th>
<th>MD</th>
<th>OD</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ernteertrag (dt TM ha⁻¹)</td>
<td>213</td>
<td>240</td>
<td>241</td>
<td>236</td>
<td></td>
</tr>
<tr>
<td>Energiebindung Biomasse (GJ ha⁻¹)</td>
<td>390</td>
<td>440</td>
<td>444</td>
<td>435</td>
<td></td>
</tr>
<tr>
<td>Energieeinsatz – gesamt (GJ ha⁻¹)</td>
<td>8,4</td>
<td>12,9</td>
<td>9,2</td>
<td>10,7</td>
<td></td>
</tr>
<tr>
<td>1. Maisproduktion (GJ ha⁻¹)</td>
<td>1,5/0,0</td>
<td>5,8/0,0</td>
<td>1,5/4,9</td>
<td>3,3/2,1</td>
<td></td>
</tr>
<tr>
<td>2. Bau &amp; Betrieb der Biogasanlage (GJ ha⁻¹)</td>
<td>15,5</td>
<td>17,4</td>
<td>17,5</td>
<td>17,2</td>
<td></td>
</tr>
<tr>
<td>Energieoutput (Strom brutto) (GJ ha⁻¹)</td>
<td>84,0</td>
<td>94,7</td>
<td>95,1</td>
<td>93,3</td>
<td></td>
</tr>
<tr>
<td>Energieintensität (Energieeinsatz pro kWh erzeugt) (MJ kWh⁻¹)</td>
<td>1,0</td>
<td>1,2</td>
<td>1,0</td>
<td>1,1</td>
<td></td>
</tr>
<tr>
<td>Output/Input-Verhältnis</td>
<td>2,5</td>
<td>2,1</td>
<td>2,6</td>
<td>2,3</td>
<td></td>
</tr>
</tbody>
</table>

* Null: Nullparzelle mit 30 kg N ha⁻¹ zur Saat, MD: Mineral. Düngung, OD: Organ. Düngung mit Gärrest, MW Mittelwert


Die Nutzung von Silomais zur Stromerzeugung aus Biogas führte zur Reduktion von klimarelevanten Emissionen in Höhe von etwa 8400 kg CO₂eq ha⁻¹ durch die Substitution einer entsprechenden Strommenge unter den Bedingungen des deutschen Strommixes (Tab. 2). Die C-Freisetzung des Bodens schlug mit nahezu 70 % der CO₂-Emissionen aus der Maisproduktion sehr stark zu Buche. Zwischenfrüchte und weitgestellte Fruchtfolgen sind daher beim Maisanbau unabdingbar für eine klimafreundliche und nachhaltige Energieproduktion.
**Tab. 2: Kennzahlen der CO₂-Bilanz von Silomais zur Stromerzeugung aus Biogas in Abhängigkeit der Düngart**

<table>
<thead>
<tr>
<th>Kennzahl</th>
<th>ME</th>
<th>Null*</th>
<th>MD</th>
<th>OD</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ernteertrag</td>
<td>TM dt ha⁻¹</td>
<td>213</td>
<td>240</td>
<td>241</td>
<td>236</td>
</tr>
<tr>
<td>Energiebindung</td>
<td>GJ ha⁻¹</td>
<td>390</td>
<td>440</td>
<td>444</td>
<td>435</td>
</tr>
<tr>
<td>Methanertrag</td>
<td>m³ ha⁻¹</td>
<td>6665</td>
<td>7517</td>
<td>7545</td>
<td>7408</td>
</tr>
<tr>
<td>Stromertrag</td>
<td>kWh el ha⁻¹</td>
<td>23328</td>
<td>26308</td>
<td>26407</td>
<td>25928</td>
</tr>
<tr>
<td>Einsatz fossiler Energie</td>
<td>GJ ha⁻¹</td>
<td>8</td>
<td>13</td>
<td>14</td>
<td>13</td>
</tr>
<tr>
<td>N-Zufuhr (ohne NH₃-Verluste)</td>
<td>kg N ha⁻¹</td>
<td>49</td>
<td>163</td>
<td>151</td>
<td>142</td>
</tr>
<tr>
<td>Δ C Humus</td>
<td>kg Hu-C ha⁻¹</td>
<td>-1177</td>
<td>-1177</td>
<td>-818</td>
<td>-1023</td>
</tr>
<tr>
<td>CO₂-Emissionen Energieeinsatz</td>
<td>kg CO₂eq ha⁻¹</td>
<td>573</td>
<td>835</td>
<td>621</td>
<td>706</td>
</tr>
<tr>
<td>N₂O-Emissionen</td>
<td>kg CO₂eq ha⁻¹</td>
<td>286</td>
<td>948</td>
<td>879</td>
<td>824</td>
</tr>
<tr>
<td>C-Freisetzung Boden</td>
<td>kg CO₂eq ha⁻¹</td>
<td>4321</td>
<td>4321</td>
<td>3001</td>
<td>3755</td>
</tr>
<tr>
<td>CO₂-Emissionen Maisanbau</td>
<td>kg CO₂eq ha⁻¹</td>
<td>5179</td>
<td>6105</td>
<td>4501</td>
<td>5285</td>
</tr>
<tr>
<td>CO₂-Emissionen Bau &amp; Betrieb</td>
<td>kg CO₂eq ha⁻¹</td>
<td>2286</td>
<td>2578</td>
<td>2588</td>
<td>2541</td>
</tr>
<tr>
<td>CO₂-Emissionen Substitution dt. Strommix</td>
<td>kg CO₂eq ha⁻¹</td>
<td>-14626</td>
<td>-16495</td>
<td>-16557</td>
<td>-16257</td>
</tr>
<tr>
<td>CO₂-Bilanz–Saldo</td>
<td>kg CO₂eq ha⁻¹</td>
<td>-7161</td>
<td>-7813</td>
<td>-9468</td>
<td>-8431</td>
</tr>
</tbody>
</table>

* Null: Nullparzelle mit 30 kg N ha⁻¹ zur Saat, MD: Mineral. Düngung, OD: Organ. Düngung mit Gärrest, MW Mittelwert
Zusammenfassung


Summary

Biogas plants as well as big dairy farms have to harvest a few thousand tons of biomass every year to ensure the feeding of the cows or the plant. This handling of the biomass spends a lot of time and money. Thereby the optimization of the harvest in economical and ecological aspects gains in importance. In the point of view of the author, the optimization has to base on farm-specific key figures. It’s the task of the manager to acquire the required data and to calculate and interpret these farm-specific key figures. This paper discusses an applicable method to do this in a convenient way. The data acquisition focuses on the required machine-hours and man-hours, the consumption of fuel, the cash flow and last but not least the mass of the fresh biomass with its specific content of dry matter. The data evaluation focuses on key figures, optionally specified at different levels of detail (whole farm, machines, per ton biomass). This year the method was introduced on several farms of Bavaria with success in order to prove its practicability.

Schlüsselwörter:

Biomasse, Logistik, Bewertung, Optimierung

biomass, logistics, evaluation, optimization
1 Einleitung


![Biomasse-Erntelogistik](image)

Abb. 1: Biomasse-Erntelogistik

2 Zielsetzung


3 Methode


Die Bewertung der Biomasse-Erntelogistik erfordert die Erfassung der sechs in Tabelle 1 dargestellten absoluten Kenngrößen. In der Tabelle sind ebenfalls die Einheiten sowie Vorschläge zur Art der Erfassung und Dokumentation angegeben.


Der horizontale und vertikale Vergleich mit anderen Ernteketten wird ermöglicht, indem die absoluten Kenngrößen je Tonne Erntemenge (Frisch- oder Trockenmasse) ausgewiesen werden. Das Ergebnis sind abgeleitete, von der Größe der Erntekette unabhängige Kennwerte mit direkter Vergleichbarkeit.
Im folgenden Beispiel werden alle Kenngrößen aggregiert auf die gesamte Erntelogistik diskutiert. Für Detailanalysen können sie aber auch getrennt nach einzelnen Prozessgliedern oder Maschinen erfasst und später ausgegeben werden.

4 Praxisbeispiel

Praktisch angewendet wurde diese Methode bereits bei einigen Ernteketten auf Pilot-Biogasanlagen der Bayerischen Landesanstalt für Landwirtschaft. Im vorliegenden Beispiel handelt es sich um eine siebentägige Maisernte mit gut 160 Hektar Erntefläche bei durchschnittlich sechs Luftlinien-Kilometer Transportentfernung.

Tab. 1: Absolute und abgeleitete Kenngrößen


Die daraus abgeleiteten Kennwerte sind in den Spalten „Kennwert: 1/t FM“ und „Kennwert 1/t TM“ aufgelistet. Für das vorliegende Beispiel wurden in diesem Sinne für die Erntelogistik einer Tonne Frischmasse aggregiert 1,97 Liter Kraftstoff verbraucht, 0,09 Stunden Maschinen eingesetzt, im Umfang von 0,10 Stunden Personen beschäftigt und in Höhe von 5,83 Euro Auszahlungen verursacht.

5 Ausblick

Experiences and regulations for the use of off-farm source materials as co-substrates for farm based digesters in the Province of Ontario, Canada

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2 Ministry of the Environment, 2 St. Clair Avenue West, Floor 12A, Toronto, ON, M4V 1L5, Canada

Summary

Farm based biodigesters using some off farm source co-substrates are operating effectively in Ontario, Canada. Recent changes to legislation improve the volumes and broaden the types of co-substrates that can be utilized.

Ontario’s new FIT Program gives a 20 year contract, which should foster continued development of biogas systems. The result is that farmers can treat their manure to reduce odour and pathogens as well as capture economic opportunities in the new green economy.

1 Introduction

The Province of Ontario is located in the central part of Canada, bordering the Great Lakes. Ontario is a center of significant livestock production, and has a moderate climate suitable for extensive grain and oilseed production. By the middle of 2010 Ontario should have over 20 farm based digesters operating with almost all blending manure or food processing byproducts with off farm source material such as grease trap wastes. This paper describes an example of a farm based digester and outlines recent regulation developments that enable these systems. Finally, this paper describes the effect of the new Green Energy Act (GEA) in the development of farm based biogas systems projects.

2 Ontario example – Biogas system blending dairy manure with grease trap waste

2.1 Initial phase (manure only)

Fepro Farms near Cobden, Ontario (located North East of Ottawa) installed a biogas system (Figure 1) in 2003 at their 140 cow dairy barn. This system ran only on manure and produced about 35 kW of power continuously (about 0.25 kW per milking cow). The digester was built into a side of an existing tank, with a capacity of about 450 m3, and an average retention time of 30 days.
2.2 First expansion (adding some of off-farm materials)

In 2007, Fepro Farms installed a system to add off-farm material (Figure 2). They obtained a Certificate of Approval (C of A) from the Ontario Ministry of the Environment (MOE). One condition of the C of A was that any Fats, Oils and Grease (FOG) such as Dissolved Air Floatation (DAF) material or grease trap material brought to the farm must be pasteurized prior to entry into the digester and blending with the manure.
2.3 Second expansion (500 kW (el) production)

In 2008, Fepro Farms initiated an expansion of the biogas facility including construction of three kilometres of 3 phase electrical lines to allow the production of 500 kW continuously (Figure 4). Construction was completed in early 2009.

Since June 2009, the system has been successfully operating at a continuous 500 kW (el) (>3 kW per cow). Predominate inputs are 15 tonnes per day of FOG (typically grease trap waste at 70% moisture) per day and 15 tonnes per day of dairy manure (no change from initial phase). The only operational issues experienced so far, are shutdowns caused by the anti-islanding grid protection system. At the time of writing, the operation is experiencing about 3 shutdowns per week. The system reboots automatically however the farmer is concerned about the effect of the fast shutdowns on the engine.

Surplus heat from the generation unit is used to heat 2 farm homes and a grain drying system. The farmer is considering setting up a process to dehydrate digestate with the remaining available heat.
2.4 Treatment effect of adding off-farm materials on example farm

A project was completed by the University of Guelph to measure the treatment effects. Table 1 shows the results of the testing of treatment effects of digestion between the input raw manure and the effluent (called digested manure). The effect of adding FOG is shown in the second set of columns. Note that any additional input of bacteria from the FOG materials is not included in the raw manure concentrations.

Tab. 1: Pathogen reductions in the Fepro farm digester (Crolla, 2008)

<table>
<thead>
<tr>
<th>Pathogen</th>
<th>Geometric Mean Bacteria Concentrations (CFU 100 mL^-1)</th>
<th>Fepro Farm Digester Without FOG</th>
<th>Fepro Farm Digester With FOG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw Manure</td>
<td>Digested Manure</td>
<td>Log Reduction</td>
</tr>
<tr>
<td>E.coli</td>
<td>4.33 E+08</td>
<td>2.26 E+05</td>
<td>3.29</td>
</tr>
<tr>
<td>Log STDEV</td>
<td>0.82</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>Salmonella</td>
<td>2.04 E+04</td>
<td>2.43 E+03</td>
<td>0.92</td>
</tr>
<tr>
<td>Log STDEV</td>
<td>0.94</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>C.perfringens</td>
<td>3.82 E+06</td>
<td>6.71 E+05</td>
<td>0.75</td>
</tr>
<tr>
<td>Log STDEV</td>
<td>0.54</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>Enterococci</td>
<td>1.69 E+07</td>
<td>1.53 E+06</td>
<td>1.05</td>
</tr>
<tr>
<td>Log STDEV</td>
<td>0.29</td>
<td>0.31</td>
<td></td>
</tr>
</tbody>
</table>

1 Mean is calculated based on 55 samples (n=55)
2 Mean is calculated based on 23 samples (n=23)
2.5 Odour Effect of Adding Additional Materials on Example Farm

Table 2 compares total volatile fatty acid reduction that the author (Crolla, 2008) used as a measure of odour reduction. Note that the reduction is higher when the FOG is added and this does not include the acids added due to the addition of the FOG.

Tab. 2: Volatile fatty acids (odours) reduction at the Fepro farm digester (Crolla, 2008)

<table>
<thead>
<tr>
<th></th>
<th>Raw Manure</th>
<th></th>
<th></th>
<th></th>
<th>Digested Manure</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetic Acid (mg L⁻¹)</td>
<td>Propionic Acid (mg L⁻¹)</td>
<td>Butyric Acid (mg L⁻¹)</td>
<td>TVFA (mg L⁻¹)</td>
<td>Acetic Acid (mg L⁻¹)</td>
<td>Propionic Acid (mg L⁻¹)</td>
<td>Butyric Acid (mg L⁻¹)</td>
<td>TVFA (mg L⁻¹)</td>
</tr>
<tr>
<td>Fepro Digester Without FOG as Co-substrate (n = 45)</td>
<td>Mean</td>
<td>4760</td>
<td>1248</td>
<td>911</td>
<td>6919</td>
<td>252</td>
<td>78</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>STDEV</td>
<td>1713</td>
<td>496</td>
<td>347</td>
<td>2471</td>
<td>165</td>
<td>63</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>% Red.</td>
<td>95</td>
<td>94</td>
<td>99</td>
<td>95</td>
<td>95</td>
<td>94</td>
<td>99</td>
</tr>
<tr>
<td>Fepro Digester With FOG as Co-substrate (n = 19)</td>
<td>Mean</td>
<td>4988</td>
<td>1432</td>
<td>734</td>
<td>7154</td>
<td>92</td>
<td>42</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>STDEV</td>
<td>1231</td>
<td>649</td>
<td>413</td>
<td>1221</td>
<td>38</td>
<td>35</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>% Red.</td>
<td>98</td>
<td>97</td>
<td>&gt;99</td>
<td>98</td>
<td>98</td>
<td>97</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

3 Use of off-farm source materials as co-substrates for farm based digesters

Almost all farm based biogas projects in Ontario are utilizing co-substrates. Utilization of these materials improves the economic viability of the operations. Proper use of these materials helps solve Ontario’s waste management issues as well.

3.1 Recent Ontario legislation dealing with adding off-farm source materials to on-farm biogas systems

A facility that receives and processes off farm source co-substrates must obtain a C of A under the Environmental Protection Act (EPA). In addition, sites where digestate (not designated as fertilizer by the Canadian Food Inspection Agency) is land applied also need to have a C of A (Hilborn and Keyvani, 2008).

There are exemptions to the above legal requirements if the farm biogas system is designated as a “Regulated Mixed Anaerobic Digestion Facility” under the Nutrient Management Act – 2002 (NMA). To achieve this designation the facility must be located on a farm unit and must complete a strategy showing it meets a number of criteria including:

- Off-farm material volume limits (including no more than 25% of total inputs or 10,000 m³ per year, whichever is lower)
- Specific off-farm material types,
- Minimum manure content requirement
- Need for pre-treatment for certain types of inputs
In addition, under the NMA, anaerobic digestion (AD) output is defined as agricultural source material (i.e. no C of A is required for land application) if the treatment is completed in a mixed AD facility (defined as on a farm unit on which an agricultural operation is carried out) and at least 50% of the inputs by volume are on-farm AD materials (materials generated in a farm operation).

### 3.2 Use of legislation

Up to now, most on-farm AD systems have selected to obtain a C of A under the EPA. This allows the facilities to accept materials such as grease trap wastes from restaurants. Recent legislative changes in Ontario allow these desired materials to be included at a “Regulated Mixed Anaerobic Digestion Facility” under the NMA without requiring to obtain a C of A. It is expected that more facilities will use the NMA approach especially since a higher Feed-In Tariff (FIT) price can be obtained (see section 4).

### 3.3 Available off-farm source co-substrates in Ontario

A study (DeBruyn, Hilborn, Dick (2008)), commissioned by Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA), concluded there are between 1.2 and 9.8 million wet tonnes per year of suitable food-based inputs that are produced in Ontario. This study determined that if the estimated 50 per cent of available food-based inputs are used in biogas systems a 30% efficient co-generation unit would produce from 53 to 697 gigawatt-hours/year (GWh/yr) of electrical production. This is equivalent to 6.1 to 80 megawatts (MW) of continuous electrical capacity, or 27 to 350 MW of peak power production.

### 4 Ontario feed-in tariff program

The Feed-In Tariff (FIT) program is Ontario’s new electricity price program for power from renewable energy sources. The FIT program is being deployed by the Ontario Power Authority to support the GEA. FIT is the next generation of pricing, following in the footsteps of the former Renewable Energy Standard Offer Program (RESOP). FIT offers a range of prices for electricity from different technologies based on the cost of power production from those systems. Table 3 provides the currently proposed FIT prices for biogas.

<table>
<thead>
<tr>
<th>Location Restrictions</th>
<th>Size</th>
<th>Price (¢/kWh)</th>
<th>Average</th>
<th>On-Peak Hours</th>
<th>Off-Peak Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-Farm</td>
<td>≤ 100 kW</td>
<td>19.5</td>
<td>26.325</td>
<td>17.55</td>
<td></td>
</tr>
<tr>
<td>On-Farm</td>
<td>&gt;100 kW ≤ 250 kW</td>
<td>18.5</td>
<td>24.975</td>
<td>16.65</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>≤ 500 kW</td>
<td>16</td>
<td>21.6</td>
<td>14.4</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>&gt;500 kW ≤ 10 MW</td>
<td>14.7</td>
<td>19.845</td>
<td>13.23</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>&gt;10 MW</td>
<td>10.4</td>
<td>14.04</td>
<td>9.36</td>
<td></td>
</tr>
</tbody>
</table>
There are many details associated with securing a contract with these prices. Check FIT program documentation at http://www.powerauthority.on.ca/fit/. Several important factors related to the prices:

- Twenty percent (20%) of the FIT price will be increased year to year based on the Consumer Price Index (society’s inflation factor).
- There are additional bonuses for community projects (0.4 ¢/kWh) and for projects with Aboriginal Community participation (0.6 ¢/kWh) at biogas projects.
- The on-peak hours are 11:00 am to 7:00 pm on business days, and off-peak hours are any other time. Biogas systems should be able to capture virtually all on-peak hours.
- To satisfy the “On-Farm” designation, biogas systems must be a “Regulated Mixed Anaerobic Digestion” facility under the NMA.

4.1 Streamlined grid connections: Capacity allocation

The Ontario Energy Board (OEB) has established streamlined connection rules for “capacity allocation exempt” generation facilities, that is, for facilities which have a name-plate rated capacity of:

- \( \leq 250 \text{ kW} \) and connected to a less than 15 kV electrical line; or
- \( \leq 500 \text{ kW} \) and connected to a 15 kV or greater electrical line;

and which are not a micro-embedded generation facility. (Micro-embedded generation facilities are smaller than 10 kW, and have additional allowances in the OEB Distribution System Code).

4.2 Setbacks from conflicting uses

The new Renewable Energy Approvals Regulation (O. Reg. 359/09) made under the GEA sets out the process for obtaining Renewable Energy Approval (REA) for biogas systems. The regulation also outlines the setbacks between new biogas systems and their neighbours.

Farms that operated under the NMA “Regulated Mixed Anaerobic Digestion” rules are exempted from the REA requirements, but will typically still have to comply with a Minimum Distance Separation formula used for livestock facilities and manure storages.

Under the new REA, non-manure based farm biogas systems and green house operations that process agricultural materials, as well as off-farm materials must be sited at least 250 m from neighbouring dwellings. These systems can achieve reduced setbacks down to 125 m for some components of the system by meeting specified best management practices; or if the facility is designed to minimize the odour to at least the same extent of specified best management practices. Non-farm-based biogas systems or systems that cannot meet the requirements listed above are required to undertake a series of air, noise and odour studies and reporting activities to demonstrate that they minimize nuisance and environmental risks.
References


http://www.omafra.gov.on.ca/english/engineer/facts/food_input.htm


http://www.omafra.gov.on.ca/english/engineer/facts/nm_ad.htm