RESEARCH IN LOGISTICS & PRODUCTION

LOGISTICAL ADVANTAGES DUE TO THE USE OF AN INNOVATIVE SENSOR UNIT FOR CONTROLLING OPTIMUM BIOGAS PROCESSES

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Abstract. For imaging of the biogas process fast and long-term stable measurement methods misses for certain parts of the process. Thus, it is necessary to know the development of organic acids. These metabolites, which are generated during the bacterial degradation, are important indicators. The process is generally very confusing, not only in terms of the number of occurring bacteria and chemical compounds, but also their variabilities. For the knowledge of such changes a direct, low-wear and permanent monitoring of organic acids would be extremely useful. Upon the occurrence of a change like hyperacidity we could react quickly. There are already some proven methods. However, these methods have several disadvantages: the information gathering is logistically difficult by long journeys, by process conditions informations are delayed and distorted, quickly worn sensors, etc. Therefore, a innovative development is presented here, which avoids all the disadvantages listed. The sensor unit has been developed in cooperation with KSI Meinberg, Logic Way Schwerin, IBZ Hohen Luckow, University of Rostock and a polish colleague. According to Raoult law a characteristic is

used in principle, which is typical of some liquid and gaseous media that are touching. This means volatile substances, which for example, are also in the fermenter broth, among others organic acids, are also detectable in the gaseous phase. If in the gas phase such acids can be detected, conclusions about the acid content in the substrate broth are possible. In different experiments evaluable matches between the developments of organic acids on the one hand in the liquid phase (broth) and on the other hand, in the gaseous phase were found. These results are based on an acid sensor unit with which distant standing biogas plants can be controlled remotely. A project regarding this topic is supported by research programme ZIM. Project executing organization is AiF (Arbeitsgemeinschaft industrieller Forschungsvereinigungen "Otto von Guericke" e.V.).

Paper type: Research Paper

Published online: 28 October 2016
Vol. 6, No. 5, pp. 407–418
DOI: 10.21008/j.2083-4950.2016.6.5.3

ISSN 2083-4942 (Print)
ISSN 2083-4950 (Online)

Keywords: *remote control, biogas process, sensor unit*

1. INTRODUCTION

The availability of energy is in any economy of outstanding importance. However, forecasts and world prices show that availability decline. We are looking for alternatives – some countries call the renewable energy. Biogas – a renewable energy – shall help in Germany to cover the demand. In the last 15 years a lot of biogas plants were built. After this quantitative development qualitative developments must follow now. This also means that plants that already exist need to be more profitable. Here are two categories of improvements to be distinguished. They are already summarized in Germany under the term repowering: the first improvement concerns the biological efficiency of the biogas generating process. Secondly, we need an improvement regarding the processes around the fermenter (for example, substrate and logistics costs, energy costs, etc.). This article is intended to deal with the reduction of logistical expenses.

The parameter organic loading rate (OLR) is still an important measure in the control of biogas plants. He sets the amount of degradable organic substance by bacteria in a reference to the fermenter space and to the required degradation time. Microbiological processes remain stable if they do not exceed a "certain" OLR (kg organic dry matter per cubic meter fermenter volume and day). The term "certainly" is chosen because it is not clear at which OLR a biogas plant remains stable.

Many factors have an influence on it (plant type, type of substrate, etc.). Although the operator of a biogas plant does not know the value exactly, he must try to achieve a maximum gas yield. For this, he feeds the fermenter with a larger amount of organic substrate. The result is a rising OLR. In that case it may happen that the microorganisms cannot multiply so quickly. Now the risk of acidification increases, which means that the pH-value decreases and bacteria die or become inactive. This process is sometimes referred to in common parlance as "overturning" of the fermenter.

Only the knowledge that this condition (overturning) just is adjusting, there is the possibility to stop the supply of substrates – the fermenter may no longer be "fed". The OLR is reduced so far in such a case that pH no longer falls and the bacteria can survive. Under the neutral becoming environment it can be formed methane again. In the worst case, if the acidification is detected too late, and then the procedure of reducing the substrate supply is too late, the fermenter "overturning", he must be emptied, refilled and inoculated. This may take a period of up to several months. The biogas production declines, the resulting economic consequences may be able to be ruinous.

We have the fact that the OLR has often been found to be inaccurate for predicting the situation in the fermenter. Additional we have the fact that the information cannot be delivered often if and when it is needed – the results come too late. The reason is that the complex analytics to be realized in laboratories. But first someone has to go to plant and pick up the sample. The sample comes often too late. Here a logistically faster and more reliable method is needed. In this context, information on the so-called volatile fatty acids (VFAs) pushes in the spotlight. The abrupt increase in concentration of VFAs is responsible for overturning. Contrary to this undesirable consequence, these acids are normal metabolites in the degradation of substrates, which shows the Figure 1.

The bacteria involved in the entire biogas process can be roughly divided into four population groups. In those that disintegrate the supplied substrate particles with so-called exo-enzymes – enzymes that are released on the bacterial outer surfaces. Polymers are disintegrated in this process called hydrolysis into monomeric structures. Their metabolic products – the monomers (monosaccharides, lipids, amino acids) – are used by another population group as food.

These bacteria group break down these monomers to different VFAs and other insignificant products – this phase is called acidogenesis. The following population group is named after its main metabolite: Acetic acid is the product of the acetogenic bacteria – acetogenesis. In the last step the acetic acid in turn is converted mainly in methane – methanogenesis.

Before a fermenter overturns always an extremely rapid rise of these volatile fatty acids (VFAs) can be recorded. It is probably a consequence of the rapidly increased supply of substrate whose subsequent rapid degradation by the bacteria of first two phases hydrolysis and acidogenesis. But the methanogenic bacteria (last process phase) couldn´t grow with this speed. They couldn´t remove the occurring

acids in order to generate methane. Since under these acids, acetic acid comprises the largest portion, this situation is called “acid accumulation” sometimes. However, it can be recorded other acids too.

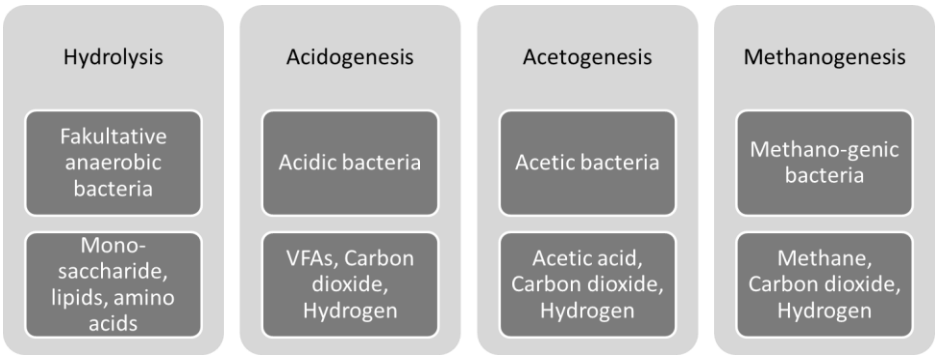

Fig. 1. Scheme of four phases of biogas process, involved bacteria and their degradation products

To be able to measure permanently the acid level, a special measurement technology is required. Measurement of today does not provide satisfactory results. Biogas fermenters underlie an extraordinary stress, according to experience the bacteria coat all surfaces – even those of sensors – In the form of a biofilm. After a short time, the sensor is unusable. This is true for different measurement principles. In order to be able to measure the states in the fermenter, it is necessary to keep the potential sensor of this fermenter content with living bacteria therein.

For this, a physical individuality of these substances is used. The fact that the organic acids are volatile, they change into their gas phase; they should not be found only in the fermenter broth, but also in escaping biogas. The Raoult’s Law explains this relationship between the concentration of a volatile liquid and the concentration of the volatile part in its gas. Everything we can find in gaseous form in biogas we condense by reducing the temperature. Now the condensate contains our VFAs for measuring.

The great advantage of such a gas-based sample collection is that in this condensate VFAs can be found, but no bacteria are almost in it. That means that this sample of condensate with the VFAs is fed a suitable sensor which detects the concentrations. This can no longer be fatally damaged by the formation of a biofilm.

A precondition for such a determination of VFAs is a good correlation between the concentration in the fermentation broth and the biogas. Acid concentration, pressure and temperature of the gas in the fermenter are important factors. This paper presents first results to this relationship. Later, the results will be the basis for the development of an acid sensor unit, with which more precise remote control of biogas plants are possible.

2. METHODS

Conceptual design of investigation:

1. Extraction of condensate
   - Continuous biogas trial
   - Process of condensate extraction
2. Tests for VFAs concentration in…
   - condensate samples
   - fermenter broth samples
3. Evaluation of concentrations
   - Comparison between condensate and fermenter broth
   - Interpretation of results

Retrieval of condensate

In a continuous biogas experiment (Fig. 2) a blend of corn and sedges was fermented (Mehl, 2014). This experiment was complemented by the actual condensate extraction, with which VFAs were separated from the biogas stream (Kade, 2014).

For the biogas experiment two heatable fermenters (38°C) with a volume of 10.5 l were operated independently. In their caps are openings for feeding and gas outlet and an agitator shaft are embedded. Additional sensors are integrated and other measurements.

The experiment was conducted over a period of 60 days; the fermenters were fed once a day and stirred automatically and regularly. First, every day 0.5 g organic matter (oS) per liter fermenters was supplied (OLR (Organic Loading Rate) = 0.5). Then every other week the OLR was increased by 0.5 g oS/(l · d). All values were determined by standard specifications (Author collective, 1999; Author collective, 2001a, b).

The reason for the gradual increase was that about the rising level critical acid impacts should be produced in the fermenter. For the calculation of OLR the parameters like dry matter, organic dry matter and total organic acid content are determined weekly. The determination of VFAs in the substrate broth was carried out according Buchauer (1998). The ratio between VFA and total inorganic carbon (TAC) was calculated by Burchard et al. (2001). The TAC has a buffering effect in the acidic nascent milieu. The relationship between VFAs and TAC should not increase above 0.4, because from this value increases the risk of overturning. Also for monitoring the pH-value of the fermenter broth were recorded continuously automated.

The amount of biogas produced was recorded daily by reading a drum gas meter type TG 05/05 Fa. Ritter. The gas which is permanent formed was passed after passing through the drum gas meter in gas-tight plastic bags. Once a day this stored gas was measured in terms of its individual gas components methane, carbon dioxide, oxygen and hydrogen sulfide with a biogas monitor type BM 2000 from Ansyco.

Time-independent of the procedure above explained, the resulting gas was passed constantly through a cooled condensate trap – and a bypass path. To avoid condensation until to the cooled condensate trap the way was partially heated. The bypass path consisted of a t-fitting in biogas tube and an intermediate pump. The latter should increase the biogas amount which should pass the condenser and thus also the amount of condensate. After condensate extraction process, the gas was fed back into the headspace of the fermenter back. The accumulated condensate was removed in the morning (before feeding) every day, frozen and stored until sample analysis. This procedure was carried out simultaneously with the sample of the fermenter broth. In this way, we have condensate (gas phase) as a bulk sample of a full day and a corresponding sample of the fermentation broth.

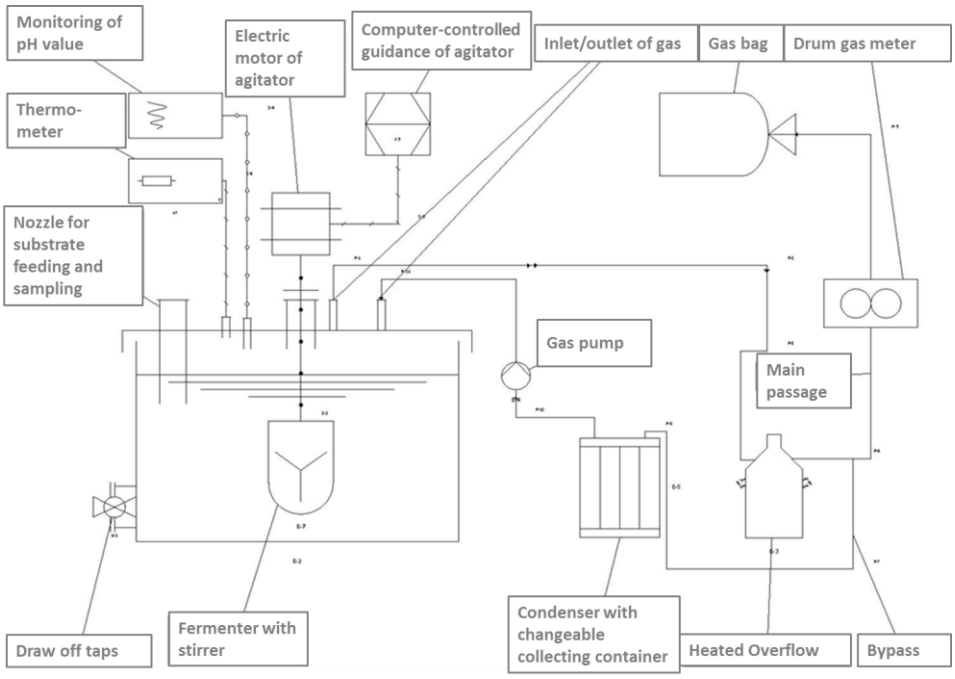

Fig. 2. Scheme of experiment design for extraction of condensate

Tests for VFAs concentration

For the second main part of the experimental approach, tests for VFAs concentration in condensate and broth samples, it was used a gas chromatograph (GC) type GC 1000 from Dani. Before examining the fermenter broth to their VFAs-concentration it was used a centrifuge type Labofuge 200 Heraeus to separate the solids and suspended solids from the liquid. The condensate samples, however, could be investigated without a purifying pretreatment. Before analyzing

by GC to each of the two samples was added 4-methylvaleric acid/isocaproic acid (internal standard).

Evaluation of concentrations

The results of the GC-analysis (chromatograms) were evaluated and the concentrations determined. These values of condensate samples were compared with the corresponding results of fermenter broth. Focus of this analysis was to acetic acid concentrations. In this study, primarily the detection of a concentration match of one of the organic acids in the two samples was important. For this purpose, acetic acid is suitable, because in an optimally running process (acetogenesis) acetic acid in relation to the other VFAs should record a surplus in the substrate solution. The accumulation of higher VFAs indicates towards a disturbed process (Görisch & Helm, 2007).

3. RESULTS

The development of OLR can be read in Table 1 and Table 2, also the values of pH and the ratio between VFAs and total inorganic carbon (TAC).

Table 1. Selected process parameters at selected times of fermenter 1 (F1)

Parameters	**Unit**	**Process values according test day (d)**				
		5	**20**	**34**	**48**	**60**
OLR	g oS/(l · d)	0.49	0.50	1.66	2.65	2.95
pH-value	–	7.94	8.13	7.93	7.96	8.08
VFAs/TAC	–	0.21	0.14	0.24	0.11	0.15
oS	**– Organic substance**					
VFAs/TAC	**– Volatile organic acids/Total inorganic carbon**					

It is noted that the increase has no clear effect on the respective pH-values – they do not sink. Also the FOS/TAC values show nearly no indication to an environment becoming more acidically, until that value after 20 days in the fermenter 2 (Tab. 2). The reason was an air leak into the fermenter, which had an influence on the anaerobic methanogenic bacteria. Thus, the degradation of higher VFAs (for example, propionic acid to acetic acid) was inhibited.

For the general valuation about small influence of increasing OLR on the shown process parameters can be registered that the amount of generated acid was not sufficient yet – the OLR was too small.

Table 2. Selected process parameters at selected times of fermenter 2 (F2)

Parameters	Unit	Process values according test day (d)				
		5	20	34	48	60
OLR	g oS/(l · d)	0.48	0.49	1.55	2.64	2.94
pH-value	–	8.62	7.78	8.00	7.94	8.09
VFAs/TAC	–	0.20	0.72	0.11	0.12	0.14
oS	**– Organic substance**					
VFAs/TAC	**– Volatile organic acids/Total inorganic carbon**					

Or the total inorganic carbon (TAC) was sufficient to buffer the acid attack and so the acids could transform in methane gas. The pH value or FOS/TAC value do not indicate – at least in this chosen range of OLR – to an unusual biological situation.

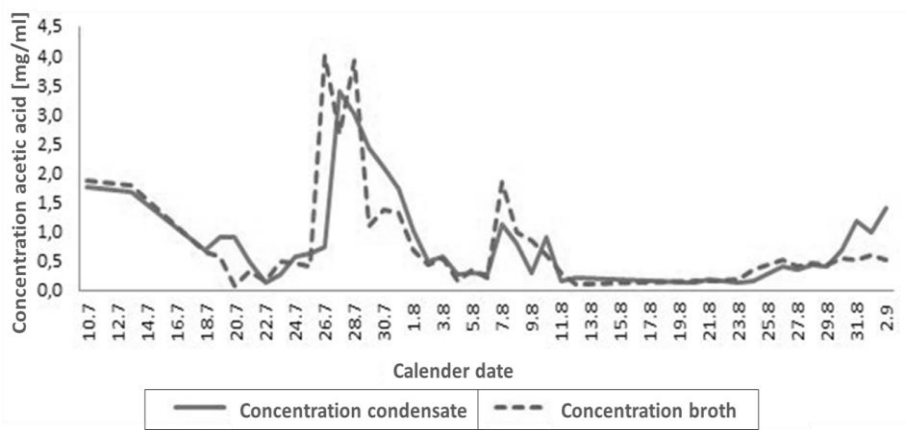

Fig. 3. Course of acetic acid concentration of the substrate and of the condensate during the experiment (F1)

In Figure 3 are shown the acetic acid concentrations of fermenter broth together with those of the gas phase over the entire test period from the fermenter 1. Again, the OLR increase (Tab. 1) is not reflected either in the fermentation broth or in the overlying gas phase.

This also points to the correctness of the assessments made above: in this range of OLR the acids which are formed are degraded biologically, the methanogenic bacteria work without disruption, there is no biologically critical situation.

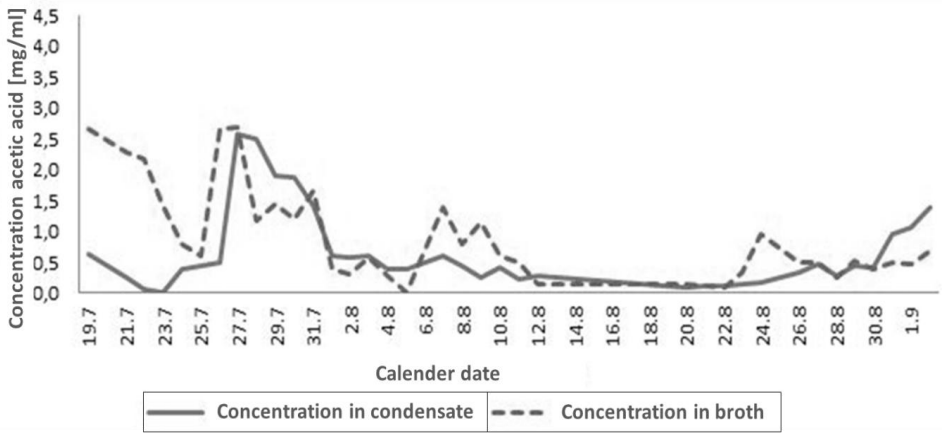

Fig. 4. Course of acetic acid concentration of the substrate and of condensate during the experiment (F2)

Identical statements as before those for the fermenter 1 can be taken for the concentrations of the two media in the fermenter 2 (Fig. 4).

4. CONCLUSION

1. Acid concentrations have a greater variability than it can imagine if we reflect the values of pH and VFAs/TAC. Although this test with the chosen OLR increase has not led to a critical biological state, it can be assumed anyway that the high volatility can be an indication of the suitability for rapid imaging of abnormal acid development than the other two process parameters pH and FOS /TAC could do.
2. The concentration courses of the condensate (gas phase) correspond approximately to those of the fermentation broth. Thus, a fundamental objective of the experiment is reached. On the other hand, sometimes the compliance of the two courses is not satisfactory. Reasons can be find firstly in the experimental setup, and secondly in the experimental realization. In experimental setup has to be considered in the future the full heating of all gas components (for example, hoses) to avoid condensation prior to the condensation trap. In experimental realization the fact is to be considered that the compared samples come from a sampling that is truly comparable. The condensate collection must not be permanent throughout the day in the future (sample is an average per day), while the sampling of the fermenter broth to a single time of day occurs (sample represents current state).

3. Indicatively, it can be seen in the two last figures that the concentration course of condensates follow slightly later the concentration course of fermenter broth. The biological situation in the fermenter broth cannot be immediately reflected in the concentration levels of the gas phase. A just-adjusting state in the fermentation broth cannot show due to the inertia of the mass transfer at the same time in the gas phase. However, to be prepared for future experimental setups shall be changed to harmonize the concentration courses. For example, the fermentation broth should be actively perfused with recirculated biogas. It should also be observed in the future, that the pressure on the substrate broth remains the same, as this will permanently change the solubility of gases in the fermentation broth.
4. With a remote control of fermenters it is possible to control this complex biological process in the most remote regions without traveling. So it is possible to get information about the process in time. Logistical expenses for traveling can be significantly reduced.

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BIOGRAPHICAL NOTES

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