

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/276833464>

Multiposition Sensor Technology and Lance-Based Sampling for Improved Monitoring of the Liquid Phase in Biogas Processes

ARTICLE in ENERGY & FUELS · MARCH 2015

Impact Factor: 2.79 · DOI: 10.1021/ef502816c

CITATION

1

READS

83

9 AUTHORS, INCLUDING:



Erich Kielhorn

Technische Universität Berlin

3 PUBLICATIONS 1 CITATION

[SEE PROFILE](#)



Hans Oechsner

Hohenheim University

57 PUBLICATIONS 294 CITATIONS

[SEE PROFILE](#)



Peter Neubauer

Technische Universität Berlin

224 PUBLICATIONS 3,239 CITATIONS

[SEE PROFILE](#)



Stefan Junne

Technische Universität Berlin

61 PUBLICATIONS 363 CITATIONS

[SEE PROFILE](#)

Multiposition Sensor Technology and Lance-Based Sampling for Improved Monitoring of the Liquid Phase in Biogas Processes

Erich Kielhorn,[†] Sandra Sachse,[‡] Matthias Moench-Tegeder,[§] Hans-Joachim Naegele,[§] Christian Haelsig,^{||} Hans Oechsner,[§] Winfried Vonau,[†] Peter Neubauer,[†] and Stefan Junne^{*,†}

[†]Chair of Bioprocess Engineering, Department of Biotechnology, Technische Universität Berlin, Ackerstraße 76, ACK24, 13355 Berlin, Germany

[‡]Kurt-Schwabe-Institute Meinsberg, Kurt-Schwabe-Straße 4, 04736 Waldheim, Germany

[§]State Institute of Agricultural Engineering and Bioenergy, University of Hohenheim, Garbenstraße 9, 70599 Stuttgart, Germany

^{||}teleBITcom GmbH, Potsdamer Straße 18A, 14513 Teltow, Germany

Supporting Information

ABSTRACT: The current installations of sensors in the liquid phase in digesters are usually not sufficient for the fast detection of disturbances. Thus, the application of strategies for process control is restricted. In this paper, multiparameter (micro-) sensors as novel process analytical tools are introduced, which are coupled with wireless data transmission and are designed for an easy integration into digesters. Furthermore, the combination with a lance-based sampling system, which enables sampling in the core of the liquid phase, is described. The monitoring and sampling devices allow for the measurement at various positions in the liquid phase for the purpose of the identification of gradients. Three case studies were performed: (i) at an open hydrolysis basin, (ii) a mid-sized biogas plant with a concrete roof, and (iii) a larger biogas plant equipped with a flexible roof. Online measurements of the redox potential and offline analysis of the dry matter, ammonia, and acetic acid concentrations indicate plant-specific gradients, which appear in the liquid phase. Thus, the concept is not only suitable to improve the monitoring in digestion processes but also to identify the most suitable locations for installing sensors and sampling ports for a fast detection of process disturbances.

INTRODUCTION

Currently, only very few or even no equipment for the online observation in the liquid phase is installed at biogas plants. The importance of monitoring the composition of the culture broth, e.g., the concentration of key metabolites, such as short-chain fatty acids, is well-known.^{1,2} However, the limitation of technical solutions and the efforts for their maintenance, such as cleaning and calibration of sensors, causes poor acceptance. The insufficiency of the installed sensor capacities was observed with a survey at 400 plants in Germany.³ As result, the current practice is restricted to the application of the temperature and level control; sometimes, the pH value is monitored in the liquid phase.⁴ The restriction to monitor the gas phase composition, though, is likely insufficient, because process disturbances are detected with a significant time delay. Two mass transfer barriers have to be crossed by a metabolite intermediate from the interior of the microbial cell to the extracellular liquid phase and then to the gas phase. This causes a late recognition of concentration changes in the off-gas stream.

To overcome the current limitations of measurements in the liquid phase in industrial scale, several constraints have to be considered: (i) the monitoring devices need to withstand the harsh conditions during digestion; (ii) the installation has to be easy and affordable; (iii) maintenance needs have to be manageable by the staff of the plant; and finally, (iv) monitoring and sampling has to be conducted in zones, in which disturbances can be detected as early as possible.

The latter aspect is very important when assuming concentration gradients from the vessel wall to the inner core of the liquid phase and from the top to the bottom part of a digester.

The heterogenic distribution of substrate and dissolved gases is a well-known issue in many biotechnological processes, which are operated at an industrial scale of several hundred cubic meters or more.⁵ Intensive research has been conducted mostly in aerobic processes, which addressed the observation of impacts on the cellular metabolism and the process performance at oscillating cultivation conditions.⁶ Impacts because of gradients have also been observed in the anaerobic beer fermentation process, which is usually not stirred.⁷ It can be assumed that concentration gradients also occur in the culture broth in digesters because of the high viscosity and restricted volumetric power input.

Despite other biotechnological processes, the way biogas digestion is conducted varies strongly between different plants. Neither a standard procedure for stirring and mixing in a biogas digester exists nor a standard bioreactor design itself. The application of stirring (continuously or pulse-wise) and stirrer design and position remains a current matter of research^{8,9} and influences the economic benefits of operation. If gradients were

Special Issue: 2nd International Scientific Conference Biogas Science

Received: December 15, 2014

Revised: February 25, 2015

not considered for monitoring and control purposes, zones might be observed, which are not representative for the bulk of the liquid phase. Hence, monitoring tools should be applicable in a wide range of plant sizes and designs. Solutions should exist for the measurement at different positions to decrease the efforts for the identification of gradients.

Because many compounds, which are relevant for the scientific evaluation of the current process state and for control purposes, cannot be measured online thus far,¹⁰ the development of (multiposition) sampling systems for offline analysis is of importance for the characterization of the liquid phase too. Once gradients are identified, the locations that are most suitable for monitoring and sampling can be defined. Locations are regarded as most suitable if process disturbances were detected there at the earliest time whenever possible. Additionally, strategies for the improvement of the reactor design and mixing procedure can be evolved.

This research paper addresses the development and application of multiposition sensors and lance-based sampling systems for the application in biogas plants. Because hydrolysis is a key process for improvements, solutions for monitoring and sampling in an open hydrolysis basin are described too. Finally, the current methods are evaluated concerning their suitability to monitor gradients in the liquid phase online and offline.

MATERIALS AND METHODS

Features of the Observed Biogas Plants. Among the investigated plants was the research biogas plant of the University of Hohenheim (BGP1). It has a capacity of 192 kW. The feedstock solid and liquid manure as well as energy crops were applied. The BGP1 consisted of a digester covered with insulated concrete and a secondary digester that was equipped with a foil inflation dome for gas storage. Every digester had a diameter of 14 m, a height of 6 m, and a maximum volume of 923 m³. Further details have been described elsewhere.⁸

The second biogas plant (BGP2) that was examined had a capacity of 500 kW, and the applied feedstock were grass and corn silage as well as solid turkey manure. BGP2 consists of an open basin for pre-hydrolysis (from now on called the hydrolysis basin) as well as main and secondary digesters, both covered with a foil inflation dome for gas storage. The hydrolysis basin was designed with the following dimensions: a length of 22 m, a width of 10 m, and a depth of 2.4 m, with, thus, a maximum volume of 528 m³. It was equipped with three stirrers (two located opposite to each other and one located at the substrate addition). The stirrers were operated each 90 min for 30 min. The dry mass content was 2% (w/w). The basin was roundly accessible and enclosed by a railing for safety reasons. The main digester had a diameter of 20 m and a height of 6.4 m, which resulted in a maximum volume of 2000 m³.

No special safety measures had to be considered while working at the different reactors besides using a safety belt at head-space measurements in the main digester of BGP2. All reactors were accessible outdoors, so that adequate ventilation was ensured.

Sampling Procedure. Samples were taken with a probe sampling system designed at the University of Hohenheim⁸ at two locations, numbers 2.2 and 3.3 (Figure 1), in the BGP1. It was designed to take samples from the liquid phase via ports at the concrete roof.

The sampling procedure at BGP2 was part of the developments described in the Results. Sample volumes of 50 mL were taken and immediately inactivated by adding a 30% (w/w) KOH solution into the sample to achieve a final concentration of 2% KOH, which resulted in a pH value of >10. The samples were frozen at -20 °C prior to analysis.

Newly Developed Sensor and Sampling Devices. A multiposition sensor device (manufactured by the Kurt-Schwabe-Institute, Meinsberg, Germany) was developed for the application in hydrolysis basins (Figure 2) that consists of three sensor arrays, which were

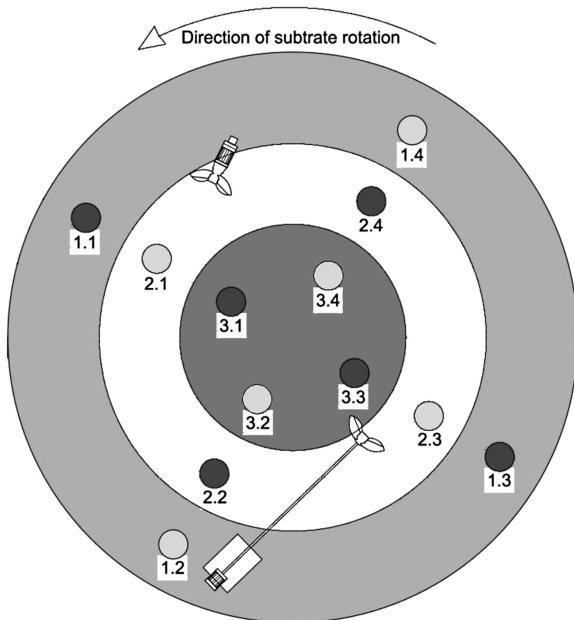


Figure 1. Schematic top view on the roof of the digester of the research biogas plant of the University of Hohenheim, Sampling ports are numbered from 1.1 to 3.4.⁸

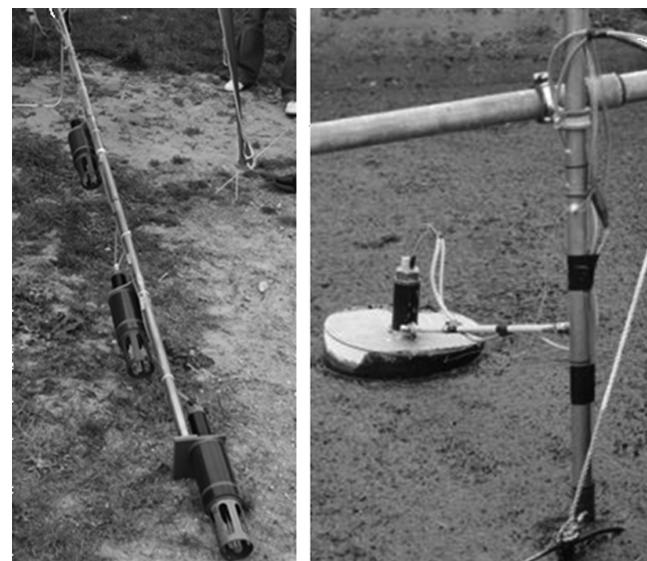


Figure 2. Multiposition sensor lance: (left) three multisensor devices, each encapsulating three electrodes, are mounted on an immersion lance; (right) installation in a hydrolysis basin with a floating measuring head on the liquid surface. Parameters measured are the temperature, pH (potentiometric measurement with a glass electrode), and redox potential with platinum and an Ag/AgCl reference electrode.

mounted at different heights at a steel tube (so-called sampling lance). The measuring heads were equipped with a cage that protected the electrodes from mechanical damage. The parameters temperature, pH value, and redox potential were measured simultaneously. The sensor performance was steadily determined for proving long-term stability. PT1000 probes were used for monitoring the temperature. The pH electrodes consisted of glass, and the redox electrodes consisted of platinum. Impedance converters were necessary for the pH measurements, because the cables were approximately 10 m long. The silver chloride reference electrodes, of which one was installed in each sensor head, were used for measuring the pH value and the redox potential.

Several diaphragms were implemented in each pH electrode. A system driven by a pressure drop enabled a continuous KCl flow. Because of these factors, blockage of the diaphragms was minimized, so that the long-term stability of the electrodes was improved.

A multiparameter electrode, which consists of five miniaturized electrodes, was developed for the multiposition investigation in anaerobic digesters (Kurt-Schwabe-Institute). A PT1000 device was applied to measure the temperature. The pH electrode consisted of glass, and the redox electrode consisted of platinum. The silver chloride reference electrode, which is necessary for the measurement of the pH value and redox potential, is equipped with a removable cup to refill or exchange the inner electrolyte. At the front side of the reference electrode was a porous ceramic diaphragm to ensure the electrolytic contact to the measurement solution.

For the simultaneous measurement of samples in a hydrolysis basin, a tray was constructed (upper left corner of Figure 4), at which four 50 mL plastic sampling tubes were mounted into tube holders on a metallic tray. This tray was equipped with an electromagnetic valve, which allowed for opening and closing all sampling tubes simultaneously. To sample in the center of the basin, the tray was mounted at a wire, which was crossing along the width of the basin.

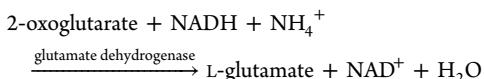
Monitoring at various depths in the liquid phase of an industrial digester with a flexible roof was performed by drilling a hole through the concrete wall of the upper part of the main digester. The hole was closed with a gate valve. This installation could be mounted during operation of the digester. Further, a supporting tray was installed outside the valve to hold the lance with the mounted sensor head at a flange. The lance itself was of a total length of 6 m, consisting of three 2 m long tubes made of carbon-fiber-reinforced plastic (CFRP). The sensor head was mounted on a tensile data transfer cord and could be locked to the lance tip by pulling the cord and strain relief. To minimize the risk of cord breakage, the sensor will be attached to an additional steel cable in the next stage of development. The lance was connected to the gate valve via a metal sleeve pipe adaptor. The lance containing the sensor head on its tip could be pushed into the reactor. As soon as the sensor head was reached into the headspace of the digester, it was located at greater depths by data cord relief.

Data Transmission during Online Monitoring. The electrodes were connected directly to a radio transmission unit, which allows for an easier retrofitting at operating plants. For transmission, unlicensed short-range radio measurements were guided to a database via the GSM network. They were available through a web portal (teleBITcom GmbH, Teltow, Germany). Thus, a decentralized data collection and evaluation was feasible.

Determination of Insoluble Dry Matter Content. Culture broth was centrifuged at 18500g for 10 min, and the resulting pellet resuspended in 30 mL of distilled water and centrifuged again at 18500g for 10 min. After the supernatant was discarded, the pellet was dried for 3 days at 75 °C and weighted.

Enzymatic Determination of the Ammonia Content. The nitrogen content in the supernatant was measured via the ammonia content applying an enzymatic test kit (Boehringer/R-Biopharm AG, Darmstadt, Germany). The test was scaled down with a factor of 20 from the standard cuvette to a microwell plate (MWP).

The principle of the enzymatic test was based on the following reaction:



The NAD⁺ concentration decreased linearly in accordance with the ammonia content. It was determined spectrophotometrically at a wavelength of 340 nm. A total of 100 μL of the reagent mixture was transferred to each well of a MWP. A total of 20 μL of the supernatant was added and mixed, then incubated for 5 min at room temperature, and measured on a plate reader Synergy Mx (BioTek Inc., Winooski, VT). Afterward, 2 μL of glutamate dehydrogenase was added, incubated for 20 min, and measured spectrophotometrically at a wavelength of 340 nm. The differences in the absorbance were applied for the determination of the ammonia concentration.

Determination of Volatile Fatty Acids with High-Performance Liquid Chromatography (HPLC). Volatile fatty acids in the supernatant were measured with a HPLC–refractive index detector (RID) (1200 series, Agilent Technologies, Waldbronn, Germany) equipped with a H⁺, 8 μm column (Hyper REZ XP, Fisher Scientific, Germany) using 10 mM H₂SO₄ as the liquid solvent. The supernatant from the culture was centrifuged at 21500g for 10 min at 4 °C and diluted with demineralized water, if necessary. Afterward, the sample was transferred to HPLC vials (Fisherbrand, Schwerte, Germany) prior to analysis.

All analyses were performed in duplicates or triplicates.

RESULTS

Online Monitoring in a Hydrolysis Basin. Although the design of hydrolysis basins varies, they usually have in common no closed roof. They are stirred in most cases, but the volumetric power input varies because of different designs and operation procedures. The multiparameter probes were submerged into the liquid phase at three different depths (0 m, surface; 1.0 m, center; and 1.6 m, bottom).

The performance of the electrodes was proven several times before and after the application in the hydrolysis basin. The electrodes were measured against a saturated silver/silver chloride reference electrode (SSE) in buffer solutions (pH 4.01, 6.86, and 9.18). The electrodes had a sensitivity of -58.2 mV pH⁻¹ prior to installation. The asymmetries were in a range between -5 and 1 mV. Because of the operation times of 150, 173, or even 232 days, the changes were negligible. The maximum of the slopes decreased or increased about 1 mV pH⁻¹, and the asymmetries varied between 3 and 5 mV.

The calibration of the redox electrodes was conducted in solutions of three different potassium hexacyanoferrate (II) and (III) concentrations. The measurements were performed against a SSE before and after the application in the hydrolysis basin. The redox electrodes showed changes between 0 and 7 mV after 323 days of operation.

The reference electrodes were proven against a SSE in 3 M potassium chloride (KCl) solution before and after the installation. The first calibration resulted in potentials in the range between 8 and 10 mV. After an operation time of 135, 150, or 173 days, the potentials changed only between 1 and 5 mV. Performances of various electrodes before and after installation are depicted in the Supporting Information.

Measurements obtained with the multiposition sensor device as described above and in the materials are depicted in Figure 3. Because the upper sensors are mounted close to the surface, measurements are affected by changed weather conditions and day to night fluctuations (e.g., the air temperature). Additionally, the redox potential indicates a much more fluctuating measurement at the top spot because of the inconsistent stirring, when oxygen is dissolved unevenly. The redox potential near the surface is 10 mV higher than at deeper zones. The temperature in the center part is higher too. There is a deviance of up to 3 °C toward the top phase, in which cooling originating in the temperature of the environment has the greatest impact.

Fluctuations of the pH value are due to freshly added feedstock, which locally disturbs the pH value and influences the microbial activity. In general, crucial parts in a hydrolysis basin are those that exhibit a high release of protons from an accelerated short-chain fatty acid production source. If the release exceeds the buffer capacity, a changed pH value influences the enzymatic activity and harms microbes. Most critical parts are assumed to be located at either the center or

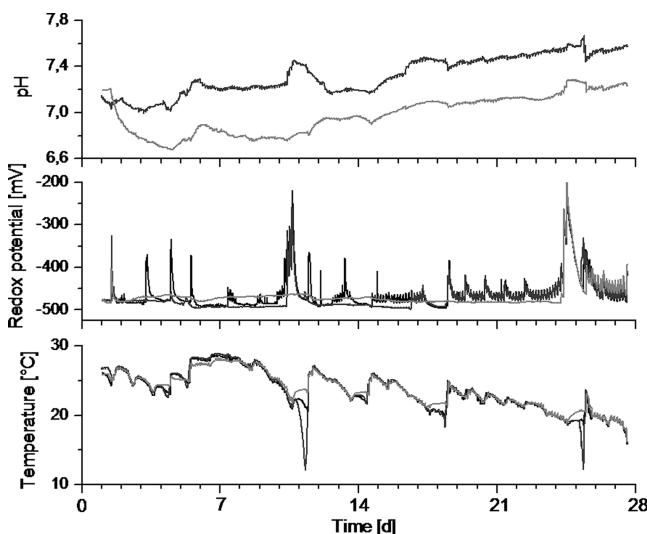


Figure 3. Monitoring of the temperature, pH value, and redox potential in different depths of the liquid phase in a hydrolysis basin with the multiparameter sensor device: (black line) 0 m, surface; (dark gray line) 1 m, center; and (light gray line) 1.6 m, bottom.

the bottom part of the liquid zone as a result of the multiparameter measurements.

Offline Measurements in a Hydrolysis Basin. A novel sampling device was designed for parallel offline analysis, with which several samples were taken at different depths simultaneously (upper left corner of Figure 4). Because of

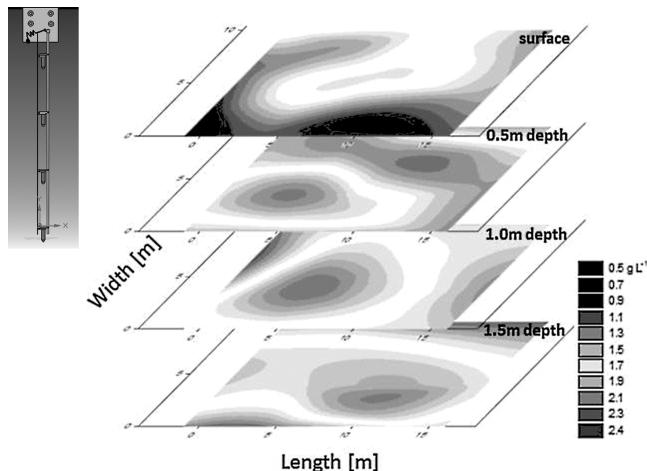


Figure 4. Distribution of the acetic acid concentration in a hydrolysis basin. Values of samples collected at four layers in parallel with a multiposition sampling unit (schematic drawing in the upper left corner) are shown (0, 0.5, 1, and 1.5 m of depth).

multiposition sampling, offline analysis enabled the detection of the concentration distribution of relevant metabolites, such as acetic acid. As seen in Figure 4, concentration gradients of about 2 g L⁻¹ were detected in between the center part compared to the zones at the edges. The observed concentration gradients were in agreement with the assumed mixing behavior because of the location of the stirrers. Gradients were less profound nearby the stirrers. Indeed, the highest accumulation of fatty acids was detected in the zones, in which a lower pH value was detected when the online monitoring was applied. Thus, the method of monitoring at

different positions is suitable for the detection of critical spots and for advanced monitoring in a hydrolysis basin. The optimum location for a sensor device can be defined as the area in which concentration changes are significantly larger than the accuracy of the determination method, as is the case in this example. Thus, the optimal position for fixed sensors and sampling would be the center part at a depth between 0.5 and 1.5 m.

Research Plant Biogas Digester of a Size of 1000 m³.

Online Measurements. The application of the multiposition sensor and sampling devices is more challenging in closed digesters. The overpressure of biogas in the headspace requires special attention for a suitable design, because the risk of methane loss has to be minimized. In contrast to the previous application in open hydrolysis basins, dimensions matter because of the sealed construction. The combination of several sensors to one probe is beneficial when the number of holes are restricted, which is the case at most biogas plants. To minimize the diameters of ports, multiparameter sensor heads equipped with miniaturized electrodes for the determination of the temperature, pH value, and redox potential were developed (Figure 5). These probes were incorporated into a portable



Figure 5. Miniaturized electrodes: (left upper corner) temperature sensor (Pt1000), redox (platinum), reference, and pH (glass) electrodes, with a maximum diameter of 4 mm, length of 40 mm, and service intervals of > 4 weeks without recalibration; (left lower corner) built-in sensor head; and (right) lance coupled to a vertically flexible multiparameter probe for the measurement in the liquid phase.

lance system, which allowed for the movement of the sensors into the bulk of the liquid phase up to 4 m. The diameter of the whole multiparameter sensor head was as small as 55 mm.

The miniaturized electrodes were calibrated before and after the application at 50 °C. The pH electrode was measured against a miniaturized silver/silver chloride reference electrode (3 M KCl) in buffer solutions (pH 4.01 and 9.18). Prior to installation, the electrode had a sensitivity of -61.8 mV pH⁻¹ and an asymmetry of 26.3 mV. The slope increased by 0.3 mV pH⁻¹, and the asymmetry decreased by 0.8 mV. The redox electrode showed changes of only a few millivolts between 0 and 3 mV after 42 days of operation. The reference electrodes were proven against a SSE at 50 °C in 3 M KCl solution before and after operation. Because of the necessity of two measuring devices, two reference electrodes were required. The first calibration resulted in potentials in a range between 4 and 8

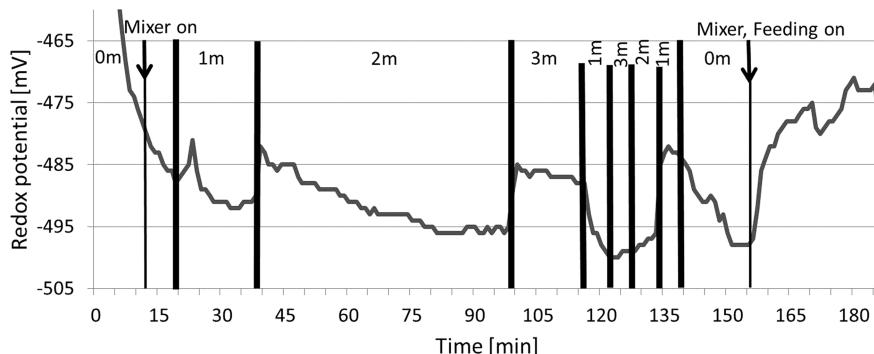


Figure 6. Time course of the redox potential in a 1000 m³ biogas digester in dependence upon the submersion depth of the electrode (up to 3 m from the top; depth measure indicated above). The measurement spot is located half way from the center to the wall of the digester (spot number 2.2, as shown in Figure 1).

mV. After 42 days, the potentials of operation changed by about 31–40 mV. This is a change of 0.7–1 mV per day and cannot be neglected; however, a repeatability of this change would allow for an online adjustment. The repeatability is currently proven during the operation in industrial biogas plants. Selected plots, which show the behavior of the electrodes prior to and after operation, are provided in the Supporting Information.

Gradients in the vertical direction were investigated at the BGP1. The concrete roof was equipped with a total of 12 DN200 openings for depth measurements at the digester. They consist of a gastight lock, which was mounted on the port valve as previously described.⁸ The sensor head was vertically submersed with a lance of a length of 6 m. The continuous measurement with the multiparameter sensor is demonstrated at the redox potential. As expected, the measured values changed with the immersion depth of the measurement probe (Figure 6). At the measurement port number 2.2 (Figure 1), which was located at about half the distance between the vessel wall and the center of it, fluctuations of the measured value of about 10% could be determined. The measured redox potential was influenced by agitation, because it changed quickly after agitation had started. The distribution along the height of the liquid phase indicated a delay time in the order of several minutes after a new position was reached. In the case of a quick change of the position, no steady state was obtained during the measurement time. However, if sufficient time was applied at one position, distinct differences could be determined. The measured profiles at this sample port differed from profiles obtained at other spots. Only negligible deviances were measured along the height of the liquid phase at the center of the vessel (sampling spot number 3.3). This observation indicates a better mixing at this point because of the installation of a stirrer nearby. Similar changes of the signal caused by agitation were not detected for the temperature and the pH value. Thus, monitoring of the redox potential close to the stirrer might be more suitable, while far away from the stirrers, settlement of particles in the fluid could lead to non-representative values if stirring was interrupted.

Offline Measurements. A system that was recently designed by the University of Hohenheim was applied for sampling at different depth layers of the digester.⁸ The dry matter content was ranging from 8.5 to 9.5 g L⁻¹. Although no distinct differences were observable at the different sample ports concerning the dry matter content, concentration gradients for several metabolites could be determined at different depths

(Figure 7). For example, the values of the ammonia content varied up to 20% (w/w) and, for acetic acid, still up to 10% (w/w)

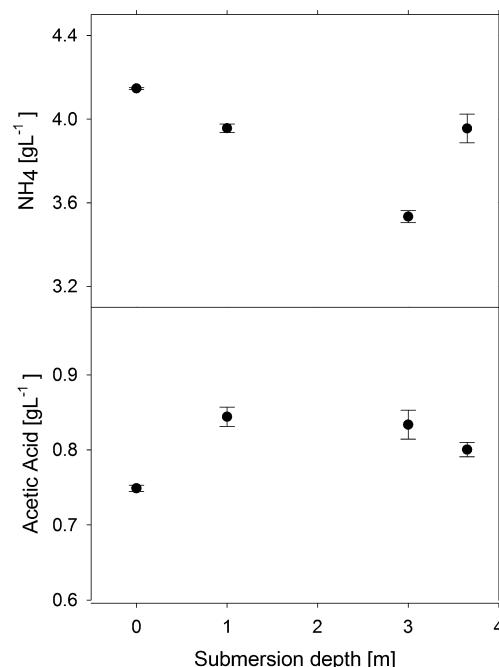


Figure 7. Concentration of (top) ammonium and (bottom) acetic acid in a 1000 m³ biogas digester depending upon the distance of the sampling point to the liquid surface. The sampling point 3.3 is located in the center of the reactor.

w). Samples taken from the bottom and surface parts indicated different concentration levels, while the core of the liquid phase seemed to be rather homogeneous. This leads to the assumption that a suitable sampling port should be located in the bulk of the liquid phase. Usually, sample ports at main digesters do not reach so far into the reactor. In this case, wrong assumptions of the state of the liquid phase might be made.

Industrial-Scale Biogas Digester of a Size of 2000 m³. **Online Measurements.** In this case, sensors could not be installed from the top as in the previous example, because a flexible roof was installed at BGP2. Therefore, ports at the side walls were used. A special challenge is the design of a lance equipped with microsensors and sampling ports that can be installed during plant operation. To overcome the restrictions

of a stiff lance, which can move the sensor head only in one direction, alternative ways had to be found to locate the sensors at vertically variable positions from the top part of the digester. Therefore, a novel solution for the application of a mobile unit was developed that permits the horizontal movement by a lance and the simultaneous vertical movement into various depths (Figure 5).

The distribution of the redox potential indicated a change of the sensor signal after a change of the position of the electrodes. The measured values differed between -200 and -250 mV inside the reactor. This measurement indicates that there are certainly differences along the depth of the liquid phase (data not shown). Relevant gradients were not observable when monitoring the pH value and temperature. In any case, further investigations are necessary to obtain more detailed results from the vertically flexible measurement and concomitant statistical analyses.

Offline Measurements. To take samples from the 2000 m^3 digester, lances made of CFRP were manufactured. The lance consists of three tube parts of a diameter of 45 mm and a length of 2 m , resulting in a total length of 6 m . Five sample chambers of up to 200 mL sample volume were distributed evenly along the length of the lance, allowing for the simultaneous sampling of five samples within a distance of 4 m in the liquid phase. It thus enabled the sampling of layers that are clearly outside the laminar flow near the vessel wall. Two ports are currently installed at the BGP2 that can be used for sampling: (i) a 50 mm ball valve located at 2.20 m beneath the liquid level of the digester and (ii) the previously described gate valve, approximately 0.5 m beneath the liquid surface. There is also a sample port located at 4.5 m below the surface of the liquid layer, which is thus far used as a regular sampling spot.

Initial measurements were performed at a penetration depth of 2.2 m . Samples were taken in the horizontal direction at different distances to the digester wall to identify gradients between the wall and the core of the liquid phase. There existed a concentration gradient of the dry matter from the wall to the liquid core. The dry matter was reduced to 5% in a depth of 0.5 m , while 6% of dry matter was measured near the vessel wall (data not shown). This indicates a viscosity gradient between the vessel wall and the liquid core. As a consequence, accumulation of intermediate products might appear near the wall because of low flow velocities.

Ammonia concentrations were measured because this compound can inhibit biogas production.^{11,12} Additionally, the distribution of acetic acid was measured in the liquid phase (Figure 8). The results show substantial differences between the conditions close to the wall from those in deeper areas in the bulk of the liquid phase. The values of the ammonia concentration vary up to 30% , and the values of the acetic acid concentration vary up to 50% . The highest concentrations were measured close to the wall in each case, the lowest concentrations were measured at 1.5 m distance from the vessel wall. The multiple measurements appear more consistent at the triplicate determination with a larger distance to the vessel wall, as the data spread decreases among samples taken there. Also, the measured values of the samples from the external ports differ significantly from each other. This indicates a poor reproducibility as is typical for samples taken from poorly mixed regions.

The results indicate the importance of the selection of the measurement ports in digesters. Although the examined reactor is almost continuously stirred, gradients are observed.

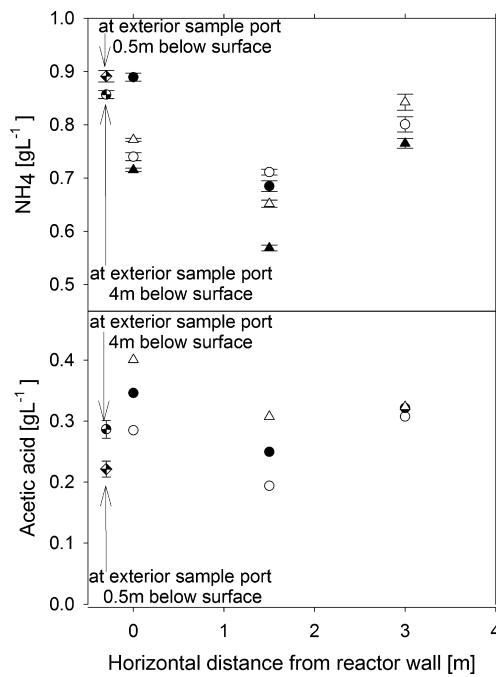


Figure 8. Concentration of (top) ammonia and (bottom) acetic acid in a 2000 m^3 biogas digester depending upon the distance of the sampling point from the reactor wall (depth of penetration). The samples were taken at 3.8 m above the vessel ground (2.2 m immersion depth). For comparison, samples have been taken from exterior sample ports (quartered dots shown at the left edge of the graph) near the vessel wall at a height of 2.0 m (4.0 m below the liquid surface) and at the top of the reactor at a height of 5.5 m (0.5 m below the liquid surface). Different symbols indicate different samples.

Monitoring and sampling in the core of the liquid phase seems to be preferable, instead of commonly applied monitoring and sampling close to the vessel wall.

■ DISCUSSION

Thus far, the stable operation of a biogas process, which is a prerequisite for a sufficient biogas yield, is not feasible at every plant and still a difficult task.¹³ The application of organic residues, in which compositions per batch are highly fluctuating,¹⁴ or, in general, a changing feedstock can cause considerable process instabilities. Any disturbance occurs in the reaction phase at first, i.e., in the microbial cell. Therefore, monitoring of the process should take place as close as possible to the place where the disturbance occurs first, that is, in the liquid phase. The development of (mobile) sampling and sensor systems that are both cost-efficient and easy to install is described in this paper. These tools should be a contribution to close the large gap that still exists between the knowledge-based process optimization in the lab scale and the trial and error practice in industrial scale. As described, miniaturized sensors can be applied to minimize the effort needed for their installation and/or achieve mobility of the sensor probes. An identification of areas that are suitable for monitoring is feasible.

It has been demonstrated that relevant process parameters vary depending upon the position at which samples were taken or a sensor was installed. This leads to the question if lab-scale experiments under homogeneous conditions are able to reflect properly the conditions in the large scale. This question can only be solved if the impact of gradients was investigated more intensively. In particular, a higher resolution of gradients in the

liquid phase allows for the investigation of their role in the biogas production process. Gradients because of biofilm formation near the wall and the usual differences in density and composition at various depths of the liquid phase are only considered when sample ports can be adjusted to various positions or at the most critical region rather than at one single spot.

In many biogas plants, laminar flow prevails because of the viscosity of the culture broth. The flow near the wall is slowed by friction. However, many ports for typical sampling at biogas plants are located very close to the vessel wall, which might lead to a false representation of the conditions in the core of the liquid phase. The spreading of values obtained near the vessel wall (e.g., for the concentration determination for acetic acid) can be based on the uneven formation of pockets. The formation of pockets within the reactor can occur under laminar flow conditions.¹⁵ Within these pockets, the formation of microbial granules can evolve, so that the intercellular metabolite exchange is accelerated.¹⁶ This can even cause a positive effect on the gas production. Thus, zones of poor mixing do not necessarily have a bad effect on the process performance.

Gradients observed for the dry matter content are only measured at the larger biogas plant. One reason might be that the relative power input is approximately 20% smaller compared to the mid-size biogas plant. A low power input generally supports the formation of gradients. This underlines the necessity to observe a large number of plants with reinstallable monitoring and sampling solutions. The solutions presented in this study demand less than €10 000 for installation, whereas a single loss of productivity by 30% (e.g., caused by acidification) in a mid-size biogas plant during 4 weeks usually leads to higher expenditures.

CONCLUSION

The presented tools can be applied widely at industrial-scale plants, which support the idea of a knowledge-based process optimization and operation. Extended sampling efforts with lances might not be applied regularly but in periods of process disturbances. Several promising strategies are being pursued, including the application for model-based process control and sampling. Improved mixing, process monitoring, and control support the acceptance of more flexible feedstock utilization by plant operators, because the presented strategies are suitable to counteract increased risks for process failures.

ASSOCIATED CONTENT

Supporting Information

Comparison of slopes and asymmetries of the pH electrodes installed in the lance for the hydrolysis basin before and after the application (Figure S1), comparison of the potentials of the redox electrodes installed in the lance for the hydrolysis basin before and after the application (Figure S2), comparison of the potentials of the reference electrodes installed in the lance for the hydrolysis basin before and after the application (Figure S3), comparison of slopes and asymmetries of the micro-pH electrode installed in the lance before and after the application (Figure S4), comparison of the potentials of the micro-redox electrode installed in the lance before and after the application (Figure S5), and comparison of the potentials of the micro-reference electrodes installed in the lance before and after the application (Figure S6). This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: stefan.junne@tu-berlin.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors kindly acknowledge the funding of the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (Grant 03KB059) and the German Federal Ministry of Education and Research (Grant 03SF0455A).

REFERENCES

- (1) Nielsen, H. B.; Angelidaki, I. Codigestion of manure and industrial organic waste at centralized biogas plants: Process imbalances and limitations. *Water Sci. Technol.* **2008**, *58* (7), 1521–1528.
- (2) Stockl, A.; Oechsner, H. Near-infrared spectroscopic online monitoring of process stability in biogas plants. *Eng. Life Sci.* **2012**, *12* (3), 295–305.
- (3) Weiland, P. *Biogas-Messprogramm II*; Fachagentur Nachwachsende Rohstoffe e.V.: Gützow, Germany, 2009; ISBN: 978-3-9803927-8-5.
- (4) Ward, A. J.; Bruni, E.; Lykkegaard, M. K.; Feilberg, A.; Adamsen, A. P. S.; Jensen, A. P.; Poulsen, A. K. Real time monitoring of a biogas digester with gas chromatography, near-infrared spectroscopy, and membrane-inlet mass spectrometry. *Bioresour. Technol.* **2011**, *102* (5), 4098–4103.
- (5) Enfors, S. O.; Jahic, M.; Rozkov, A.; Xu, B.; Hecker, M.; Jurgen, B.; Kruger, E.; Schweder, T.; Hamer, G.; O'Beirne, D.; Noisommit-Rizzi, N.; Reuss, M.; Boone, L.; Hewitt, C.; McFarlane, C.; Nienow, A.; Kovacs, T.; Tragardh, C.; Fuchs, L.; Revstedt, J.; Friberg, P. C.; Hjertager, B.; Blomsten, G.; Skogman, H.; Hjort, S.; Hoeks, F.; Lin, H. Y.; Neubauer, P.; van der Lans, R.; Luyben, K.; Vrabel, P.; Manelius, A. Physiological responses to mixing in large scale bioreactors. *J. Biotechnol.* **2001**, *85* (2), 175–185.
- (6) Neubauer, P.; Junne, S. Scale-down simulators for metabolic analysis of large-scale bioprocesses. *Curr. Opin. Biotechnol.* **2010**, *21* (1), 114–121.
- (7) Nienow, A. W.; Nordkvist, M.; Boulton, C. A. Scale-down/scale-up studies leading to improved commercial beer fermentation. *Biotechnol. J.* **2011**, *6* (8), 911–925.
- (8) Lemmer, A.; Naegele, H.-J.; Sondermann, J. How efficient are agitators in biogas digesters? Determination of the efficiency of submersible motor mixers and incline agitators by measuring nutrient distribution in full-scale agricultural biogas digesters. *Energies* **2013**, *6* (12), 6255–6273.
- (9) Shen, F.; Tian, L.; Yuan, H.; Pang, Y.; Chen, S.; Zou, D.; Zhu, B.; Liu, Y.; Li, X. Improving the mixing performances of rice straw anaerobic digestion for higher biogas production by computational fluid dynamics (CFD) simulation. *Appl. Biochem. Biotechnol.* **2013**, *171* (3), 626–642.
- (10) Yekta, S. S.; Gonsior, M.; Schmitt-Kopplin, P.; Svensson, B. H. Characterization of dissolved organic matter in full scale continuous stirred tank biogas reactors using ultrahigh resolution mass spectrometry: A qualitative overview. *Environ. Sci. Technol.* **2012**, *46* (22), 12711–12719.
- (11) Yenigün, O.; Demirel, B. Ammonia inhibition in anaerobic digestion: A review. *Process Biochem.* **2013**, *48* (5–6), 901–911.
- (12) Rajagopal, R.; Massé, D. I.; Singh, G. A critical review on inhibition of anaerobic digestion process by excess ammonia. *Bioresour. Technol.* **2013**, *143*, 632–641.
- (13) Costa, J. C.; Moita, I.; Abreu, A. A.; Ferreira, E. C.; Alves, M. M. Advanced monitoring of high-rate anaerobic reactors through quantitative image analysis of granular sludge and multivariate statistical analysis. *Biotechnol. Bioeng.* **2009**, *102* (2), 445–456.

- (14) Álvarez, J. A.; Otero, L.; Lema, J. M. A methodology for optimizing feed composition for anaerobic co-digestion of agro-industrial wastes. *Bioresour. Technol.* **2010**, *101* (4), 1153–1158.
- (15) Sindall, R.; Bridgeman, J.; Carliell-Marquet, C. Velocity gradient as a tool to characterise the link between mixing and biogas production in anaerobic waste digesters. *Water Sci. Technol.* **2013**, *67* (12), 2800–2806.
- (16) de Bok, F. A.; Plugge, C. M.; Stams, A. J. Interspecies electron transfer in methanogenic propionate degrading consortia. *Water Res.* **2004**, *38* (6), 1368–1375.