APPLICATION REPORT
LABORATORY ANALYSIS & PROCESS ANALYSIS
BIOGAS
PLANT MONITORING



Lellbach biogas plant, 1.2 $MW_{el.}$
(Source: EnerCess)

Monitoring of digesters in biogas plants

Renewable sources of energy are gaining steadily in importance. Leading the way is the use of methane gas obtained from fermentation processes in biogas plants. Overloading such plants with excessive biomass may have drastic economic consequences and may even inactivate the biomass, necessitating a cost-intensive restart. Adding too little biomass also has financial consequences, as less electricity and heat are generated and revenue is therefore lost. All plant operators therefore have a crucial interest in running their biogas plant as efficiently as possible. To be able to do this, reliable on-site analysis is needed in combination with continuously operating process instruments.

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Analytical control of fermentation processes in biogas plants

Introduction

Against the background of finite fossil fuels and the contentious use of nuclear energy, renewable sources of energy are steadily gaining in importance. Leading the way is the use of methane gas obtained from fermentation processes in biogas plants. Plant operators in Germany receive a high return for feeding electricity generated from renewable raw materials into the national grid – up to 0.18 € per kWh.

All plant operators therefore have a vested interest in running their biogas plant as efficiently as possible. If excessive amounts of biomass are fed into such plants however, this may have drastic economic consequences and may even inactivate the biomass, necessitating a cost-intensive restart. On the other hand, long-term underloading of a plant also has financial consequences, as less electricity and heat are generated and revenue is therefore lost.

A precise and reliable analysis of the fermentation processes using photometric cuvette tests, easy-to-use titrators and process measurement technology for online monitoring ensures stable process management cost effectively.

Structure of a biogas plant

In a biogas plant, natural fermentation and decomposition processes produce biogas, which is used to generate electricity as efficiently as possible [2].

In the first phase the substrate is made available, stored and treated in accordance with requirements and fed into the bioreactor (Fig. 1). In the second phase, anaerobic fermentation processes take place in the digester, producing biogas. In the third phase the gas is treated, stored and utilised. Finally, in the fourth phase, the fermentation residues are utilised (e.g. as fertiliser in the agricultural sector).

The main component of biogas is methane (about 50-70 %). One cubic metre of biogas contains about six kilowatt hours of available energy and is equivalent to about 0.6 litres of fuel oil in terms of its average calorific value [3]. The heat generated during its combustion is fed into the fermentation process as process heat or used to heat on-site living and working quarters and livestock buildings or sold to external customers (e.g. operators of local heat networks).

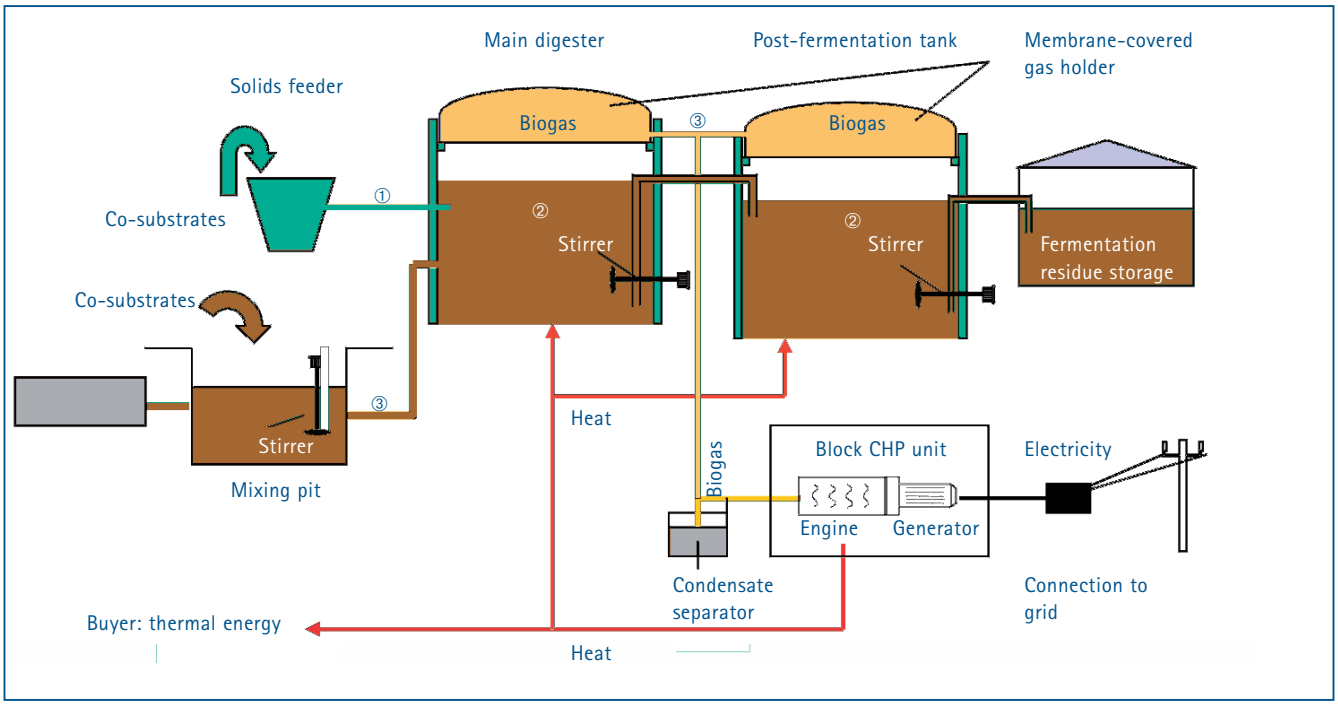


Fig. 1: Design of a typical biogas plant (CHP = combined heat and power)
① Eluate analysis: N_{tot}, COD, NH_4, heavy metals
② Digester analysis: NH_4, org. acids, COD, acid capacity
③ Online process analysis: pH, temperature, redox and TS

There are basically two types of plants in which wet fermentation processes take place: plants that use renewable raw materials and co-fermentation plants. The former use renewable raw materials such as maize, grass, complete cereal plants and grains, sometimes together with manure slurry.

In co-fermentation plants, substrates of non-renewable raw materials are used, such as residues from fat separators, food residues, flotation oil, industrial waste products (glycerol or oil sludge) and domestic organic waste. Manure slurry is also usually used.

Biogas is produced by a highly sensitive and complex process. Without instrumentation, biogas plants are often underloaded, i.e. the biomass feed rate is too low, so that electricity generation isn't cost effective. This can result in substantial financial shortfalls (see Table 1, [4]). The effects of overloading are especially drastic. Such unintentional "overfeeding" slows down or stops the biological fermentation process and may cause a total system breakdown. A cost-intensive plant restart is then necessary.

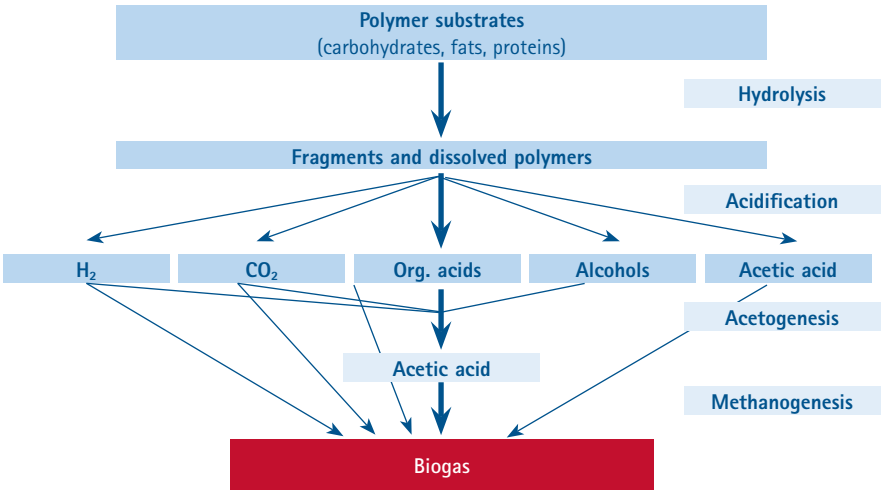


Fig. 2: Anaerobic digestion steps resulting in the production of biogas [5]

The anaerobic fermentation process

The fermentation of biomass is a four step anaerobic digestion process, which is brought about by the complementary activities of several species of bacteria.

The first step is hydrolysis (Fig. 2). First of all, long chain substances, carbohydrates, proteins and fats are broken down into smaller fragments such as simple sugars, glycerol, fatty acids and amino acids. In the second step (acidification, acidogenesis), fermentative microorganisms convert these products into short chain fatty acids such as acetic acid, propionic acid and butyric acid. Lactic acid, alcohols, hydrogen and carbon dioxide are also formed. The third stage of acetic acid formation (acetogenesis) combines the prior acidification with methane formation. The starting substrates are a number of final products from the acidification phase, i.e. short chain fatty acids, propionic acid, polymer substrates (carbohydrates, fats, proteins) and butyric acid. Together with lactic acid, alcohols and glycerol, these substances are converted by the acetogenic microorganisms into acetic acid, hydrogen and CO_2. In the final step, methane is formed. The methane bacteria produce biogas, which contains up to 70 % methane.

All the described processes run almost simultaneously in a biogas plant. They are in a sensitive state of equilibrium, which is dependent on the pH and temperature. Changes may have a negative effect and drastically disrupt the total biogenic process.

Lost income due to underloading

	Unit	Plant A (underloading)	Plant B (comparison)
Energy yield	%	80	90
Energy production per year	kWh	3504000	3942000
Energy revenue (9.9 ct/kWh)	€/a	346896	390258
Renewable raw materials bonus (6 ct/kWh)	€/a	210240	236520
Bonus for utilisation of heat (2 ct/kWh)	€/a	70080	78840
Revenue per year	€/a	627216	705618
Revenue per month	€/a	52268	58802

Tab. 1: Loss of income due to underloading, as shown by a 500 $kW_{el.}$ biogas power plant

Control parameters for a cost effective process

Control parameters for a cost effective process

To achieve optimal control of the degradation process in a biogas plant, a detailed knowledge of the key chemical and physical parameters is necessary.

Temperature

Temperature plays a crucial role. Biogas plants are usually mesophilic or thermophilic. The former function most efficiently in the temperature range from 35 to 41 °C, while the latter prefer 57 °C. Methanogenic bacteria in particular are extremely sensitive to temperature fluctuations. The temperature of the fermentation process should therefore be kept constant to within a maximum of ± 1 °C.

TS/TOS content

The total solids content (TS) or total organic solids content (TOS) is used to estimate the volumetric loading of the digester for the purpose of managing the solids streams. Wet digesters are usually run with a TS content of 8-10 %, while special digesters may be operated with a TS of up to 20 %. The total organic solids content is very important for the operation of the plant. If it is too high (e.g. > 3 kg oTS/(m^3·d)), there is a danger of overloading the digester. In this case the substrate input must be immediately reduced.

Redox potential

The redox potential of a digester is a measure of the oxidisability or reducibility of its content. Biogas production only proceeds efficiently in an anaerobic environment, i.e. the redox potential must be less than 330 mV. In general the use of oxidation promoting substrates, i.e. substrates that contain oxygen, sulphate or nitrate groups, may significantly change the redox potential and thus cause a shift in the pH. Such a negative development for the fermentation process can be triggered by, for example, a change of substrate. Continuous redox measurements give an early warning, i.e. before the shift in pH occurs.

pH

Just like the temperature there is more than one optimum pH value. During hydrolysis and acidification, the best pH is between 4.5 and 6.3. The optimal pH range for methane formation is the narrow window between 7.0 and 7.7.

Continuous pH metering gives an early indication of any acute disruption of the process. However, the plant cannot be controlled reliably simply on the basis of the current pH. This is especially true of plants whose digester has a high buffer capability, as an unintentionally large input of organic acids does not necessarily result in a drop in pH.

Acid capacity

The acid capacity is a measure of the buffering capability of the digester. The greater the acid capacity, the less rapidly the pH can rise or fall. The acid capacity is measured in mmol/l or mg/l $CaCO_3$.



Fig. 3: Central pumping station of a biogas plant in Lelbach with online sensors (front)

COD

The chemical oxygen demand is the amount of oxygen required to oxidise the oxidisable components of the fermentation substrate. All oxidisable organic compounds are totally chemically oxidised to CO_2 and H_2O. COD is a reliable indicator of the energy potential of a fermentation substrate.

Organic acids/Fatty acids

Low molecular fatty acids, in particular acetic acid, propionic acid and butyric acid are formed during the first and second steps of the fermentation process. If the fermentation process is proceeding efficiently, the values for these compounds, expressed as an equivalent amount of acetic acid, lie between 500 and 3,000 mg/l. In this case, the processes in the digester, the production of acid by hydrolysis and the degradation of acid by methanisation are in equilibrium. If the acid concentration rises above 10,000 mg/l, the pH usually falls below 7. According to Bischofsberger [6], a drop in pH to 6.4, at an acetic acid concentration of 1,000 mg/l, reduces the methane concentration by half. Acetic acid concentrations below 1,000 mg/l should be determined by the titrimetric VOA/TAC method.

Ammonium

During the fermentative degradation of protein rich substrates in particular, e.g. grass silage or chicken droppings, high concentrations of ammonium ions may be generated. Ammonium exists in a pH dependent equilibrium with ammonia, which is toxic to the bacteria. If the pH increases the equilibrium shifts, favouring ammonia. Regular checks of the ammonium content of the digester ensure the trouble free operation of a biogas plant.

Process monitoring in practice

The suitability of the process probes was tested in a biogas plant in north Hesse, Germany. The parameters temperature, total solids, pH and redox were measured [7].

pH/Redox measurement

The digital pHD electrode used to measure pH and redox is fully encapsulated so that it does not come into contact with the fluid being measured. A special, soil resistant salt bridge forms the direct contact to the fluid to enable the measurements to be made. In contrast to conventional membrane based electrodes, this electrode can be used for very long periods even in fluids with a high particulate content, e.g. digester water. The intervals between cleaning are especially long. Electrode poisoning, e.g. by any H_2S that may be present, is prevented and dilution of the electrolytes is avoided.

Figure 4 shows examples of time-course curves obtained from pH and redox measurements. Through appropriate positioning in the control zone of a pump station, the conditions in the digester or post-digester can be accurately determined and monitored. During the test period (8 months), the pH readings remained in the range from 6.9 to 7.4. In the post-digester the average was 7.38, with a minimum of 7.20 and a maximum of 7.50. These results confirm that the pH in a digester is not constant, but undergoes fluctuations. A similar result was obtained from the readings of the redox potential. The average value was -392 mV, with fluctuations between -250 and -476 mV.

These values show that fermentation processes must be properly understood and closely monitored to ensure optimal and therefore profitable operation of a biogas plant.

Online measurement of pH and redox potential

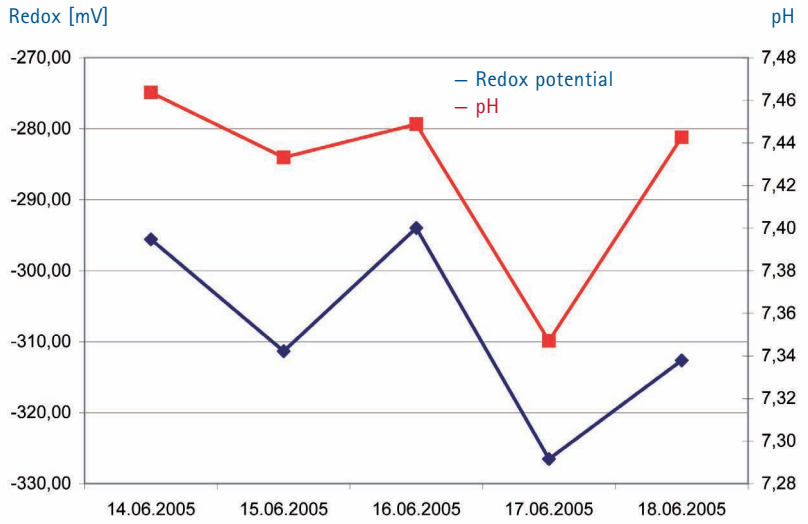


Fig. 4: Measurements from the pressure pipe line of a biogas plant digester in north Hesse, Germany

Process monitoring in practice

Comparative measurement Total solids

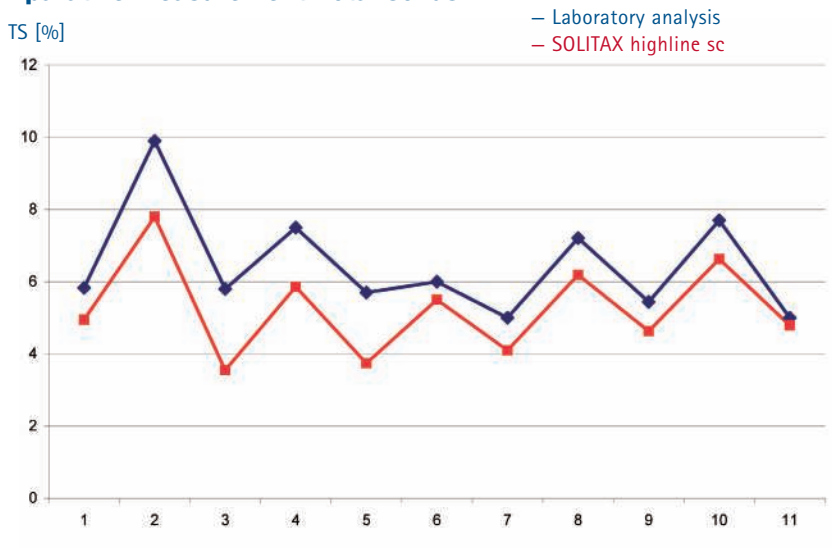


Fig. 5: Comparative measurement of digester and post digester samples: SOLITAX highline versus gravimetric laboratory analysis (filterable substances)

Total solids (TS)

The time course curves shown in Figure 5 were produced from some of the comparative measurements carried out in a biogas plant over a period of six months. The total solids content was determined precisely by a SOLITAX highline sc probe, which uses a colour independent combined infrared dual scatter light measurement method. In parallel to the online measurements, the TS content was determined gravimetrically in an external reference laboratory. Due to the varying particle size distribution in the sludge, a plant-specific correction factor has to be used to calibrate a TS probe. The determined TS values were in the range from 3.8 to 10 % and the results obtained in the laboratory were slightly higher than the equivalent results of the online measurements carried out on site. Both time course curves accurately reflected the fluctuations in the TS content within the fermentation process and therefore enable the plant to be monitored and precisely controlled.



Fig. 6: Photometric measuring station: HT 200S thermostat, cuvette test, DR 2800 photometer

Monitoring digesters with photometric tests

The most important parameters in the fermentation process, which can be monitored using chemical or photometric methods, are the organic acids formed as intermediates, the COD and the ammonium concentration. Until now, the necessary measurements have been carried out in external service laboratories, with the associated high costs and sometimes considerable delays between sampling and the availability of the results.

A late response to negative processes in the digester may enable considerable inhibition of the biogas productivity to occur, even to the extent that the biomass may be inactivated, bringing the total plant to a halt.

For this reason, it is advisable to monitor the digester directly and as quickly as possible with photometric cuvette tests, which have been regarded as the “state of the art” in wastewater monitoring for several years.

The suitability of photometric cuvette tests for monitoring organic acids, ammonium and COD was tested on numerous samples from a co-fermentation biogas plant (1.5 $MW_{el.}$) in Lower Saxony. Reference analyses were carried out by the contract laboratory of a nearby mechanical biological waste treatment plant. A decisive factor for the assessment was the comparability of the results to those obtained using corresponding standard methods and the consistency of the results obtained from diluted and spiked samples.

Samples taken from a digester may remain biologically active. The possibility of post sampling formation of acetic acid in the samples cannot therefore be excluded.

For the comparability of the results of the two methods it was especially important that the period between on-site analysis (using the cuvette test) and laboratory analysis (using the standard method was as short as possible). Besides the samples from the co-fermentation biogas plant, numerous samples from the mechanical-biological waste treatment plant were analysed.

In addition, the concentrations of the organic acids in digester samples from various biogas plants were analysed using ion chromatography (IC) and the fast photometric test. The sum of the individual components determined using IC was compared with the total organic acids determined with the photometric test.

Dilution series for LCK 365 Organic acids

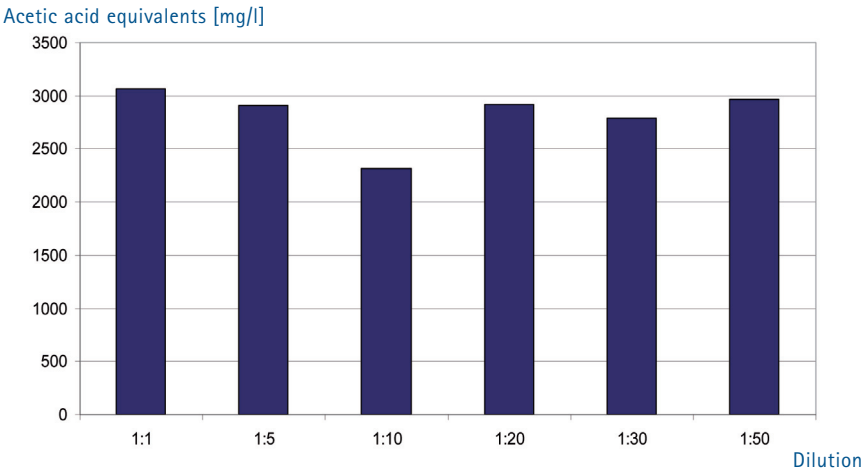


Fig. 7: Dilution series for checking the plausibility of the measurements of organic acids in a post digester sample

Sample preparation

Colourless, clear solutions are required for photometric tests. For this reason it is important that the preparation of the digester samples, which have a high particulate content, is carried out carefully and in line with good practice. The samples from the digester and post-fermentation tank were diluted in the ratio 1:20. To do this, the tip of a single-use pipette tip was cut off and the appropriate volume was added step by step (25 ml, 5 x 5 ml) to a 500 ml round flask. The diluted sample was then split up and passed through a 0.45 µm polycarbonate membrane filter under a pressure of 6 bar in the reference laboratory. The standard analyses were carried out on the filtrate. For each photometric cuvette test, 20 ml of the filtered sample was centrifuged in a table centrifuge for 10 minutes at 13,500 rpm, providing approximately 20 ml clear and almost colourless centrifugate, with which the cuvette tests were then carried out.

Plausibility of the measurements

There are two relatively simple methods of determining the plausibility of the results: dilution and spiking [8]. For the first of these, a dilution series is prepared from the measured original sample. If any interference is present in the original sample, its effect is weakened as the level of dilution of the sample increases. The concentration of the original sample can be calculated from the measurement results obtained from the dilutions. The presence of any interference is revealed by a significant deviation between the concentration of the undiluted original sample and the concentrations calculated from the measurements of the dilution series. If there is virtually no deviation, no sample specific interference is present.

The spiking method requires steadily increasing concentrations of a standard to be added to the measured sample. The concentration determined by measuring the spiked samples, (corrected to take account of the dilution factor), should correlate to the known concentration of added standard.

Figure 7 shows the results obtained from a dilution series prepared from a post digester sample from a biogas plant during the course of long-term comparative measurements. Except for the result from the 1:10 dilution, all the results are within the range of tolerance, which is higher for samples with a high particulate content than for samples that contain no particles. This is a consequence of the unavoidable dilution error. The cause of the low result obtained from the 1:10 dilution is unknown, but may be associated with the above mentioned uncertainty of the volume reduction. The presence of any interference can be excluded, as the following dilution steps did not confirm this trend.

Comparative measurements

Spiking test with acetic acid

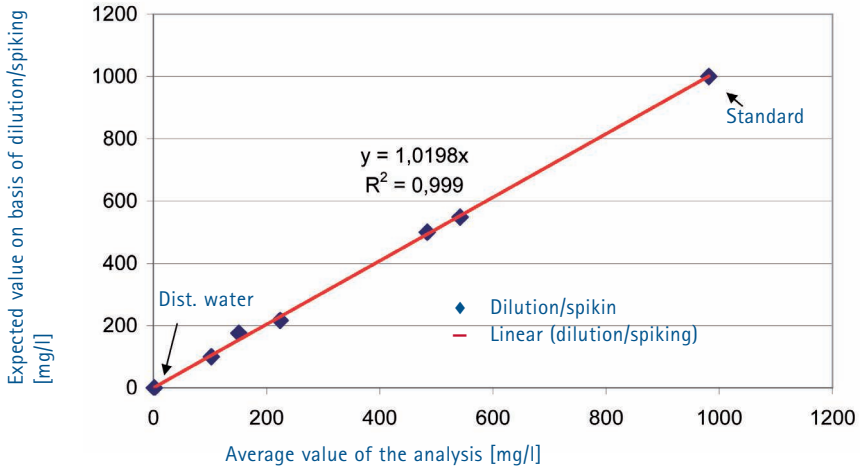


Fig. 8: Spiking test to check the plausibility of the measurements of organic acids in a post-digester sample

The spiking test was carried out using a sample from the post digester of a co-fermentation biogas plant. Glacial acetic acid was used as the standard, which was diluted with distilled water to a concentration of 1,000 mg/l. The lowest and highest spiking values were those of the distilled water and the dilute solution of glacial acetic acid. The plot of measured values against the expected values gives a straight line with a correlation of 0.999. This almost linear relationship indicates that no interference is present in this sample (see Figure 8).

Comparative measurements – photometric and standard methods

The comparative measurements from the photometric cuvette tests and the corresponding standard methods were carried out in the operations laboratory of a mechanical biological waste treatment plant and the on-site reference laboratory.

The organic acids were measured using the German standard method DEV H21. The operations laboratory used the LANGE cuvette test LCK365 Organic acids [9]. The hydrolysis needed in order to determine the acetic acid equivalents was carried out by heating the sample for 10 minutes at 100 °C in a preheated dry thermostat. The clear and colourless sample was then cooled to room temperature before being evaluated with the cuvette test. As with all photometric methods, particles and strong colours can influence the measurement result and must therefore be removed if necessary, e.g. by passing the sample through a 0.45 µm filter or diluting it still further.

The ammonium concentration of a sample from a post digester was determined with the LANGE cuvette test LCK302 [10] and the photometric DEV E5 method.

The COD (chemical oxygen demand) was determined with the German standard method DEV H44 and the LANGE cuvette test LCK514 [11]. The two methods use the same reagents but differ in terms of the digestion time. A special high-temperature thermostat (HT 200S) reduces the usual 2 hour digestion period to 15 minutes.

Figure 9 shows the time course curves of the almost simultaneous comparative measurements obtained with the cuvette test and the standard method. Due to the predefined measuring range of the cuvette tests and the relatively high concentration of the measured parameters, the samples subjected to the photometric tests had to be diluted. The COD samples and the samples for the determination of the organic acids were diluted in the ratio 1:20, centrifuged and measured. A few ammonium samples still had some slight intrinsic colour after being centrifuged, and therefore had to diluted still further (1:50).

The comparative measurements were carried out over a period of several months. In the case of the ammonium measurements and the determination of the organic acids, the correlation between the measurements obtained with the two methods was very similar in terms of their accuracy. Both cuvette tests are therefore suitable for monitoring these very important control parameters in biogas processes.

The results of the COD methods differ from each other somewhat, i.e. when they are plotted, one curve is above the other. They nevertheless accurately reflect the changes in concentration of the organic load in the digester and post digester. In this case a plant specific correction factor should be introduced.

Ion chromatography (IC) measurements

The cuvette test for organic acids and the standard method (steam distillation and titration of the acetic acid equivalents) both determine the sum of the individual substances. They do not give the concentrations individual substances, e.g. propionic acid, butyric acid or acetic acid. In order to obtain the concentrations of these substances and to clarify whether the sum of their concentrations correlates with the results obtained using the cuvette test and steam distillation, a number of digester samples were also subjected to ion chromatography and the results were compared with those of the fast photometric test.

In view of the lower total solids content of the samples (clearly below 10 %), sample preparation was much easier than for the previous comparative measurements. Simple filtration through a folded filter usually sufficed.

The measurements were carried out by Ingenieurbüro Stahmer, Bremen. It analyses up to 100 digester samples each week for ammonium nitrogen, COD and organic acids. The ion chromatogram for sample I shows a total of four individual organic substances in the digester sample: acetate, lactate, propionate and n-butyrate. The sum of the individual concentrations is 2,234.73 mg/l organic acids (Tab. 2). The photometric test gave a sum of 2,530 mg/l. The difference in the results for this sample is therefore 13 %. Given the already mentioned dilution error associated with substances containing a high level of solids, this is a very good value. The following ion chromatographic analyses gave much smaller differences.

Comparative measurements – cuvette test and standard analysis

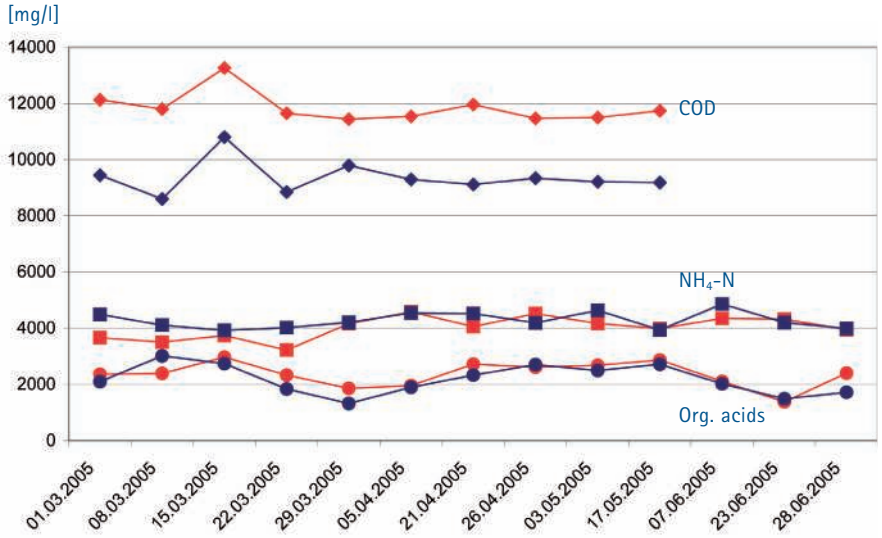


Fig. 9: Comparative measurements photometric cuvette test (red) and standard method (blue) – post digester sample from a biogas plant

Ion chromatographic analysis

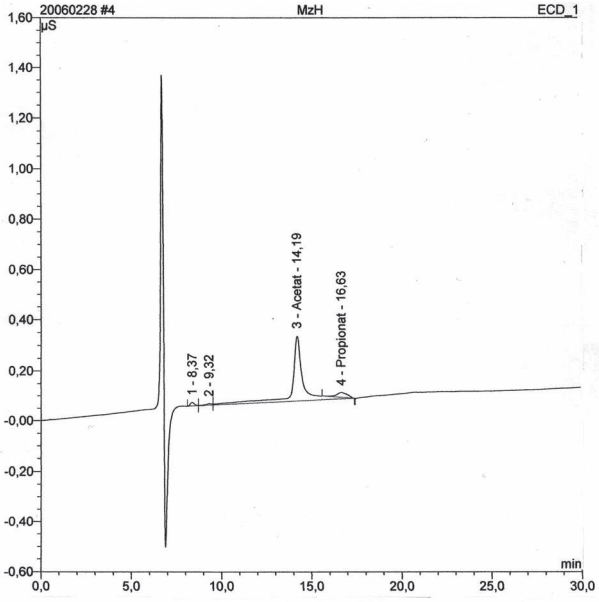
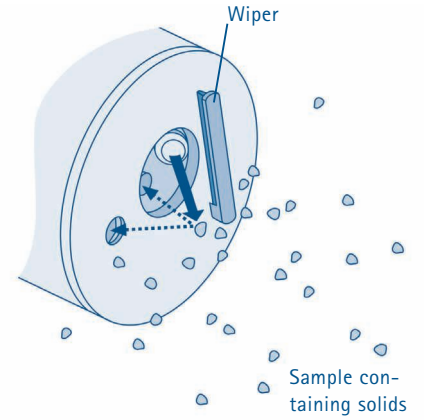


Fig. 10: Ion chromatogram of a digester sample showing the individual components acetate, lactate, propionate and N-butyrate

Measurement technology for biogas plants



Self cleaning SOLITAX highline sc probe for determination of the solids content

Components	Concentration [mg/l]	Organic acids Fast test [mg/l]	Difference [%]
Sample I			
Acetate	1768.7		
Lactate	81.63		
Propionate	296.4		
n-Butyrate	88		
Total	**2234.73**	**2530**	**13**
Sample II	**1227.45**	**1340**	**9**
Sample III	**3937.93**	**4130**	**5**
Sample IV	**1941.69**	**2070**	**7**

Tab. 2: Ion chromatography results for individual components and the results of the photometric fast test



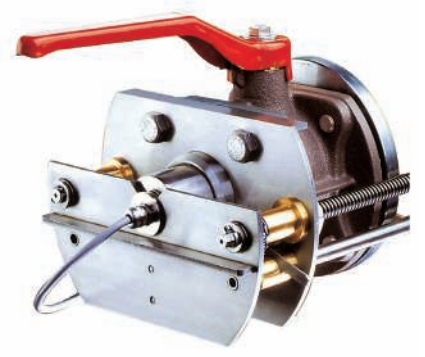
pHD sc sensor for pH or redox measurement

These results demonstrate that the results obtained using the cuvette test for the determination of organic acids correlate well with the results of the IC standard method and that the sum of the individual substances determined using the IC method also correlates very well with the result of the photometric test and the steam distillation.

Summary

The degradation processes in commercially operated biogas plants take place in a sensitive microbiological system. High, profitable gas yields and a fermentation product that can be readily used for agricultural purposes can only be obtained if the plant process is controlled.

The described online measurement technology for metering pH, redox, total solids and temperature, together with the photometric cuvette tests used in operations laboratories, allow cost effective, precise, real time monitoring of the fermentation process so that biogas plants can be efficiently controlled. The required investment is relatively low, compared with the risks associated with an uncontrolled fermentation process.



Safety fitting for mounting the SOLITAX highline sc

Measuring station for laboratory analysis

DR 2800	Compact, powerful spectrophotometer with a wavelength range from 340 to 900 nm for routine analysis and user applications; barcode reader (IBR) for automatic evaluation of cuvette tests; backlit graphic display with touchscreen menu guidance; mains and battery operation
LT 200	Dry thermostat for standard and special digestions; preprogrammed for digestion for the analysis of COD, total N, total P, TOC, organic acids and metals
Cuvette tests	Ready-to-use reagents for maximum user safety; highly precise; approved methods; more than 80 parameters and measuring ranges



DR 2800 spectrophotometer with various water analysis reagents

Installation for online measurement in central pumping line

SOLITAX highline sc	Stainless steel probe with combined infrared absorption scattered light process for in-pipe measurement of coloured liquids and sludge. Measuring range: 0.001....150.0 g/l TS Art. no. LXV 424.99.00200 Accessories: Safety fitting LZX 337 (can be mounted/dismounted without emptying the pipe)
pHD sc pH	Rugged, digital differential pH probe Process probe; material: PEEK Measuring range: 0...14 pH Art. no. DPD2P1.99 Accessories: insertion mount for pHD, stainless steel, 6136800
pHD sc ORP	Rugged digital differential redox probe Process probe; material: PEEK Measuring range: -2000...2000 mV Art. no. DRD2P5.99 Accessories: insertion mount for pHD, stainless steel, 6136800
SC 1000 Controller	A SC 1000 digital controller system consists of a single LXV 402 display module and one or more LXV 400 probe modules. The controller is modularly configured in accordance with the customer's specifications and can be expanded by additional measuring stations, sensors, inputs, outputs and BUS interfaces at any time. Each module controls up to eight sensors
Alternative	
SC 100 controller	Controls up to two sensors



Dry thermostat for all standard digestions



LCK 365 cuvette test LCK 365 for determining organic acids

Literature

Literature

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Cuvette test LCK 114 for the determination of COD

DOC 040.52.00447.May07