Process monitoring in biogas plants

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1. Introduction

1.1 Why is process monitoring necessary?

Biogas plants are biological systems involving various interacting microorganisms that anaerobically degrade organic matter. The main product is biogas, a gas rich in methane (CH₄) that can be used as a renewable fuel for vehicles or to generate heat or electricity for local use or for use via energy distribution grids. The degradation involves four consecutive biological processes: hydrolysis, acidogenesis, acetogenesis and methanogenesis (see Figure 1). If one of these processes is negatively affected in any way there is an immediate influence on the other processes and the biogas plant can become unstable. Typical process failures include, among others, organic overload, hydraulic overload and ammonia inhibition (see section 2 for details).

Process monitoring can help to understand what happens in a biogas plant and help to maintain a stable process. In many cases, a strongly inhibited microorganism population or a total crash of the whole plant can have severe financial consequences for the biogas plant operator.

In general, process monitoring can help to:
- give an overall picture of the biogas process
- identify upcoming instabilities in anaerobic digesters before a crash happens
- accompany a successful start-up or re-start of a plant

The costs of basic monitoring are often much lower than the costs and lost revenue associated with re-establishing a biologically destabilised plant. For example, if a biogas plant has totally crashed it may have to be emptied and filled again with new inoculum. This, together with the necessary start-up period, means that several months can be lost during which the plant could have operated at full load (Henkelmann et al., 2010). The financial consequences can be devastating for the plant operator.

1.2 What is meant by process monitoring in this brochure?

This brochure focuses on the monitoring of parameters that are concerned with stability of the anaerobic degradation process. These parameters are mainly driven by biological interactions and as a result the monitoring of a biogas plant is very different from many other industrial processes. This brochure describes the different monitoring methods, the way they are applied and how monitoring data are obtained. In addition, advice

![Figure 1 Degradation steps in anaerobic digestion (adapted from Speece, 1996)]
regarding the amount and frequency of monitoring is given.

In addition to the biological parameters, there are also technical parameters that need to be monitored in a biogas installation. This means a regular check of the functionality of equipment (e.g. pumps, valves, CHP – combined heat and power plant, etc.). Another important point to take into account is the monitoring of plant safety, for example emissions of explosive gas mixtures and toxic gases (e.g. hydrogen sulphide). Whilst important, monitoring of technical equipment and safety is not described in this brochure.

Another aspect not covered in this brochure is detailed process optimisation of, for example, gas production and economic performance.

1.3 How can process monitoring be established?

Every biogas plant develops its own unique process conditions and as a result there is no single value for each process parameter that can be referenced to all plants. For each plant it is therefore important that values of relevant process parameters, such as temperature and pH, are established during stable operation. By recording these process parameters over the life of the plant, any change from “normal” can be identified quickly. Apart from recording these parameters, general process information such as mass of input, organic loading rate and operational problems should be documented (Schriewer, 2011). Whilst much of this information is recorded automatically in automated plants, it is recommended to keep a manual operational logbook.

Apart from the off-line analysis of parameters, which means analysis of samples in a laboratory, a minimum of on-line process monitoring equipment will have to be installed in every biogas plant. In general, the level of investment in on-line equipment should always be made in relation with the economic risks in the biogas plant (Henkelmann et al., 2010).

2 Possible Reasons for Process Instabilities

In order to better understand the reasons for implementing biological process monitoring, the possible causes for process instabilities in biogas plants are summarised in this section. These causes can include feeding problems, temperature variations, lack of trace elements that support a healthy community of microorganisms and the presence of inhibitory or toxic substances. As the microbial community within each digester is able to adapt to changes to a certain extent, it is often not possible to state definitive stability limits.

Before going into detail, it should be stated that many process imbalances can be avoided by good operation practice. Therefore, adequate training of the operating staff of a biogas plant is an important matter (see section 4.4). The following general recommendations are given so that a biogas plant operator can avoid process imbalances (Clemens, 2012):

- Continuous feeding rate
- Consistent feedstock mix (e.g. manure and biowaste)
- Gradual and careful change of feedstock mixes when required
- Avoid temperature changes
- Constant intervals and intensity of stirring or agitating
- Continuous process monitoring and control

2.1 Problems caused by changing feeding loads and intervals

2.1.1 Unstable feed

If large variations of the daily organic loading rate (see section 3.3.1) to the biogas occur, this will result in variable rates of gas production. Whilst this is often not a real problem with regard to process stability, it can result in decreased productivity of the biogas plant. In addition, if the energy contents of two different batches of feedstock, for example grass silage, are different, biogas production will change, although the nominal feeding rate has not been changed. Another aspect can be interrup-
tions of the feed to the biogas plant. Depending on the feedstock and the specific plant, feeding interruptions of some days (Gallert and Winter, 2008; Drosg, 2012) or sometimes even hours (according to Forstner and Schlachter, 2012) can cause considerable problems with process stability. This is, however, very plant-specific, depending on feedstock and process.

2.1.2 Organic overload

An organic overload occurs when the amount of organic matter fed to the biogas plant exceeds the total degradation capacity of the microbes to produce biogas. As a consequence the organic matter is only partially degraded to volatile fatty acids (VFA) which then accumulate in the reactor. In this situation, methane concentration in the biogas normally declines. If the concentration of the accumulated VFA exceeds the buffer capacity in the reactor, acidification of the digester occurs and the pH decreases. If no countermeasures are taken, acidification will reduce biogas production to a point where it is zero. In practice, typical causes of organic overload (and consequently acidification) are changes in feedstock mixture and composition, incorrectly measured inputs or increased mixing which suddenly leads to inclusion of unreacted material (e.g. floating layers) into the digestion process (Schriewer, 2011).

2.1.3 Hydraulic overload

In addition to organic overload, hydraulic overload is also a possible cause of process instability. If the hydraulic retention time (see section 3.3.2) does not allow enough time for multiplication of the anaerobic microbes, their concentration will decline and they will gradually be washed out of the reactor. This will logically pose a problem as biogas production is directly proportional to the concentration of the anaerobic microbes. Hydraulic overload is especially problematic in anaerobic processes because some of the microorganisms involved can have very long reproduction times. Methane-forming microbes can show doubling times (doubling of the population) up to 30 days (Gerardi, 2003), and if inhibition is involved doubling time will even increase beyond that. The washing-out of microbes will finally lead to accumulation of VFA in a manner similar to organic overload, as acidifying microbes grow faster than methanogens. Washing out will finally result in biogas production ceasing. It is therefore important that all liquid inputs, as well as solid inputs, to a digester are measured and recorded.

2.2 Temperature changes

In general, microbes and microbial consortia operate optimally at specific temperatures. In biogas plants, where mixed cultures are involved, the composition of the different microbes will adapt to the fermentation temperature. For this reason it is necessary that the fermentation temperature is kept stable and no major variations occur during the process. According to Gerardi (2003) it is recommended to keep daily temperature variations <1°C for thermophilic biogas processes and within 2-3°C for mesophilic processes. For the start-up of a biogas plant, an inoculum should be used that is already adapted to the future operation temperature, in order to reduce the adaptation time, and by that the duration of the start-up.

In contrast to the conditions described above, a strategic increase in process temperature, for example from psychrophilic (<25°C) to mesophilic (36 to 43°C) temperatures, can make sense. This is because a mesophilic process is much more efficient. If a planned increase in temperature is carried out, feeding rate should be reduced as temperature sensitivity increases with loading rate (Speece, 1996). In addition, microbes normally need a time span of several weeks to adapt to the new temperature. Such a strategic temperature shift should be a very rare event, and afterwards temperature must be kept stable again. For more data on temperature shifts, see Lindorfer et al. (2008).

2.3 Ammonia inhibition

Ammonium nitrogen (NH₄-N) is produced by the degradation of proteins during anaerobic digestion of feedstocks containing nitrogen. In an aqueous environment such as in a digester, NH₄-N is present as ammonium ions (NH₄⁺) and as free ammonia (NH₃(aq)). With rising pH or temperature, the percentage of NH₄⁻ present as free ammonia (NH₃(aq)) increases. The free ammonia (NH₃(aq)) is considered to be the main cause of
inhibition since it freely passes through the cell membrane of the microbes (Chen et al., 2008). Several mechanisms for inhibition have been proposed, including a change in the intracellular pH, an increase in maintenance energy required for metabolism and inhibition of a microbial enzyme reaction (Chen et al., 2008).

In addition to the influence of temperature and pH on ammonia inhibition, adaptation of the microbes to high ammonia concentrations is an important factor. In practice, high nitrogen feedstocks can frequently pose problems on process stability in biogas plants. Rapid changes from low nitrogen feedstocks to high nitrogen feedstocks can be especially problematic. As this depends on the specific mixed culture and its adaptation to ammonia, it is very difficult to define stability limits. Consequently, in the literature very different inhibitory concentrations of ammonium nitrogen are given. According to Bischofsberger et al. (2005), inhibition starts at 1.5 to 3.0 g NH₄-N L⁻¹. However, there are other reports that inhibition starts at substantially higher concentrations: 5.0 g NH₄-N L⁻¹ (Braun, 1982), 8.5 g NH₄-N L⁻¹ (Speece, 1996) and 14 g NH₄-N L⁻¹ (Chen et al., 2008). The difficulty of defining stability limits for NH₄-N is also discussed in section 4.2.1 and Table 4. According to Drosg (2013), for a stable anaerobic process at high ammonia concentrations, the following parameters are a prerequisite: sufficient adaptation time for the microbes (adaptation can take several weeks and is done at low organic loading rate), good trace element availability (see section 2.6) and low to medium hydrogen sulphide concentrations (see section 2.4).

2.4 Hydrogen sulphide inhibition

Hydrogen sulphide inhibition starts at about 30 mg H₂S(aq) L⁻¹ according to Bischofsberger et al. (2005), whereas Braun (1982) states that inhibition does not normally occur below 100 mg H₂S(aq) L⁻¹ and even 200 mg H₂S(aq) L⁻¹ can be tolerated after sufficient adaptation time. According to Chen et al. (2008), the range of inhibitory limits for H₂S(aq) in the literature is even wider: 40 to 400 mg H₂S(aq) L⁻¹. Nonetheless, practical experiences have shown that H₂S(aq) can become problematic at much lower concentrations, especially when coupled with other inhibitory components such as ammonia (Chen et al. 2008) or low iron concentrations (Speece, 1996).

2.5 Further inhibitory substances in feedstocks

2.5.1 Heavy metal ions

With regard to heavy metals, the situation is similar to other biological organisms. At low concentrations they can be essential for microbial activity (see section 2.6), whereas at higher concentrations they can be toxic. Heavy metals can be measured by ICP-MS (inductively coupled plasma mass spectrometry) or AAS (atomic absorption spectrometry) in samples removed from the digester. Usually, low levels of heavy metals are readily tolerated because they form poorly soluble precipitates with sulphide and carbonate which reduces their bioavailability. Therefore, monitoring for toxicity reasons is only necessary in feedstocks where higher concentrations are expected (e.g. biowaste). Normally heavy metals are analysed regularly in biowaste treatment plants in order to monitor digestate quality rather than process stability. The lowest limits of reported negative effects for heavy metals are Cu (40 mg L⁻¹), Cd (20 mg L⁻¹), Zn (150 mg L⁻¹), Ni (10 mg L⁻¹), Pb (340 mg L⁻¹) and Cr (100 mg L⁻¹), according to Bischofsberger et al. (2005). Braun (1982) describes the following concentrations to cause 20% inhibition at pH 8: Cd (157 mg L⁻¹), Ni (73 mg L⁻¹), Cu (113 mg L⁻¹) and Zn (116 mg L⁻¹).

2.5.2 Antibiotics and disinfectants

It is obvious that most detergents and chemicals that are designed to inhibit or kill microbes will have a negative effect on anaerobic digestion. Antibiotics, for example, can be present in manure or other animal residues. While there are some antibiotics that show no effect on
anaerobic digestion (e.g. erythromycin), there are others that show partial inhibitory effects (e.g. aminoglycosides) or others that show strong effects (e.g. chlortetracycline) (Sanz et al., 1996). Disinfectants are often used on farms or in the food industry. According to Poels et al. (1984) disinfectant doses should not be higher than recommended for farm use and only low-toxicity antimicrobial agents should be used in order to minimise possible digester failures. Concentrations of antibiotics and disinfectants in feedstock are not usually monitored.

2.6 Trace element limitation

A lack of micro elements / trace elements can be responsible for decreasing performance in biogas plants, which is then called “trace element limitation”. Figure 2 illustrates how a single essential trace element can become the limiting factor of microbial activity if its availability is too low. Essential trace elements in a biogas process can be Ni, Co, Mb, Se according to Henkelmann et al. (2010), but also iron (Fe) has to be available for a stable process. Trace elements are often necessary for the build-up of enzymes, and are therefore essential for the microbes. The presence of certain trace elements in the fermentation broth can be determined, similar to heavy metal measurements (see section 2.5.1). However, apart from their physical presence in the reactor, they also need to be biologically available for the microbes.

In order to be bioavailable trace elements first have to be soluble, and secondly they should neither be present in the form of precipitates (e.g. sulphides, carbonates) nor adsorbed. According to Ortner (2012) for analysis with regard to estimations on bioavailability, different solvents can be applied one after another to the digester samples. Subsequently, the presence of the different trace elements in the different solvents is analysed, which indicates their bioavailability.

A lack of trace elements is more likely to occur in mono-digestion (e.g. the by-product stillage from ethanol fermentation), but it can also occur in co-digestion. Normally, if a high percentage of manure is used as feedstock, a lack of trace elements rarely arises (Schriewer, 2011). Testing for trace element limitation is not regularly carried out, so it has not been added to the list of process monitoring parameters presented in this brochure (see section 3). If a plant shows problems with process stability and VFA concentrations increase, the first and most obvious reasons for process imbalances (see section 2.1 to 2.5) have to be checked and eliminated. If the symptoms remain, it pays to have a look at trace element availability so that appropriate trace elements can be added. However, as mentioned above (section 2.5.1), if trace elements are added at too high an amount they can become inhibitory. In addition, land application of digestate can become problematic if trace element concentrations in the digestate exceed legal application limits in the digestate.

Figure 2 This barrel illustrates the problem of trace element limitation. Microbial growth is indicated by the water level and trace element availability is indicated by the pieces of wood of the barrel. One trace element (in this case cobalt) can limit microbial growth, even if the other elements are in excess (reproduced with the kind permission of Schriewer Biogas Consulting).
3 Process Monitoring Parameters

In this section the methods and the background of the different monitoring parameters are given. As process monitoring is quite complex and potentially expensive, the details with regard to frequency of measurements and preferable ranges of parameters will be discussed separately in section 4.2.

All together, the most important parameters for process monitoring and control can be put into the following groups (according to Weiland, 2008):

- Parameters characterising the process (section 3.1)
- Early indicators of process imbalance (section 3.2)
- Variable process parameters (section 3.3)

3.1 Parameters characterising the process

Parameters characterising the process which are considered:

- Quantity and composition of feedstock
- Biogas production and gas composition
- Fermentation temperature
- Total solids / dry matter
- pH value
- Ammonium nitrogen

These parameters describe the state of the overall biogas process. It is necessary to monitor them to identify the possible reasons for changes in process stability. However, they cannot be used as early indicators of process imbalance (Weiland, 2008). The reason is that, for example, decreases in gas production or in pH are frequent signs of already occurring process instability. Other parameters, such as changes in H₂ or VFA concentration happen before the process becomes unstable and allow the plant operator to counteract the situation before a process imbalance happens.

3.1.1 Quantity and composition of feedstock

Feedstock quantity

As changes in the amount of feeding and composition of feedstock can be responsible for process instabilities (see section 2.1), it is necessary to record the mass input to the biogas plant. For solid feedstock this can be done by an automatic feeding system (Figure 3) fitted with weighing cells (Figure 4) and data loggers. In order...
to protect the feeding system from damage by loading machinery, a small barrier should be placed in front of it (Schwieger, 2011) (see Figure 3). Although not very accurate, in less sophisticated biogas plants, the daily numbers of shovel loads, for example by a wheel loader, can provide valuable information. Feed reduction can lead to a lower biogas production and feed increase can lead to acidification, and consequently to process instability (see section 2.1).

In addition to solid feedstocks, liquid feedstocks should be recorded for two reasons. The first reason is that if they contain high amounts of organic matter they will contribute to the daily feed of organic matter to the biogas plant. The second is that high amounts of liquids (e.g. rain water) in feedstock lower the retention time and can lead to hydraulic overload (see section 2.1.3).

Many existing biogas plants use weighing equipment for measuring the input of solid feedstock. For liquid feedstock, often no quantification takes place. According to FNR (2009), almost 50% of the German biogas plants investigated do not measure input of liquid feedstock or process water. Since practically all biogas plants are continuously stirred tank reactors (CSTR) which have no special retention system for microbes, the daily input of solid and liquid feedstock determines the retention time of the microorganisms (see HRT, section 3.3.2). As the input of liquids to the digester is often not documented as indicated above, operators of such biogas plants do not know the real retention time in the plant. According to the LfL (2007), measurement of the quantity of liquid feedstock is best carried out by flow meters. Recording the levels of storage tanks can be also useful. Recording pumping time is another alternative; this will give inexact information because pump flow rate depends on the composition of the respective feedstock as well as on gradual wear of the pump (LfL, 2007).

**Feedstock Characterisation**

In addition to quantifying feedstock, characterisation of feedstock is very important. This is especially the case for waste treatment plants, where a large variety of different feedstocks are used. It is thus essential to monitor the specific feedstocks that enter the plant. If the feedstock in a biogas plant is always quite similar (e.g. manure) and the plant is working well, feedstock characterisation is normally less important. For biogas plant monitoring, a comprehensive list of the most relevant feedstock parameters can be found in Table 1, as well as the corresponding methods for analysis.

Feedstock pH is important to know, as an excess of highly acidic or alkaline feedstock can cause a deviation of the digester from its favourable pH range of pH 7-8. In this case, addition of caustic (or acid) is necessary. Nonetheless, in practice a wide pH-range of feedstocks is acceptable due to the buffering capacity of a biogas digester.

As another feedstock parameter, the volatile solids (VS) represent the organic matter which is the source from which biogas is produced and is therefore very important. In many feedstocks the ash content is quite low, so in practice total solids (TS) content can provide sufficient information (TS equals VS plus ash). For liquid feedstocks like wastewater, VS (or TS) are often not good parameters to try and follow because the volatile substances present (acetic acid, ethanol, etc.) cannot be determined. In these cases a COD (chemical oxygen demand) measurement is applied. COD measurements are rarely applied for solid feedstocks as the analysis is more complex than the VS measurement and the reproducibility is quite poor for a solid or inhomogeneous feedstock.

The total Kjeldahl nitrogen (TKN) indicates the nitrogen content of a feedstock. Monitoring TKN content of feedstocks can be important because a change from nitrogen-poor to nitrogen-rich feedstock mixtures can cause severe process instabilities. The reason for this is that nitrogen-rich feedstocks will lead to ammonia accumulation in the digester which can cause ammonia inhibition (see section 2.3).

Carrying out a BMP test (biomethane potential, see Figure 5) for a feedstock gives important information on how much biogas will be produced from the feedstock and how fast the degradation process will be. As BMP tests are rather time consuming they are applied in special cases, for example, if a completely new feedstock should be evaluated.
Table 1 Overview on relevant parameters and methods of analysis for the characterisation of biogas feedstocks
(adapted from Drosg et al., 2013)

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Standard/a)</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value</td>
<td>EN 12 176</td>
<td>Characterization of sludge – Determination of pH value</td>
</tr>
<tr>
<td></td>
<td>APHA 4500-H B</td>
<td>pH value “Electrometric method”</td>
</tr>
<tr>
<td>Total solids (TS) / Dry matter (DM)</td>
<td>EN 12 880</td>
<td>Characterization of sludges – Determination of dry residue and water content</td>
</tr>
<tr>
<td></td>
<td>APHA 2540 B</td>
<td>Total solids dried at 103 –105°C</td>
</tr>
<tr>
<td>Volatile solids (VS) / Organic dry matter (oDM)</td>
<td>EN 12 879</td>
<td>Characterization of sludges – Determination of the loss on ignition of dry mass</td>
</tr>
<tr>
<td></td>
<td>APHA 2540 E</td>
<td>Fixed and volatile solids ignited at 550°C</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>DIN 38 414 (S9)</td>
<td>German standard methods for the examination of water, wastewater and sludge – Sludge and sediments (group S) – Determination of the chemical oxygen demand (COD) (S9)</td>
</tr>
<tr>
<td></td>
<td>APHA 5220 B</td>
<td>Chemical oxygen demand (COD) “Open reflux method”</td>
</tr>
<tr>
<td>Total Kjeldahl nitrogen (TKN)</td>
<td>ISO 5663</td>
<td>Water quality – Determination of Kjeldahl nitrogen – Method after mineralisation with selenium</td>
</tr>
<tr>
<td></td>
<td>ISO 11261</td>
<td>Soil quality – Determination of total nitrogen – Modified Kjeldahl method</td>
</tr>
<tr>
<td></td>
<td>APHA 4500-Norg B</td>
<td>Nitrogen (organic) “Macro-Kjeldahl method”</td>
</tr>
<tr>
<td>Biochemical methane potential / Biomethane potential (BMP)</td>
<td>EN 11734</td>
<td>Water Quality – Evaluation of the “ultimate” anaerobic degradability of organic compounds in digested sludge – Method by measurement of the biogas production</td>
</tr>
<tr>
<td></td>
<td>DIN 38414 (S8)</td>
<td>German standard methods for the examination of water, wastewater and sludge – Sludge and sediments (group S) – Determination of the amenability to anaerobic digestion (S8)</td>
</tr>
<tr>
<td></td>
<td>VDI 4830</td>
<td>Fermentation of organic materials – Characterisation of the substrate, sampling, collection of material data, fermentation tests</td>
</tr>
</tbody>
</table>

a) VDI – Verein Deutscher Ingenieure, Düsseldorf, Germany; ISO – International Organisation of Standardization, Geneva, Switzerland; EN – European Committee for Standardisation, Brussels, Belgium; APHA – American Public Health Association, Washington DC, USA; DIN – Deutsches Instituts für Normung e. V., Berlin, Germany

Figure 5 Set-up of a simplified test for measuring the biochemical methane potential (BMP). In a temperature-regulated environment (e.g. under mesophilic temperature) a fermenter flask with a mix of inoculum and feedstock is set up. The produced biogas passes a bottle of a NaOH solution, where the CO₂ is retained. The gas which passes is considered to be CH₄ and is measured by water displacement (for details see Drosg et al., 2013).
3.1.2 Biogas production and gas composition

As usual in biotechnological processes, the detailed monitoring of the fermentation product, in this case biogas, provides valuable information. Therefore, it is recommended to monitor both the volume of gas produced and gas composition. With regard to process monitoring, a change in either gas production or gas composition can be an indicator of process imbalance.

Biogas production (biogas volume)

In general, a large variety of devices can be applied for measuring biogas production/volume:

- Ultrasonic flow meters
- Fluidistor oscillator probes
- Turbine flow meters
- Vortex flow meters
- Dynamic pressure probes
- Thermal flow meters
- Diaphragm gas meters / bellows gas meters

In practice, as biogas is of variable gas composition, dirty, corrosive, wet, and produced at low pressure, measuring biogas volume accurately is one of the most challenging parameters at a biogas plant. An overview of the advantages and disadvantages of the different measuring systems is given in Table 2. In general, gas flow meters should be placed in a way that enables easy removal and cleaning. Another important point is that the complexity of the sensor (data transfer, calculation effort, etc.) should suit the purpose of the plant.

Table 2 Overview of advantages and disadvantages of different sensors for gas volume measurement (adapted from Keitlinghaus, 2011 and Vaßen, 2012)

<table>
<thead>
<tr>
<th>Sensor Type</th>
<th>+</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrasonic flow meters</td>
<td>• Good results at low pressure</td>
<td>• Long straight measuring distance needed (15 times the diameter)</td>
</tr>
<tr>
<td></td>
<td>• No moving parts</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Very reliable even at changing process conditions</td>
<td></td>
</tr>
<tr>
<td>Fluidistor oscillator</td>
<td>• No moving parts</td>
<td>• Complex calculation to norm cubic meters</td>
</tr>
<tr>
<td></td>
<td>• High accuracy</td>
<td>• Error of 1.5%</td>
</tr>
<tr>
<td></td>
<td>• Low cost</td>
<td>• Sensitive to vibrations in the biogas caused by e.g. piston</td>
</tr>
<tr>
<td></td>
<td>• Easy handling, exchange and cleaning</td>
<td>compressors</td>
</tr>
<tr>
<td>Turbine flow meters</td>
<td>• Robust technology</td>
<td>• Deposits can become problematic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Moving parts</td>
</tr>
<tr>
<td>Vortex flow meter</td>
<td>• No moving parts</td>
<td>• Sensitive to disturbances in flow</td>
</tr>
<tr>
<td></td>
<td>• High durability</td>
<td>• Long straight measuring distance needed (30 times the diameter)</td>
</tr>
<tr>
<td></td>
<td>• Resistant to corrosion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Low pressure loss</td>
<td></td>
</tr>
<tr>
<td>Dynamic pressure probes</td>
<td>• Long durability</td>
<td>• Works better at higher gas pressure</td>
</tr>
<tr>
<td></td>
<td>• Dirty gas has little influence</td>
<td>• Large calibration effort</td>
</tr>
<tr>
<td></td>
<td>• Pressure fluctuations have no negative effect on accuracy</td>
<td>• Error of 1.5-5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• For calculation of Nm³ the density (gas composition) is needed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Long measuring distance needed</td>
</tr>
<tr>
<td>Thermal flow meters</td>
<td>• Easy handling</td>
<td>• No dirty biogas measurement possible</td>
</tr>
<tr>
<td></td>
<td>• Good for mobile applications</td>
<td>• Measurement error of 3-5% (increases rapidly if gas is dirty)</td>
</tr>
<tr>
<td></td>
<td>• Direct measurement of Nm³/mass</td>
<td>• Extremely sensitive to humidity</td>
</tr>
<tr>
<td></td>
<td>• Exact Measurement also at pressure fluctuations</td>
<td>• Long straight measuring distance needed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Calibration once a year</td>
</tr>
<tr>
<td>Diaphragm gas meters / bellows gas</td>
<td>• Simple and cheap</td>
<td>• Corrosion, fouling or deterioration of gas meter by biogas</td>
</tr>
<tr>
<td>meters</td>
<td>• Direct volume measurement</td>
<td>components and particles</td>
</tr>
<tr>
<td></td>
<td>• Robust technology</td>
<td>• Increased utilization time decreases accuracy of measurements</td>
</tr>
<tr>
<td></td>
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<td>• External calibration and maintenance</td>
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</table>
According to Vaßen (2012) the best options for measuring raw biogas are ultrasonic flow meters (see Figure 6) and fluidistor oscillator meters because water and corrosive components in the biogas can be managed and accurate measurements at low gas pressures are possible. In addition, turbine flow meters, vortex flow meters and dynamic pressure probes are useful options. However, deposits or biofilms can pose problems in long-term operation so that regular maintenance and cleaning should be facilitated. In less sophisticated or rather small-scale biogas plants diaphragm meters or bellows meters are in use (Clemens, 2012). However, in the long run such mechanical gas meters can pose considerable problems due to corrosion, fouling or general deterioration when measuring raw biogas. Biogas can also be measured after cleaning and drying in order to avoid problems caused by humidity or corrosion. However, in this case the direct on-line information of gas production is lost and this is of great interest for process monitoring. Gas drying and cleaning is a prerequisite if for example thermal flow meters are used.

Apart from monitoring the fermentation product, the biogas volume measurement can be used to calculate the biogas yield, per unit of mass input of organic material, which is an important parameter (e.g. Nm³ t⁻¹ VS). For obtaining accurate biogas yields, measurements should be made over a period of about a week and during a time where feedstock mix and OLR remain constant. This parameter gives a good overall view of the performance of the degradation process. As a comparison, measured biogas yields are in the range of 200-500 Nm³ t⁻¹ VS for cow manure, 450-700 Nm³ t⁻¹ VS for corn silage and 200-500 Nm³ t⁻¹ VS for food waste (FNR, 2004).

Maximum theoretical biogas yields possible are 746 Nm³ t⁻¹ VS for carbohydrates, 1390 Nm³ t⁻¹ VS for lipids and 800 Nm³ t⁻¹ VS for proteins (VDI 4630, 2006).

**Biogas composition**

Many biogas plant operators install on-line measuring devices for gas composition (see Figure 7), but portable gas composition measuring devices are also in use (FNR, 2004). Gas composition measurements include CH₄ and CO₂, which are measured by infrared or thermal conductivity sensors, as well as in most cases H₂S and O₂, which are determined by electrochemical sensors (LfL, 2007).

Biogas composition is a useful parameter for process monitoring. A decrease in methane content can be a first sign of organic overload (see section 2.1.2), provided that the feedstock mix has not recently changed. Similarly, a sudden increase in H₂S can provoke process instability. Yet, as changes in biogas production and composition can have various causes (not always process stability problems) they should always be interpreted together with the early indicators of process imbalance (parameters such as alkalinity ratio, VFA concentrations, etc., see section 3.2.1). In some cases H₂ is also measured within gas composition measurements. However, as H₂ concentration is considered a very early indicator of process imbalance it is therefore described separately in section 3.2.1.
3.1.3 Fermentation temperature

It is essential to control process temperature in the biogas digester, as a stable temperature is necessary for a high performance of the microbes (see section 2.2). The optimal fermentation temperature mainly depends on the microbes involved and lies between 36 and 43°C for mesophilic degradation and between 50 and 65°C for thermophilic degradation. In addition, fermentation temperature has an influence on other parameters such as the dissociation of ammonia, for example, and its inhibitory effect. At higher temperature the concentration of the undissociated form of ammonia (NH₃(aq)) increases and thermophilic fermentation is therefore disadvantageous when degrading protein-rich feedstocks.

For temperature measurements, Pt100 thermometers are normally used which are common industrial thermometers applied in food or biotech industry (see Figure 8). As faulty temperature measurements tend to occur, Weiland (2008) recommends measuring the temperature at different locations in a digester.

3.1.4 Total solids (TS) / dry matter (DM)

The TS content in a digester (for methods of analysis see Table 1) can be used as an indicator of the viscosity of the fermentation broth in the reactor. In CSTR reactors the viscosity should not increase a certain level because then stirring problems can occur or the digester content cannot be pumped anymore. In wet fermentation systems which represent the majority of the existing biogas processes, TS concentration should normally not exceed 10% (LfL, 2007). This will ensure ease of pumping and mixing of digester contents. If fibrous feedstocks are involved (e.g. grass silage), an increased TS concentration can lead to stirring problems. In these cases, dilution with fresh water, digestate, liquid feedstock or process water is often necessary (Resch et al., 2008). Monitoring the TS in the digester can give feedback to the plant operator on the sufficiency of dilution. It can also be useful to measure and compare TS and VS of feedstock TS and VS degraded (see section 3.1.1). The liquid fraction of digestate can be used as process water, for example the liquid after separation by screw press separators or centrifuges.

3.1.5 pH value

The pH value gives an approximate indication on the state of the fermentation process. Due to the buffer capacity in biogas plants, which is dependent on dissolved CO₂, carbonate and ammonia, a detectable pH change takes place only after process instability has started. Therefore the measurement of the pH value is not suitable as early indicator of process imbalance, but gives important information for process monitoring.

In most biogas plants the pH is measured off-line after taking samples from the digester by a laboratory pH-meter (see Figure 9). The reason is that on-line pH-measurement is problematic due to rapid fouling of the electrode and subsequent requirement for regular cleaning and calibration. This requires special adapters which allow the removal of the electrode without causing leaks. In practice off-line pH measurements are often not as accurate as on-line measurements due to the effects from variability of sampling, sample storage and sample temperature during measurement. If possible, the off-line pH measurements should always be carried out at similar temperatures, in order to achieve comparability.
3.1.6 Ammonium nitrogen (NH₄⁻N)

Ammonium nitrogen (NH₄⁻N) is one of the digestion products in anaerobic digestion. If nitrogen-rich feedstocks are used, inhibition by ammonia is often the reason for a process imbalance (see section 2.3). Therefore, monitoring NH₄⁻N concentrations in the digester helps to estimate if ammonia inhibition is causing the process imbalance.

The NH₄⁻N can be analysed by automated laboratory systems (see Figure 10) according to US-American standard “APHA 4500-NH₃-Nitrogen” (APHA, 1998) or the German industry standard DIN 38406-5:1983-10 (1983). Based on NH₄⁻N concentration, it is also possible to calculate the free ammonia (NH₃(aq)) which is the inhibitory form of NH₄⁻N. For NH₃(aq) calculation according to the following formula (Hansen et al., 1998), the pH and temperature in the digester are needed:

$$[\text{NH}_3(aq)] = \frac{[\text{NH}_4\text{-N}]}{(1 + 10^{-\text{pH}} / 10^{-(0.09018+(2729.92/T))})}$$

- **[NH₃(aq)]**: Concentration of free ammonia in mg L⁻¹
- **[NH₄⁻N]**: Concentration of total ammoniacal nitrogen (free ammonia + ammonium) in mg L⁻¹
- **pH**: pH value
- **T**: Temperature in K

Within this brochure it is recommended to use the directly measurable NH₄⁻N (and not NH₃(aq)) as the monitoring parameter. The reason is that the calculation of NH₃(aq) is strongly dependent on a very accurate determination of the pH inside the digester. As indicated in section 3.1.5, in practice the pH is often measured offline, which makes the determination of the exact pH inside the digester very difficult. As a consequence, even a slight deviation of the pH (e.g. 0.2 pH units) can have a big influence on the calculated NH₃(aq). On the contrary, the measurement of NH₄⁻N in the digester is very exact. It is noted that very skilled biogas plant operators may manage to establish their own monitoring system based on calculating NH₃(aq) from NH₄⁻N.

3.2 Early indicators of process imbalance

Parameters that are considered early indicators of process imbalance are:

- Volatile fatty acids (total VFA, individual VFA)
- Alkalinity ratio (FOS/TAC)
- Hydrogen
- Redox potential
- Complex monitoring of mixed parameters (NIRS or electronic nose)

These parameters can indicate in advance if a process imbalance is impending. Yet, they do not give direct information of the cause for the process imbalance. For an interpretation of the process imbalance, the recorded parameters characterising the process (see section 3.1) are to be used. In general, only one (or two) of the following parameters are used in one monitoring scheme.
3.2.1 Volatile fatty acids (VFA)

Volatile fatty acids (VFA) are short-chained volatile organic acids such as acetic acid, propionic acid, butyric acid and valeric acid or branched isomers of them (isobutyric acid, etc.). They are intermediate metabolites in the anaerobic digestion process that are produced during the acidification step (acidogenesis) and are precursors of methane (see Figure 1). As a consequence, if they accumulate this often means that methanogenesis, the biological transformation to methane, is inhibited. In general, according to Buchauer (1997) various methods can be applied for VFA measurement, such as steam distillation, colorimetric methods, chromatographic methods or titrimetric methods. This brochure will focus on the methods most commonly applied. In general, for biogas process monitoring, two VFA parameters are used: individual VFA concentration and total VFA concentration.

Individual VFA - measured by external high performance laboratory

Monitoring the concentrations of the individual volatile fatty acids (individual VFA) in the digester gives the best information on the state of the process. Their analysis can give direct feedback on the interaction and inhibition of the different groups of micro-organisms in the reactor. A moderate accumulation of acetic acid in the digester is normal, as acetic acid is the final precursor to methane. Slight accumulation of propionic acid is tolerable. The ratio of acetic to propionic acid, and especially of their branched isomers, is normally a sign of severe process instability.

The measurement of individual VFA is carried out by chromatography methods such as HPLC (high pressure liquid chromatography, see Figure 11) or GC (gas chromatography) analysis. For details of these methods see Liebetrau et al., 2012. As chromatography equipment is very expensive, such analyses are normally carried out by external laboratories. In order to obtain reliable results good sample handling, transport and storage are essential (see section 4.1.2).

Total VFA - measurement at an on-site laboratory possible

The parameter total VFA represents the concentration of the sum of all VFAs present. Total VFA can be determined by titration methods, photometric methods or, of course, by summing up the individual VFA (details indicated above). In general, titration methods are recommended for total VFA determination because they are cheap, robust and quick to carry out. An automated titration device is shown in Figure 12.

In the literature (Buchauer, 1997; Buchauer, 1998; Liebetrau et al., 2012) the titration method according to Kapp (1984) is recommended. In this method the sample has to be free of suspended solids which is achieved either by filtering the sample through a 0.45 μm membrane filter (Buchauer, 1997) or centrifuging the sample at 10,000g for 10 min (Liebetrau et al, 2012). Then, 20 mL of this sample is put through a three-point titration with 0.05 mol L⁻¹ of sulphuric acid for pHs of 5.0, 4.3 and 4.0 (for details see Buchauer, 1998). Total VFA can be calculated according to the following formula (Liebetrau et al., 2012):

$$\text{Total VFA [mg L}^{-1}\text{]} = \left[131,340 \ast \left( V_{pH4.0} - V_{pH3.0} \right) \ast N_{H_2SO_4} / V_{sample}\right] - \left[3.08 \ast V_{pH4.3} \ast N_{H_2SO_4} / V_{sample} \ast 1,000\right] - 10.9$$

Where:

- $V_{pH4.0}$ Volume of added acid until pH=4.0 in mL
- $V_{pH3.0}$ Volume of added acid until pH=4.3 in mL
- $V_{pH4.3}$ Volume of added acid until pH=4.0 in mL
- $V_{sample}$ Volume of titration sample (recommended 20 mL, see Buchauer, 1997)
- $N_{H_2SO_4}$ Normality of used acid (0.1 in case of 0.05 mol L⁻¹ sulphuric acid)
Total VFA can also be determined on-site by photometric test kits, but depending on the feedstocks these tests often do not work reliably due to the intrinsic colour of the digester content which interferes with the measurement (Buchauer, 1997). In order to overcome this interference it is possible to apply a distillation pretreatment to the photometric tests kits, where the VFA are evaporated and condensed. However, losses during distillation have to be accounted for.

In theory, the intermediate alkalinity (IA) measurement as part of the alkalinity ratio analysis (section 3.2.2) can also be used for total VFA. However, according to Rieger and Weiland (2006) the measured IA values in the alkalinity ratio are very different from actual VFA concentrations, measured for example by HPLC. Consequently, IA cannot be used as a reliable value for total VFA concentration.

### 3.2.2 Alkalinity ratio

The alkalinity ratio is a two-point titration measurement which determines the ratio of the intermediate alkalinity (IA) over the partial alkalinity (PA). The first parameter, the intermediate alkalinity, indicates the accumulation of volatile fatty acids and is an important indicator of process problems (see section 3.2.1 above). The second parameter, the partial alkalinity, represents the alkalinity of the bicarbonates and is a measure of the buffer capacity in the digester. The bicarbonate buffer capacity is important in the biogas process so that a moderate accumulation of volatile fatty acids does not cause a decrease in the pH which would ultimately lead to an end of biogas production. The alkalinity ratio is also called the IA/PA ratio, though other terms such as VFA/bicarbonate, Ripley ratio or VFA/ALK are in use. In German literature the parameter is called FOS/TAC.

The titration method most commonly applied is the FOS/TAC titration method according to Mc Ghee (1968) and Nordmann (1977). Here, the titration is first carried out until a pH of 5.0 is reached (bicarbonate alkalinity) and then until 4.4 (alkalinity caused by VFA). The titration is carried out in 20 mL of filtered (or centrifuged) sample of digester content with 0.05 mol L⁻¹ sulphuric acid. In English literature the Ripley ratio is also mentioned which is a two-point titration similar to the FOS/TAC, however, with different pH values: pH 5.75 and pH 4.3 (Ripley et al., 1986; and Jenkins et al., 1983). The FOS/TAC-alkalinity ratio can be calculated according to the following formula (Voß et al., 2009):

\[
FOS/TAC = \frac{[(B \times 1.66) - 0.15] \times 500}{A \times 250}
\]

A Volume of added acid until pH 5.0 in mL
B Volume of added acid from pH 5.0 to 4.4 in mL

The alkalinity ratio measurement can be carried out in a small laboratory on-site where either standard laboratory titration equipment or an automated titration device (see Figure 12) can be used. No matter which method is used, the absolute value for the alkalinity ratio measured at a biogas plant is unique to that plant and the value is not comparable between different biogas plants (Voß et al., 2009). Differences between plants, even if the same method is used, are due to the different feedstocks, the pre-treatment of the sample prior to titration (e.g. centrifuging, filtration) and the individual staff carrying out the titration. Nonetheless, for process control at one specific biogas plant measuring alkalinity ratio is a powerful and cheap option.

Figure 12 Automated laboratory titration device
(reproduced with the kind permission of HACH LANGE).
3.2.3 Hydrogen

Hydrogen is an intermediate metabolite and is produced at various stages of the anaerobic digestion process (Figure 1). Even a slight increase of H₂ concentration can be sufficient to impede degradation of volatile fatty acids (especially propionic acid) in the biogas process (Speece, 1996). For this reason in a stable digestion process hydrogen concentration has to be kept very low, typically at <100 ppm (Speece, 1996). This is also necessary, as according to the chemical conditions hydrogen utilising microbes can only gain energy at such low concentrations.

As a consequence, hydrogen concentration can be valuable information for process monitoring, especially as a change in hydrogen concentration occurs before VFA or alkalinity ratio measurements indicate changes. Yet, in practice accurate hydrogen measurement in biogas is challenging1 and therefore it is currently not recommended to rely solely on hydrogen for process monitoring. Nevertheless a few biogas plants exist which rely solely on H₂ measurements for monitoring process stability. In these cases the biogas plant operator should be experienced and it is very important to check the reliability of the H₂ measurements over time.

Currently, if hydrogen is monitored at a biogas plant, it is measured by electrochemical sensors in the gas phase together with standard biogas composition measurements (see section 3.1.2). In future, the measurement of dissolved H₂ inside the digester by an electrode could become an interesting alternative (Zosel et al. 2008, Liebetrau et al. 2012).

3.2.4 Redox potential

As opposed to aerobic microbes, anaerobic microbes need a negative redox potential for their metabolism. In the case of strict anaerobic microbes, which are present in a biogas plant, the redox potential should be lower than -300 mV. The redox potential is measured by a redox electrode which determines the voltage between oxidising substances (electron donors) and reducing substances (electron acceptors) that are dissolved in the digester content (Rieger and Weiland, 2006).

For process monitoring the redox potential is a very sensitive parameter to changes in the digester. According to Weiland (2008), the redox potential reacts faster to an impending process imbalance than, for example, the alkalinity ratio. However, changes in the feedstock mix or in the pH will cause a change in the redox potential, although no process imbalance is impending (Weiland, 2008). In addition, due to fouling problems the electrode will have to be taken out and cleaned frequently (Rieger and Weiland, 2006). Due to the problems mentioned and the complexity of redox measurements, redox electrodes are seldom applied in biogas plants.

3.2.5 Complex monitoring of mixed parameters

Different methods exist for on-line process monitoring, where no single substances or parameters are measured, but an overall process signal which is a mixture of different influencing parameters. Such approaches are near-infrared spectroscopy (NIRS) or an “electronic nose”. Up to now such methods have not often been in use at biogas plants. However, these methods have the big advantage of being on-line and data can be downloaded for monitoring at any time on any interfaced computer.

Near infra-red spectrometry (NIRS)

A transmitter of near infra-red radiation (800-2500 nm wavelength) is installed in a pipe of the reactor outlet or input. The transmitted radiation is partially absorbed by mainly organic molecules and depending on their molecular structure (O-H, N-H, C-H or COOH bonding) radiation with specific wave lengths are re-emitted. This radiation spectrum is measured by a detector and analysed. By comparison with known spectra of specific substances of known concentration the measured spectra are analysed using multivariate statistical methods. A range of monitoring parameters can be estimated by NIRS measurements, such as TS, VS, COD, total VFA, acetic acid, propionic acid, pH, alkalinity, etc. (Andree et al., 2008)

---

1 Unfortunately, in practice the hydrogen measurement in the biogas is often problematic due to cross sensitivity with hydrogen sulphide. Therefore, for H₂ measuring systems H₂S must be removed before the measurement. Further possible drawbacks are: increased response time due to the large headspace volumes in biogas plants, undefined reduction of the H₂ concentration by microbial activity (headspace or desulphurization unit), diffusion of hydrogen through sealing material, and reduced partial pressure due to delayed hydrogen mass transfer from the fermentation broth into the gas phase. (Liebetrau et al., 2012)
NIRS technology is already successfully applied in chemical and pharmaceutical industries (Andree et al., 2008). According to Ward et al. (2008) NIRS shows promise as an on-line monitoring technique in anaerobic digestion because the high water content does not interfere with the spectra and several parameters can be measured together with one single instrument and no sample preparation is needed. Nonetheless, until now NIRS technology has been applied to only a limited number of biogas plants. The biggest disadvantage is the substantial effort which is needed to calibrate the equipment, apart from considerable investment costs.

An intensive learning process is required to use a NIRS system, where a large number of samples are taken during operation of the plant. These samples are analysed off-line in a laboratory and then compared to the NIRS spectra taken on-line at the plant. In addition, a NIRS system has to be adapted to changes in feedstocks or measuring environment (Andree et al., 2008).

**Electronic nose**

According to Gilles (2013) an electronic nose is an electronic device which is composed of an array of non-specific gas sensors (e.g. metal oxide semi-conductors) which is used for the detection and recognition of specific compounds that are associated with odours. This device can be used on-line to detect process disorders in the digestion process. Using an electronic nose for process control has shown promising results at research scale (Gilles, 2013), but up to now it is not applied in biogas plants.

**3.3 Variable process parameters**

Parameters considered as variable process parameters are:
- Organic loading rate
- Hydraulic retention time

These parameters can be influenced by the plant operator. Yet, in a biogas plant that is running at full load these parameters are often not altered as a constant rate of biogas production or high throughput rates of feedstock in the process are required. In practice, these parameters are altered if a change in feedstock mix occurs or process instability demands a reduction of feed.

### 3.3.1 Organic loading rate (OLR)

The organic loading rate is a measure of the quantity of organic matter fed into a digester per unit volume of digester (normally given as kg VS m⁻³ d⁻¹ or kg COD m⁻³ d⁻¹). During start-up of a biogas plant the OLR is normally increased slowly to working conditions in order to adapt the microorganisms to the operating environment. The critical issue with the OLR is that if it is too low the productivity of the biogas plant is low and if it is too high it can lead to organic overload and acidification (see section 2.1.2). The average organic loading rate in mesophilic agricultural CSTR digesters is 3.0 kg VS m⁻³ d⁻¹ (FNR, 2009).

### 3.3.2 Hydraulic retention time (HRT)

The hydraulic retention time (HRT) is the average time during which the feedstock remains in the biogas digester. In practice, the large majority of existing biogas plants are CSTR reactors and do not have special retention systems for the microbes. The retention time of the microbes in such systems can be assumed equal to the HRT. For the calculation of the retention time all input (feedstocks and water) to the digester has to be considered:

\[
\text{HRT (d)} = \frac{V_{\text{digester}}}{V_{\text{input}}} \\
V_{\text{digester}} \quad \text{Total digester volume (m}^3\text{)} \\
V_{\text{input}} \quad \text{Total daily input to digester (m}^3\text{ d}^{-1}\text{)}
\]

In more complicated biogas plants characterised by designs used for wastewater treatment, the aim is to retain microbes in the reactor so that the microbe retention time (also called solids retention time) is much larger than the hydraulic retention time (retention time of the liquid). Such a reactor design is the up-flow anaerobic sludge blanket (UASB) reactor or the anaerobic filter.

Low HRT can lead to hydraulic overload (see section 2.1.3), which leads to the washing out of the microbes whereas a HRT which is too high leads to a low productivity (Nm⁻³ biogas m⁻³ of digester volume) of the biogas plant. If solid feedstocks are used, the retention time can be regulated by the amount of fresh water or process water used (e.g. process water can be the liquid fraction of digestate after solid-liquid separation, for example by
Process monitoring in biogas plants

In this section a description is given how a process monitoring scheme can be introduced. First, monitoring data have to be obtained (either on-line or off-line), which largely depends on the plant infrastructure. Then, stability limits for different monitoring parameters are presented and recommended intervals for their measurement. Finally, monitoring costs are given and the importance of training plant operators is emphasised.

4.1 Obtaining process monitoring data

Monitoring data can either be obtained on-line, which means that the measurement is done directly in the process with no time difference between the sampling and the analysis, or off-line which means laboratory analysis is carried out after sampling. The quality of on-line data is better than off-line data because process information can be derived without a loss in time and countermeasures can be taken quickly. Nevertheless, even in highly sophisticated biogas plants, some process parameters are still commonly measured off-line by sampling the digester contents.

4.1.1 On-line monitoring data

Many biogas plants have automated operating systems and on-line monitoring of process information (e.g. mass input, biogas production, gas composition and temperature) and other parameters (e.g. tank levels etc.) (Figure 13). Consideration of process monitoring in Germany where there are more than 9,000 medium- to

Figure 13 View of the monitor of the operating system in a biogas plant (such operating systems record data such as mass input, fermentation temperature, digester filling levels and biogas flow automatically. Reproduced with the kind permission of R(o)HKRAFT).
large-scale biogas plants in operation can help to describe on-line monitoring infrastructure (see Figure 14). Since in Germany the revenue earned from a biogas plant is mostly the result of electricity sales to the grid, practically all plants have a meter for measuring the quantity of electricity produced from the CHP. This, however, is not of interest in biological process monitoring. In Germany, only about two thirds of biogas plants investigated measured biogas volume and even fewer measured gas composition (Figure 1). More surprising is that only one third of the plants investigated measured the input of liquid feedstock into their plants, although this parameter is essential for determining the HRT (see section 3.3.2) in the system. Despite the fact that Germany is one of the countries with the best developed biogas technology sector, even there the plant infrastructure for process monitoring could still be significantly improved.

4.1.2 Off-line monitoring data – analysis of the digester content

At present it is not possible to monitor all process parameters on-line. For example, the analyses of VFA or VS/TS are carried out off-line by sampling the digester contents. Although there are some monitoring systems that can be used on-line for these parameters, such as NIRS technology (see section 3.2.2) or on-line VFA analysis (Boe, 2006), these technologies are rarely used in practice. The reasons are their high costs, their complexity or their limited robustness when changing the feedstock mix.

For off-line analysis, a small biogas laboratory on-site for carrying out simple laboratory analysis is advantageous (Figure 15). According to Schriewer (2011) it pays to operate a laboratory at a biogas plant if a number of digesters are operated, the plant operator has enough experience to interpret the obtained data, sampling and measuring are done accurately and feedstock frequently changes at the plant. Alternatively, off-line analysis can also be carried out by external laboratories.

Figure 14 Overview of on-line monitoring infrastructure in 413 German biogas plants investigated (adapted from FNR, 2009)
Sampling of digester content

In order to obtain accurate data, representative samples, correct sample handling and accurate measurements are essential. Standard methods are available for the sampling of sludge and wastewater (e.g. ISO 5667-13 (2011)) and for biogas digesters (e.g. VDI 4630 (2006)). To illustrate the importance of sampling and sample treatment, the effect of the different steps of an analysis on the accuracy of a result is shown in Figure 16. It can be seen clearly that the biggest error occurs during sample taking. The second biggest influence on error is sample treatment and preparation. The analysis itself normally causes the smallest error. So in practice, if a result does not seem plausible it should be checked for any possible sampling and analysis errors. If doubts still remain, a new sample should be taken and analysed.

For biological process monitoring samples are taken directly from the digester and not the final storage tank. In the case of two-step fermentation, either the final digester or both digesters are sampled. Clean re-sealable vials made of inert plastic, glass or steel should be used as sample vials. A sample size of 0.5 L is generally sufficient for a representative analysis due to the homogeneity of the material. Normally, the sample can be taken from sampling valves or after a discharge pump. In order to ensure that the sample is of fresh digestate, the first amounts of digester content should be discarded before collecting the sample (Figure 17), as the residual material in the pipes and valves is usually not representative. The samples should be immediately cooled to 4°C as they are not biologically stable, and should remain at 4°C during transport and storage. For digestor samples, good sample handling and storage is important. For example, VFA concentration can change dramatically if the sample is not cooled during transport or storage. If longer storage times (>1-2 weeks) are expected, for accurate results the samples should be frozen before storage.
As the digestate can be stored for up to several months in the final storage tank before use as a fertiliser, it does not make sense to sample it for biological process monitoring. In addition, taking representative samples from the final digestate storage tank can be quite complicated, since it is often not stirred and as a consequence, heavy particles sink to the bottom or light particles/fibres remain on the surface. In practice, sampling the final storage tank is used to determine the fertiliser value of digestate and to help ensure efficient use of digestate as a biofertiliser.

4.2 Process monitoring details and interpretation

The monitoring approaches presented are based on experiences from an Austrian biogas plant monitoring laboratory serving 30-50 biogas plants per year, interviews with biogas plant operators and literature. The stability limits shown are derived from typical European biogas plants processing for example biowaste, manure or energy crops. They can in general be applied to mesophilic CSTR (continuously stirred tank reactor) digesters for wet fermentation (in the case of two-step fermentation, the stability limits correspond to the 2nd digester). As with the presentation of the process parameters (see section 3), the process monitoring interpretation will also be divided in the following sections:

- Monitoring process characteristics
- Monitoring process stability

The approaches presented serve as a starting point guideline for a biogas plant operator who is interested in establishing process monitoring at a biogas plant. In order to achieve a good monitoring scheme they will need adaptation to their specific plant conditions. In general, the intensity of biogas monitoring which should be applied at a biogas plant depends on the following factors:

- Frequency of changes in feedstock type and composition
- Current state of the biogas plant (stable, unstable)
- Digestion / reactor type (simple versus high performance)

4.2.1 How to use the suggested stability limits

As already pointed out in section 2, process stability in biogas plants is influenced by a large number of interdependent factors, such as: temperature, pH, buffer capacity, ammonia concentration, composition and adaptation of microbial consortia, bioavailability of trace elements and retention time (see section 2). Therefore it is difficult to give clear limits for single parameters that define a stable plant.

Defining stability limits

Figure 18 illustrates why it is difficult to define clear monitoring stability limits. An ideal stability limit (Figure 18a) would indicate that all processes with lower values than the stability limit are stable, whereas processes with higher values are unstable. In-field monitoring data (Laaber, 2011) which are shown in Figure 18 demonstrate why the definition of stability limits is not so easy in practice. The presented data originate from monitoring the digesters of 51 biogas plants, over a longer period of time (in total, 273 values). According to Laaber (2011),
digesters were considered stable if during the period of sampling according to the biogas operator no indications of process instability had occurred. On the contrary, digesters were considered unstable if either the biogas plant operator had contacted the biogas laboratory directly due to process problems (mainly reduction of biogas production) or the authorities had declared the plant unstable due to excessive odour emissions caused by incompletely digested biogas slurries.

Figure 18b shows that stable digesters had a total VFA-concentration up to 4,300 mg L$^{-1}$, while unstable digesters showed VFA-concentrations from 1,100 mg L$^{-1}$ upwards. In between, there existed stable as well as unstable plants (the overall relation of stable to unstable data points was 1.3:1, the ratio of stable to unstable data points in the grey area was 1.9:1). So, in practice the stability limit for e.g. total VFA concentration, which is considered to be a good monitoring parameter, is not a single value but is a range from 1,100-4,300 mg L$^{-1}$ (see Figure 18b). As a simplification, a range from 1,000 – 4,000 mg L$^{-1}$ is used for the stability limits in Table 6.

For NH$_4$-N the range of concentrations in the grey area is even greater than for VFA (Figure 18c). This is despite the fact that increased NH$_4$-N concentrations will lead to increased NH$_3$(aq), which is considered inhibitory (see section 2.3). This large range is explained first of all by the fact that the concentration of the inhibitory NH$_3$(aq) is dependent not only on NH$_4$-N concentration, but also on temperature and pH. Secondly, anaerobic microbes exhibit the ability to adapt to high NH$_4$-N concentrations (see section 2.3). For example, if a biogas plant is accustomed to low or moderate NH$_4$-N concentration (< 3,000 mg L$^{-1}$) a sudden and rapid increase to e.g. 5,000 mg L$^{-1}$ could lead to process instabilities, whereas if the anaerobic microbes are adapted slowly, stable digestion processes could take place even beyond 5,000 mg L$^{-1}$. For all these reasons NH$_4$-N is not considered suitable for monitoring process stability, but for monitoring process characteristics (see section 3.1).
Operating biogas plants at high NH$_4$-N concentrations

An interesting aspect is that although high NH$_4$-N concentrations can lead to inhibitory NH$_3$-aq concentrations, at the same time high NH$_4$-N concentrations can lead to an increase in buffer capacity. As a consequence, anaerobic digestion processes can operate in a stable way at high NH$_4$-N concentrations. In practice, however, operating a stable process at high NH$_4$-N concentrations can be more challenging as it is more sensitive to negative process influences. Figure 19 illustrates how, for example, under low to moderate NH$_4$-N concentrations the process can withstand quite high impacts from destabilising factors, such as changes in pH, retention times, additional inhibiting factors, etc. Conversely, at high NH$_4$-N concentrations a small pH change, for example, can lead to sudden process instability. At high NH$_4$-N, process imbalances occur faster and it is more difficult to restore stable conditions. In addition, VFA may accumulate in the process (and remain in the digestate) although the degradation process is proceeding in a stable manner.

Recommendations to use stability limits

The short discussions above should help to understand the range in stability limits that can be used for process monitoring in practice. For a brief overview, see Table 4 and Table 6. The listed stability limits are given as rough guidelines in order to aid understanding of what range a good working process is expected to have. Because of the high variety of feedstocks and the high adaptability of the microbes, stable processes can be found even beyond these stability limits. On the contrary, sensitive microbes, which for example suffer from trace element limitation, can be affected below the stability limits. As indicated previously, the stability limits listed are derived from the author’s own experiences from an Austrian biogas monitoring laboratory and from literature (Laaber, 2011; Weiland, 2008; LfL, 2007 and LfL, 2013). With regard to the stability limits an important message is, if a biogas plant operates in a stable way and a process parameter is outside the recommended stability limit, attempts to reach the recommended values are inadvisable (never change a winning team). This is because every biogas plant has its specific feedstock mix and history and therefore a different composition of microbes in it. The best monitoring approach is a plant-
specific approach. Therefore, it is necessary to continuously measure and document process parameters, in order to have a history of parameters with which to compare. Only in this way it is possible to establish realistic stability limits for each biogas plant for stable operation and to detect in advance if a process imbalance is impending.

4.2.2 Monitoring process characteristics

Monitoring of process characteristics is the first part of a good monitoring scheme. The data of the plant history are gathered and changes of process parameters are documented. First, an upcoming process instability is detected by monitoring the parameters of process stability (see section 3.1 and section 4.2.3). Then, the cause for the upcoming instability can be found by analysing changes of the parameters characterising the process. Consequently, the plant operator has a hint how he/she can act to prevent the instability.

Table 3 shows the parameters which can potentially be used for monitoring process characteristics and Table 4 gives rough guidelines in which parameter range a stable process is expected to be. In addition, Table 3 gives recommended frequencies of analysis as well as additional information for using the parameters. The recommended frequency of measurement is divided into the following three scenarios, depending on the needs of the specific biogas plant:

- **Minimum monitoring**
- **Standard monitoring**
- **Advanced monitoring**

**Minimum monitoring** is considered for domestic or small-scale biogas plants (to a size of about 50 kW CHP; 500 cows). Here, financial returns limit the level of investment and it is usual to apply a minimum of monitoring, either on-line or off-line. Nevertheless, it is important that some monitoring is carried out. This should include daily feedstock inputs, daily gas production, daily digester temperature and weekly pH.

**Standard monitoring** should be applied in many small to middle-scale biogas plants in an agricultural context which use quite similar feedstocks all year round. Such plants are normally less prone to process instability, especially if manures are used, as these add new microorganisms as well as trace elements to the process. Another stabilising factor is a long hydraulic retention time (> 50 d) which reduces the possible occurrence of process instabilities.

**Advanced monitoring** is required if a high frequency of changes of the feedstock mix occurs at the plant because the risk of process instability is much higher. Feedstock changes at least once per week and large variation of composition mean high frequency can be considered. Such frequent feedstock changes are especially the case in waste treatment plants. In addition, advanced process monitoring is beneficial if a high performance biogas process is to be established. This is either the case in mono-digestion of industrial by-products or in large-scale digesters where a slight increase in performance can result in a considerable increase in revenue.
### Table 3 Overview of proposed parameters for monitoring process characteristics in a biogas plant (number of parameters and frequency of measurement depend on intensity of monitoring required: minimum (min.) — standard (stand.) — advanced (adv.))

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>FREQUENCY</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INPUT</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass of feedstock input (liquid, solid)</td>
<td>daily / on-line</td>
<td>daily / on-line</td>
</tr>
<tr>
<td>Characterisation of new feedstocks (pH, TKN, TS, VS)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Biogas potential of new feedstock (BMP)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>PROCESS PARAMETERS</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas production</td>
<td>daily</td>
<td>daily</td>
</tr>
<tr>
<td>Biogas quality (CH₄, CO₂, H₂S)</td>
<td>-</td>
<td>daily (min. 2x per week)</td>
</tr>
<tr>
<td>Temperature in the reactor</td>
<td>daily</td>
<td>continuous</td>
</tr>
<tr>
<td>NH₄-N</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TS, VS</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>1x per week</td>
<td>daily (min. 2x per week)</td>
</tr>
</tbody>
</table>
4.2.3 Monitoring process stability

Monitoring process stability is the second and core part of a monitoring scheme. This part functions as an alarm system that indicates in advance an impending process instability. Together with the monitoring data of process characteristics (section 4.2.2) the plant operator has to decide which measures to take in order to avoid a process instability.

For the establishment of a monitoring scheme the plant operator should select one (or two) from the presented parameters for monitoring process stability (see section 3.2 and Table 5). The most appropriate parameter is dependent on the local conditions of the biogas plants. Table 5 shows advantages and disadvantages of the different parameters as well as recommended frequencies of their measurement. In general, either alkalinity ratio, total VFA or individual VFA are the most common parameters for monitoring process stability. The latter, individual VFA, gives the best process information. It is, however, also the most difficult to obtain due to the expensive laboratory infrastructure needed. For this reason, analysis in an external laboratory is required. In any case, if a process imbalance is indicated by e.g. alkalinity ratio, a one-off individual VFA measurement can also be carried out to gain a more detailed picture of the process.

As an alternative, the H₂ concentration in the process also serves as a good monitoring indicator, as it is the fastest indicator of an impending process imbalance. However, due to possible measuring problems (see section 3.2.1), it is not recommended to rely only on H₂ measurements unless the plant operator is very skilled and accurate measurements can be guaranteed.

### Table 4 Important stability limits for parameters characterising the biogas process - data for mesophilic CSTR reactors and 2nd digester in the case of a two-step fermentation system (adapted from Laaber, 2011; Clemens, 2012 and LfL, 2007)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range of parameter</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄-N</td>
<td>&lt;5,000 mg L⁻¹</td>
<td>In some cases NH₄-N concentrations of 3,000-5,000 mg L⁻¹ can already pose stability problems. A stable process up to 5,000 mg L⁻¹ is commonly achievable especially if nitrogen concentration is increased slowly in order to allow microorganisms to adapt or an inoculum already adapted to high nitrogen concentrations is used for inoculation.</td>
</tr>
<tr>
<td></td>
<td>&gt;5,000 mg L⁻¹</td>
<td>It is possible to operate stable degradation processes beyond 5,000 mg L⁻¹, however, it is often not an easy task. Microorganisms have to be adapted and in good condition (e.g. no lack in trace elements). The exact limit up to which a stable degradation process is possible depends on temperature, pH and the performance of the microorganisms. VFA will often be accumulated in the biogas plant, although the degradation process operates in a stable manner. High amounts of NH₄-N increase the buffering capacity which supports a stable process. Nevertheless, the process is less robust against additional process problems and if an imbalance emerges it can be more drastic than at low nitrogen concentrations.</td>
</tr>
<tr>
<td>pH</td>
<td>7 - 8</td>
<td>A stable biogas process is normally operated between pH 7 and 8. Yet, it is important to know that in practice temperature, sampling and storage can have an influence on pH measurement. The pH itself influences the dissociation of ammonia, hydrogen sulphide and volatile acids and by that their inhibitory effect.</td>
</tr>
<tr>
<td></td>
<td>&lt; 7</td>
<td>If volatile fatty acids accumulate (e.g. by organic overload) and exceed the buffering capacity, this will lead to a decline in pH. At pH values below 7 the activity of the microorganisms which degrade volatile fatty acids is reduced so that biogas production stops.</td>
</tr>
<tr>
<td></td>
<td>&gt; 8</td>
<td>Increased alkalinity will lead to process instabilities. One reason is the pH-influence on the dissociation equilibrium of NH₃ and NH₄⁺. High pH values and increased temperature conditions favour the accumulation of NH₃aq, which is able to pass through microbial membranes, affecting the cellular osmoregulation and thus inhibits microbial performance.</td>
</tr>
<tr>
<td>TS</td>
<td>&lt; 10</td>
<td>In CSTR reactors TS concentration normally needs to be below 10% in order to prevent stirring problems.</td>
</tr>
<tr>
<td></td>
<td>&gt; 10</td>
<td>TS values higher than 10% can lead to stirring problems in CSTR reactors. In other reactor types higher TS concentrations are possible.</td>
</tr>
</tbody>
</table>
 Nevertheless, hydrogen measurements can provide very valuable additional information when monitoring by VFA or alkalinity ratio.

The more complex approaches such as redox measurement and NIRS can also be used for monitoring process stability. In these cases it is necessary to guarantee that they are working reliably at the biogas plant. In practice, due to their complexity (and costs) they are rarely applied.

For the interpretation of the obtained monitoring data with regard to process stability the stability limits in Table 6 can be used. For their usage, the indications on how these stability limits have been established and as a consequence how they should be used (see section 4.2.1) should be kept in mind.

Table 5 Overview of possible parameters for monitoring process stability in a biogas plant and the recommended frequency of their measurement

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>Frequency</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total VFA [mg L⁻¹]</td>
<td>Concentration of the sum of the volatile fatty acids</td>
<td>2-4x per month</td>
<td>• Simple, robust methods available (e.g. titration)</td>
<td>• Suspended solids in the sample can negatively influence the analysis (high removal efficiency necessary e.g. by centrifuging)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Can be carried out in on-site laboratory</td>
<td>• Intrinsic colour of sample can become problematic for photometric test kits</td>
</tr>
<tr>
<td>Individual VFA [mg L⁻¹]</td>
<td>Concentration of single volatile fatty acids</td>
<td>1-2x per month</td>
<td>• Best process information</td>
<td>• Very expensive laboratory equipment needed (e.g. HPLC)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Relation of acetic acid to propionic acid very good indicator</td>
<td>• Carried out in external laboratories (several days of waiting time)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Accumulation of longer chained VFA (and especially branched isomers) indicate severe process problems</td>
<td></td>
</tr>
<tr>
<td>Alkalinity ratio a) [-]</td>
<td>Relation of the alkalinity of volatile fatty acids to bicarbonate alkalinity</td>
<td>2-4x per month</td>
<td>• Simple, robust method</td>
<td>• Value is not directly comparable between different plants</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Can be carried out in on-site laboratory</td>
<td>• Indication of process imbalance takes place later than with other parameters (shorter time to react)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Takes buffer capacity into account</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Very commonly applied</td>
<td></td>
</tr>
<tr>
<td>H₂ [ppm]</td>
<td>Hydrogen</td>
<td>on-line</td>
<td>• Earliest indicator of process imbalance (even faster than VFA)</td>
<td>• Representative and accurate measurements cannot always be guaranteed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Any sudden and large change (even if not measured accurately) is a good indicator</td>
<td></td>
</tr>
<tr>
<td>Redox [-]</td>
<td>Redox potential</td>
<td>on-line</td>
<td>• Fast indicator of process imbalance</td>
<td>• Complex parameter</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Redox potential is also influenced by other parameters (e.g. change in pH or feedstock mix)</td>
</tr>
<tr>
<td>NIRS [-]</td>
<td>Near infrared spectrometry</td>
<td>on-line</td>
<td>• Fast and on-line (!) indicator of process imbalance</td>
<td>• Very high calibration effort is needed (consisting of establishing a data base of monitoring parameters measured off-line)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Several parameters can be measured with the same measurement</td>
<td>• If radical changes occur (other feedstock types) system has to be recalibrated</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• High costs</td>
</tr>
</tbody>
</table>

a) In German called FOS/TAC. In English also called IA/PA ratio, VFA/bicarbonate, VFA/ALK or Ripley ratio.
Process monitoring in biogas plants

Process Monitoring Implementation

<table>
<thead>
<tr>
<th>Range of the parameter</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1,000 mg L(^{-1})</td>
<td>Stable process</td>
</tr>
<tr>
<td>1,000–4,000 mg L(^{-1})</td>
<td>Range in which stable as well as unstable processes are possible. In biogas processes using feedstocks relatively hard to digest (e.g. energy crops with high TS content) where the rate limiting step is the hydrolysis step, the concentration of total VFA is normally lower than in waste digesters where the feedstock is readily degradable. Increased VFA concentrations can also be an indication of a lack of trace elements.</td>
</tr>
<tr>
<td>&gt;4,000 mg L(^{-1})</td>
<td>High VFA concentrations are normally an indication of process problems, especially if VFA concentrations are increasing rapidly. Yet, also stable degradation processes are possible at higher VFA concentrations, e.g. at higher ammonia concentrations. The concentration of VFA which will lead to a decrease in pH and consequently to process problems depends on the buffer capacity and is plant specific.</td>
</tr>
</tbody>
</table>

### Individual VFA

<table>
<thead>
<tr>
<th>VFA</th>
<th>Range of the parameter</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>&lt;1,000 mg L(^{-1})</td>
<td>Stable process</td>
</tr>
<tr>
<td></td>
<td>1,000–4,000 mg L(^{-1})</td>
<td>Stable as well as unstable processes are possible</td>
</tr>
<tr>
<td></td>
<td>&gt;4,000 mg L(^{-1})</td>
<td>High probability of unstable process</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>&lt;250 mg L(^{-1})</td>
<td>Stable process</td>
</tr>
<tr>
<td></td>
<td>250–1,000 mg L(^{-1})</td>
<td>Stable as well as unstable processes are possible</td>
</tr>
<tr>
<td></td>
<td>&gt;1,000 mg L(^{-1})</td>
<td>High probability of unstable process</td>
</tr>
<tr>
<td>Longer chained VFA (butyric, valeric)</td>
<td>&lt;50 mg L(^{-1})</td>
<td>Stable process</td>
</tr>
<tr>
<td></td>
<td>&gt;50 mg L(^{-1})</td>
<td>If longer chained VFA (and especially branched isomers) accumulate, severe process problems occur</td>
</tr>
<tr>
<td>Ratio acetic/propionic acid</td>
<td>&gt;2</td>
<td>Stable process</td>
</tr>
<tr>
<td></td>
<td>1–2</td>
<td>Stable as well as unstable processes are possible</td>
</tr>
<tr>
<td></td>
<td>&lt;1</td>
<td>High probability of unstable process</td>
</tr>
</tbody>
</table>

### Alkalinity ratio (FOS/TAC)

<table>
<thead>
<tr>
<th>Range of the parameter</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.3</td>
<td>Alkalinity ratios below 0.3 are in general considered to indicate stable processes</td>
</tr>
<tr>
<td>0.3–0.8</td>
<td>As alkalinity ratios are not comparable between different biogas plants it is very difficult to generalise. Stability limits have to be defined for every specific biogas plant. The maximum limits reported in literature for stable processes range from 0.3 to 0.8.</td>
</tr>
<tr>
<td>&gt;0.8</td>
<td>Unstable process</td>
</tr>
</tbody>
</table>

### \(H_2\)

<table>
<thead>
<tr>
<th>Range of the parameter</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;100 ppm</td>
<td>Stable process</td>
</tr>
<tr>
<td>100–500 ppm</td>
<td>In practice, it is quite difficult to guarantee accurate (H_2) measurements. For this reason the range where stable as well as unstable processes are possible is assumed to be quite big. If at a biogas plant accurate (H_2) measurements can be guaranteed, a smaller range of stability limits can be defined.</td>
</tr>
<tr>
<td>&gt;500 ppm</td>
<td>Unstable process</td>
</tr>
</tbody>
</table>

---

Table 6 Important stability limits for early indicators of process imbalance — data for mesophilic CSTR reactors and 2nd digester in the case of a two-step fermentation system (data adapted from Laaber, 2011; LfL, 2013; Weiland, 2008 and Clemens, 2012)
4.2.4 Monitoring during the start-up of a biogas plant

The start-up of a biogas plant is a very sensitive process. Due to slow multiplication of some of the microorganisms involved in anaerobic sludges and the consequent risk of hydraulic overload (see section 2.1.3), the start-up of a biogas plant can take much longer than in other biotechnological processes. A start-up time of 1-2 months is nothing exceptional in biogas plants. The start-up has two main functions. First, the number of microorganisms has to multiply from the seed material to the necessary amounts in the biogas plant. Second, the microorganisms have to adapt to the process conditions, and especially to the properties of the specific feedstock. A successful start-up is the pre-requisite for a well-functioning biogas plant. Therefore, the effort in process monitoring has to be highest during start-up. If the start-up is too fast, a sub-optimal biogas process can be the consequence because the most favourable microorganisms have not multiplied in the biogas plant. In contrast, a slow start-up can cause a possible loss of income as time is taken to reach full load capacity. For monitoring process stability during the start-up phase similar approaches should be used as indicated in section 4.2.3. Yet, the frequency of the measurements should be increased during this crucial process step.

As individual VFA give the best process information, this parameter is used to illustrate how a start-up of a pilot-scale anaerobic digester has been carried out. In practice, however, the frequency of the measurements will be much lower, and it will often not be possible to obtain individual VFA, so that e.g. total VFA or alkalinity ratio will be used.

In Figure 20 experimental data on individual VFA are shown for the start-up of a pilot-scale digester (0.5 m³) operated with the industrial by-product thin stillage as feedstock. As the process is an industrial mono-digestion and no changes in feedstock mix occur, it was aimed at achieving a very stable degradation process and consequently very low VFA concentrations. During the 1st start-up because the ratio of acetic to propionic acid was decreasing and finally lay below 1, which is not recommended as can be seen in Table 6, it was decided to undertake a second start-up. After the second start-up, by increasing the amounts of iron and trace elements added to the process, a very stable process with total VFA concentrations below 400 mg L⁻¹ could be achieved.

Figure 20 Acetic and propionic acid concentrations and organic loading rate during experimental period of a 0.5m³ pilot-scale digester operated with thin stillage, a by-product in bioethanol production. As butyric and valeric acid (or its branched isomers) were practically not present during fermentation, they are not shown in this figure. (Drosg, 2012)
4.3 Costs for process monitoring

In very simple biogas processes the cost of the on-plant technical equipment for process monitoring should be in balance with the economic risks (Henkelmann et al., 2010). If a biogas plant has totally crashed, it has to be emptied and filled again with new inoculum. Together with the long start-up period, several months of full load plant operation can be lost (Henkelmann et al., 2010). The financial consequences can be devastating for the plant operator.

The reason why specific process monitoring devices are integrated, or not, is not always a question of cost. As described in FNR (2009), in some regions of Germany many plants had an integrated gas composition measuring device, whereas in other regions the percentage of plants with on-line gas composition measurement is significantly lower. The reason for this situation was found to lie in the different opinions of the technical consultants used for individual plants. The price of an on-line gas composition measurement is very low compared to the total plant investment costs.

4.4 Training of plant operators and staff

Due to the complexity of the biological process it is important that biogas plant operators receive adequate training. They have to be able to recognise when a biogas process is becoming unstable and know which countermeasures to take. Basic knowledge of biological processes is beneficial. In countries where industrial biogas technology is already state of the art, courses for staff of biogas plants are often offered (see Figure 21). In other countries where the biogas technology has only recently started to develop, lack in skilled biogas plant operators can be a significant disadvantage.

Figure 21 Pictures from training courses of Austrian biogas plant operators and staff (© Lokale Energieagentur – LEA GmbH)
5 Summary and Recommendations

As biogas production is a complex biological process, where a mixed culture of microorganisms is involved and various consecutive reaction steps take place, biological process monitoring is essential to ensure a stable anaerobic digestion process. Different factors can influence the intensity of process monitoring required, e.g. scale of biogas plant, economic risk of process instability, frequency of changes in feedstock types, etc.

Among the process monitoring parameters, there are two different groups. The first group of parameters are early indicators of a process imbalance and they allow the biogas plant operator to react in time before a process imbalance happens. The second group are the parameters which characterise the process and can often help to detect and eliminate the cause of the imbalance. Although general guidelines for stability limits of different process parameters can be given, it is always necessary to adapt the monitoring strategy to the specific biogas plant and its feedstock.

The approaches displayed in this brochure should in principle help to achieve a stable digestion process. Nevertheless, some stability problems like for example trace element limitations will demand a more intensive optimisation effort and specialised expertise will be needed.

Many biogas plants will demand detailed process optimisation apart from pure process monitoring, which was however not possible to cover in this brochure. Nevertheless, standard monitoring of a biogas plant is a pre-requisite before process optimisation can be addressed. Last but not least, a very important factor for stable operation is that well-trained people are used to operate biogas plants.

While this brochure describes the state of the art for anaerobic digestion process monitoring (in 2013), it is clear that the monitoring techniques and equipment available will continue to be developed and refined. Potential users of monitoring equipment obviously need to take this into account.
6 References


DROSg, B. (2012). Energy recovery in grain bioethanol production by anaerobic digestion of stillage fractions. PhD Thesis at University of Natural Resources and Life Sciences, Institute for environmental biotechnology.


Process monitoring in biogas plants

7 Glossary

BMP Tests for measuring the biochemical methane potential (or biomethane potential) are mainly used to determine the possible methane yield of a feedstock. These tests also provide information on the anaerobic degradability of a feedstock, including the degradation rate. In addition, a first rough evaluation of the presence of inhibitory components can be made.

CSTR Continuously stirred tank reactor. This is a type of digester which is regularly stirred and the substrate as well as the microbe concentration should be the same throughout the entire reactor. The design concept of a CSTR is different to that of, for example, a plug flow reactor.

COD The chemical oxygen demand (COD) is a parameter which indicates the total chemically oxidisable material in the sample and therefore a parameter which indicates the energy content (or organic pollution) of a feedstock. In this analysis the sample is refluxed in a boiling mixture of sulphuric acid and potassium dichromate (K₂Cr₂O₇). In the next step, the remaining unreduced potassium dichromate is titrated with ferrous ammonium sulphate, which allows the determination of the equivalent oxygen consumed.

DM Dry matter (DM); see total solids

Alkalinity ratio The alkalinity ratio is a titration measurement with sulphuric acid and determines the ratio of the intermediate alkalinity (IA) caused by organic acids over the partial alkalinity (PA) caused by the bicarbonates. In the English literature it is called the IA/PA ratio, however, also other terms such as VFA/bicarbonate, VFA/ALK or Ripley ratio are in use. In German literature the parameter is called FOS/TAC.

Mono-digestion The term mono-digestion means that only a single feedstock is used in a biogas plant. Typical mono-digestions are carried for industrial residues such as sugar beet pulp, or for example in Germany energy crops like maize.

Mesophilic A mesophilic biogas process normally takes place between 36-43°C.

NH₄-N The ammonium nitrogen (NH₄-N) determination can be carried out using a distillation apparatus. A base is added to the sample and ammonia is distilled from the alkaline solution to an acid solution (usually boric acid) where ammonia is absorbed quantitatively and measured.

Nm³ Normal cubic meter (at norm temperature and norm pressure)

oDM Organic dry matter (oDM); see volatile solids (VS)

Off-line An off-line measurement is made when a sample first has to be taken from the digester and then the analysis is carried out in a laboratory. A considerable time elapses between the sampling and the analysis.

On-line An on-line measurement is carried out directly in the biogas plant and there is practically no time difference between the sampling and the analysis. Biogas volume and digester temperature are parameters which are practically always measured on-line. For on-line measurements no manual sampling is necessary.

OLR The organic loading rate (OLR) is given in kg VS m⁻³ d⁻¹ or kg COD m⁻³ d⁻¹, and stands for the amount of organic material which is fed daily to the biogas plant. The critical issue with this parameter is that with increased OLR the possibility of acidification by organic overload increases.

pH The pH value determines the acidity or basicity of an aqueous solution. Its unit is the negative logarithm of the concentration of hydrogen (H⁺) ions. The pH value can be determined in a liquid feedstock with a standard potentiometric electrode.

Psychrophilic A psychrophilic biogas process normally takes place below 25°C.

HRT The hydraulic retention time (HRT) is the average time during which the feedstock remains in the biogas digester. As in practice, the large majority of existing plants are CSTR reactors and do not show special retention systems for microbial biomass, the retention time of the microbes in the system can be assumed equal to the HRT.

Stability limit In the text the value of a monitoring parameter above which a process is considered unstable is referred to as the stability limit. In practice, the stability limit is however a value range rather than a fixed value.

TN The nitrogen content of a feedstock can be determined approximated by the total Kjeldahl nitrogen (TKN) determination. In this analysis, organic nitrogen is converted to ammonium nitrogen by boiling the feedstock sample in the presence of sulphuric acid and a catalyst. After that, similar to the NH₄-N analysis, a base is added and ammonia is distilled from the alkaline solution to an acid solution (usually boric acid) where ammonia is absorbed quantitatively and measured.

TS For the estimation of the water content of a feedstock the total solids (TS) are determined; this parameter is also called dry matter (DM). Analysis involves drying the sample to constant weight in a drying chamber at 103 to 105°C.

Thermophilic A thermophilic biogas process normally takes place between 50-65°C.

VFA Volatile fatty acids (acetic acid, propionic acid, butyric acid, valeric acid,...) are intermediate metabolites of the anaerobic digestion process. Therefore, their accumulation can give direct feedback on the interaction of the different groups of micro-organisms in the reactor.

VS In order to determine the amount of organic material in a sample the volatile solids (VS) are determined, this parameter is also called organic dry matter (oDM). In general, this determination is carried out together with the TS/DM determination described above. The sample is dried to constant weight in a drying chamber at 103 to 105°C. Then the sample is ignited to constant weight in a muffle furnace at 550°C. The VS is calculated by subtracting the ash from the total solids.
Task 37 – Energy from Biogas

IEA Bioenergy aims to accelerate the use of environmentally sustainable and cost competitive bioenergy that will contribute to future low-carbon energy demands. This report is the result of work carried out by IEA Bioenergy Task 37: Energy from Biogas.

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