International Gas Union Research Conference 2011

OPTIMISATION OF BIOGAS PRODUCTION BY INFRARED SPECTROSCOPY BASED PROCESS CONTROL

Main author

Dieter Wolf

Harald von Canstein

Cathrin Schröder

Germany

SUMMARY

Biomethane being a storable and base load capable energy carrier has an important role in the energy policy of the German government. The high targets for future production levels require an efficient production of biogas to yield the most biogas from either energy crops or organic waste, and to fully utilise the gas production capacity of biogas plants. Both processes can yet be optimised, and the two novel measuring technologies presented here may play an important part in this. The continuous analysis of biomass as input for a biogas plant and of the media inside the digesters was conducted by near infrared-based spectroscopy. First results indicate a high degree of accuracy for key process parameters compared to laboratory analyses. The measurement of the volumetric flow of raw biogas in the different stages of the process was performed with ultrasonic biogas meters. First results show a high degree of precision. The results will be used to develop a model towards process automation.

Key words: biogas, biomethane, near infrared spectroscopy (NIRS), process automation, raw biogas, ultrasonic volumetric flow meter

1. INTRODUCTION

Biogas is the product of the anaerobic digestion (AD) of biomass and thus a renewable energy carrier which can be produced continuously in so called biogas or AD plants. In 2009 approximately 4,900 biogas plants had been installed in Germany alone [1]. Most biogas plants were operated by farmers with a utilisation of the biogas in combined heat and power (CHP) plants. The electric power is fed into the power grid whereas the heat is used on site though only few sites utilise significant proportions of the heat [2].
The upgrading of biogas to biomethane and its subsequent injection into the natural gas grid offers numerous advantages compared to the on-site utilisation in CHP plants. The grid-injected biomethane is the renewable substitute of fossil natural gas and can be used not only for the base load production of heat and power in CHP plants but also as fuel for industrial gas turbines, industrial and domestic gas boilers and in cars running on compressed natural gas (CNG). By substituting power, heat and fuel from fossil sources biogas and biomethane contribute strongly towards climate change mitigation. Biomethane is thus an important milestone on the way to a renewable and sustainable energy society. The German federal government's target to supply 6 bio m^3 of biomethane by 2020 and 10 bio m^3 by 2030 requires a tremendous increase of injection capacity up from 0.28 bio cbm as of end of 2010 [3].

E.ON Ruhrgas AG is one of Europe's leading gas suppliers; its subsidiary E.ON Bioerdgas GmbH operates currently four biomethane plants with a total injection capacity of 3,300 Nm^3 /h with renewable energy crops as predominant substrates. Further plants are in planning or under construction. Along with biomethane acquired through long term contracts E.ON Ruhrgas supplies the market with 500 GWh_{Hs} of biomethane in 2011.

This article presents the enhancement of the biomethane plant Schwandorf (Germany) with a novel measuring system with near infrared spectroscopy (NIRS) and ultrasonic flow meters at its core. NIRS is based on the emission of infrared light and the detection of the spectrum of the reflected light which depends on the concentration of its constituents like organic and inorganic matter. Along with the metering of the mass flow rates of substrates, residues and raw biogas, the analysis of key parameters like concentration of organics and total energy content enables the calculation of mass and energy flows and hence the efficiency of the conversion of biomass to biogas. Further analyses of e.g. volatile fatty acids (VFAs), pH, or temperature allows for on-line process control. This is a considerable improvement to the usual process control based mostly on CHP power metering and discontinuous sampling followed by chemical analyses that take hours to days to complete, and thus often fail the biogas plant operator to react rapidly to serious process conditions like overloads and acidification [2]. Therefore operators tend to a safe but sub-optimum operation of the plant.
In contrast, the on-line process control technology presented here provides a detailed picture of the microbial processes inside the digesters. This enables the development of a model that describes the biological and physical interactions with the digesters which in turn serves the automation of the process and allows for the rapid adjustment of key operational parameters to optimise the economy of the plant. The economy can be optimised in three ways: 1) by increasing the methane yield per unit of substrate used, 2) by increasing the organic load to maximise the absolute biomethane production, and 3) by decreasing the down times and periods of diminished productivity.

2. LOCATION AND INSTALLATION OF MEASURING SYSTEM

The measuring system was installed and tested at E.ON's biomethane plant in Schwandorf (Figure 1) which is in operation since 2008. The plant operates solely on energy crops with the following figures for 2010: silages of maize (65% of total mass), grass (21%) and whole cereal crops (14%). The annual amount of 80,000 t of wet weight was grown, harvested and delivered by the vicinal farmers.

The plant was constructed by Schmack Biogas GmbH and consists of two gas production lines, each consisting of two sets of primary plug flow digester (2* 1,000 m^3), two secondary digesters (2* 3,600 m^3) and one tertiary digester (3,600 m^3). The liquid digestate is collected in a series of six digestate storage tanks (27,700 m^3 total) until the farmers retrieve it to fertilise their fields. The solid digestate – produced by separation of the native digestate – is either stored temporarily near the separation unit, or inside a silo, or directly transported as fertiliser and humus precursor onto the fields.

Each line is fed once per hour by two automated dispensers with a combined daily load of approximately 100 t per line. The raw biogas is produced at appr. 2,000 Nm³/h and subsequently upgraded by pressure swing adsorption, conditioned, analysed, metered and compressed to appr. 1,000 Nm³/h of biomethane that are injected into the 16 bar high pressure grid. This corresponds to an annual production of 90 GWh (higher calorific value). When commencing operation in 2008 it was Europe's largest biomethane plant.

The measuring system was installed in line 1 of the two identical lines. The data were transferred to, visualised and stored in the plant's process control system.

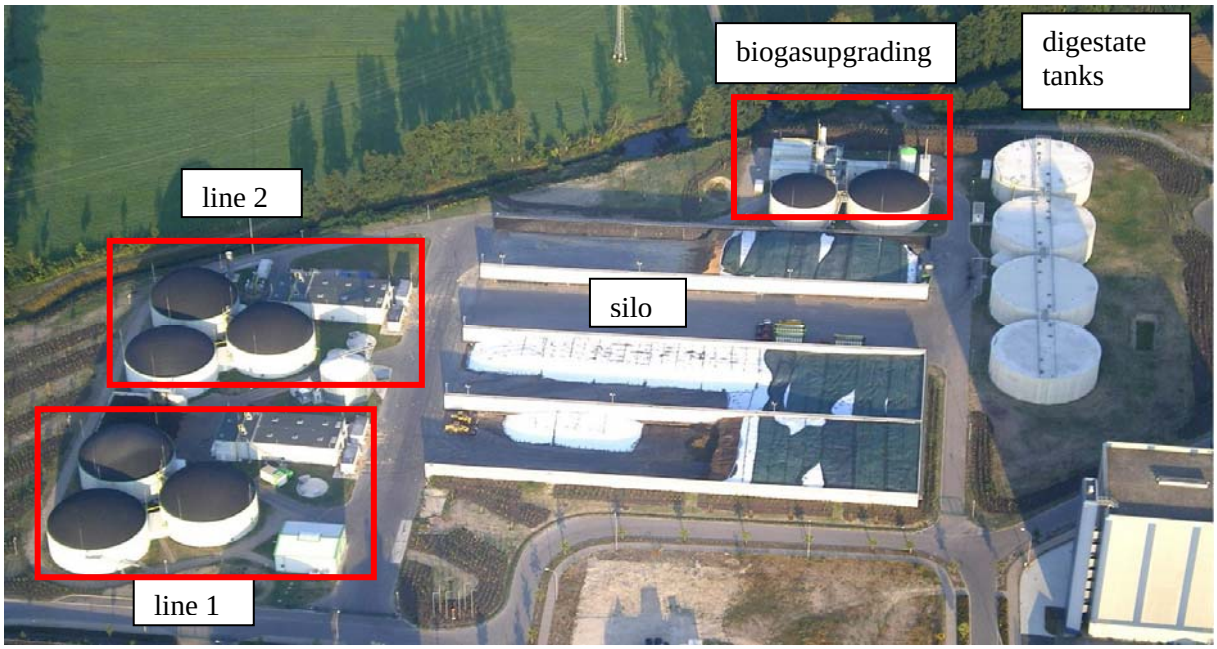

Figure 1: Aerial view of E.ON's biomethane plant Schwandorf

Figure 2 shows the flow of substrate and digestate in the production line 1 and its measuring system. The TENIRS-system contains four sensors; one was placed between feeder 1 and primary digester 1 to analyse the substrate that is fed into the system, particularly the energy and organic content. One sensor each was installed between the primary and secondary digesters to analyse the digester medium, particularly the content of remaining organics and VFAs. The fourth sensor was placed on the pressure side of the central substrate allocator pump to analyse e.g. the content of organics, VFAs, and ammonia in the various media pumped through. The central allocator enables pumping of media between all digesters and has thus a key role in the operating control. Further continuous analyses are of the pH, volumetric flows, temperatures inside the digesters and their filling levels. All data are stored in a data bank.

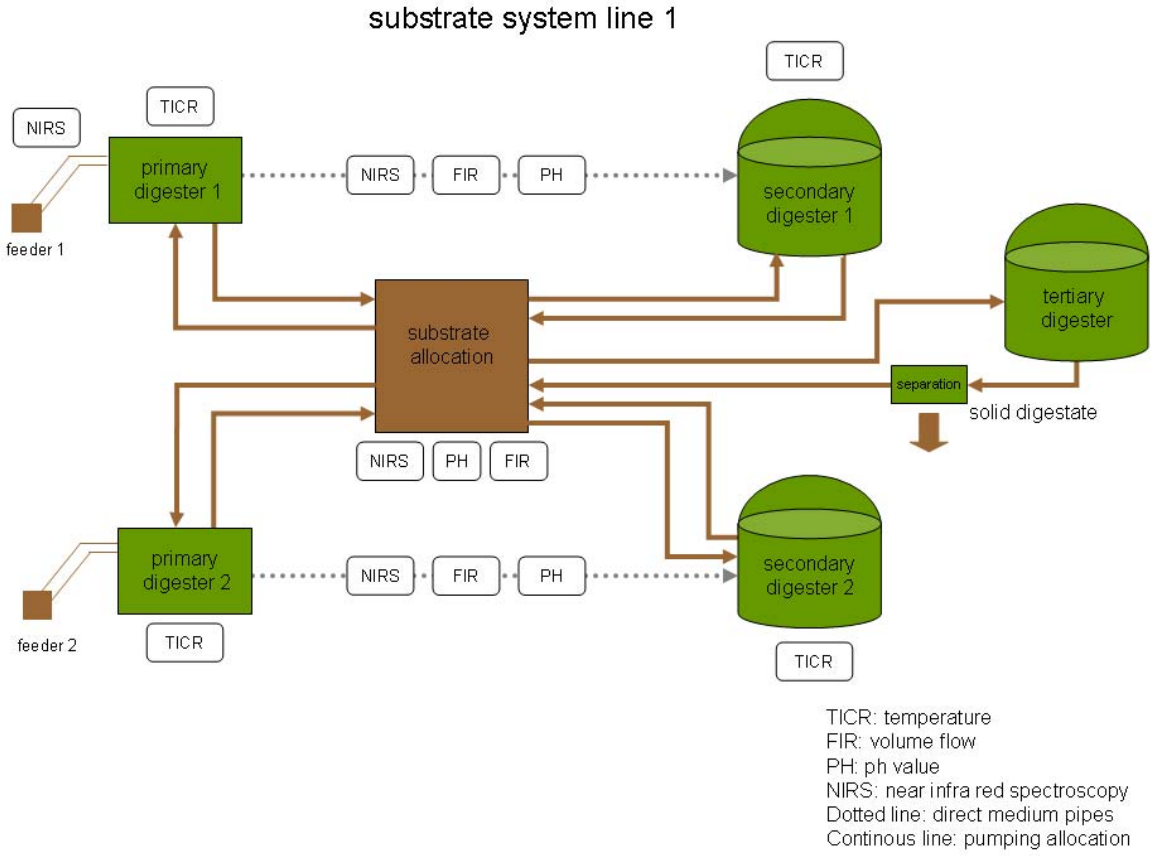

Figure 2: Substrate flow pathways and selected meters of the production line 1 of the Schwandorf biomethane plant.

Figure 3 shows the biogas production line 1 and selected parts of its measuring system. Further to the original equipment of sensors for temperature, gas quality and gas pressure, novel ultrasonic gas flow meters were installed. The ultrasonic gas flow meters were selected for their good performance with raw biogas with its high carbon dioxide concentration, low pressure and saturation with water vapour. The primary digesters have concrete ceilings and thus only limited space for biogas storage. Instead, biogas is stored in the flexible membrane domes on top of the two secondary digesters and the tertiary digester. The gas pipes coming from the secondary digesters are combined and lead to the pre-compressor to increase the gas pressure for the upgrading plant.

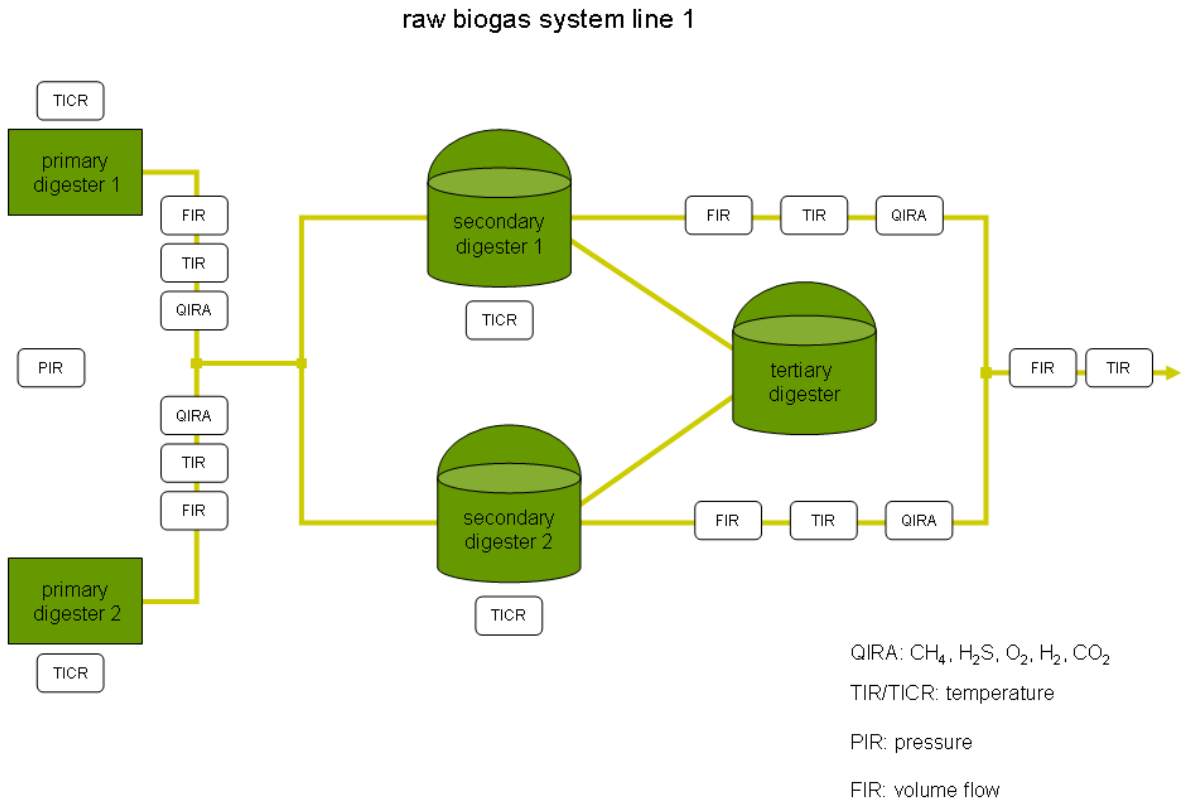

Figure 3: Biogas flow pathways and selected meters of the production line 1 of the Schwandorf biomethane plant

3. BIOLOGY OF ANAEROBIC DIGESTION

The target of optimising the plant economy requires the continuous measurement and recording of key process parameters and their interpretation in a mathematical model. This model is still under development. It is based on the empirically founded assumption that the anaerobic degradation of the biomass occurs in several steps facilitated by different microbes. These steps are the hydrolysis of polymers to monomers, e.g. starch and cellulose to monosaccharides, of proteins to amino acids, and of fats to fatty acids and glycerol. These monomers will be degraded to acetic acid, carbon dioxide and hydrogen. All of these serve methanogenic bacteria as substrate for the production of methane and carbon dioxide [4], [1].

Each biochemical reaction has a certain thermodynamic optimum, i.e. a cell can only gain energy if a reaction happens at a certain concentration of substrates and products, temperature and pH. This is especially true for anaerobic processes involving hydrogen as substrate or product [4]. To achieve an equilibrium of substrates, intermediates and products and thus avoid the accumulation of inhibitory substances like organic acids, all functional groups of microbes have to work synchronously. Unless the operator has detailed knowledge of the processes within the digesters his only way out of process inhibition is the reduction of feeding. This will inevitably cause a drop in gas production and should thus be avoided at all costs.

4. NIRS

Near infrared spectroscopy allows for the continuous analysis of various constituents in solid and liquid media [5]. In this study the system was supplied by M.U.T. AG, Wedel and comprised of the central unit with a Tristan OEM NIR spectrometer and four NIR sensor heads AMIMEKO. Figure 4 shows the

principle of NIRS. The sensor head contains a tungsten lamp whose light is focused through a sapphire glass disc into the passing substrate. The light reflected from the substrate is collected and transmitted via fibre optics to the detector in the central processing unit with a detection range of 900 to 1700 nm. NIRS requires an intensive calibration as the accuracy of the results depends strongly on a large number of samples from all substrates and media tested. The calibration requires the detection of the spectrum from a sample and its subsequent chemical analysis. Based on the results of the chemical analyses and their corresponding spectra mathematical models were developed to translate a spectrum into the concentrations of the parameters of interest. The models were then uploaded into the central processing unit. Parameters of interest were to name but a few, dry matter content, volatile substances, chemical oxygen demand, acetic and propionic acid, and ammonia. The model is only true for the range of concentrations within the calibration samples. If a parameter occurs outside that range a recalibration becomes necessary.

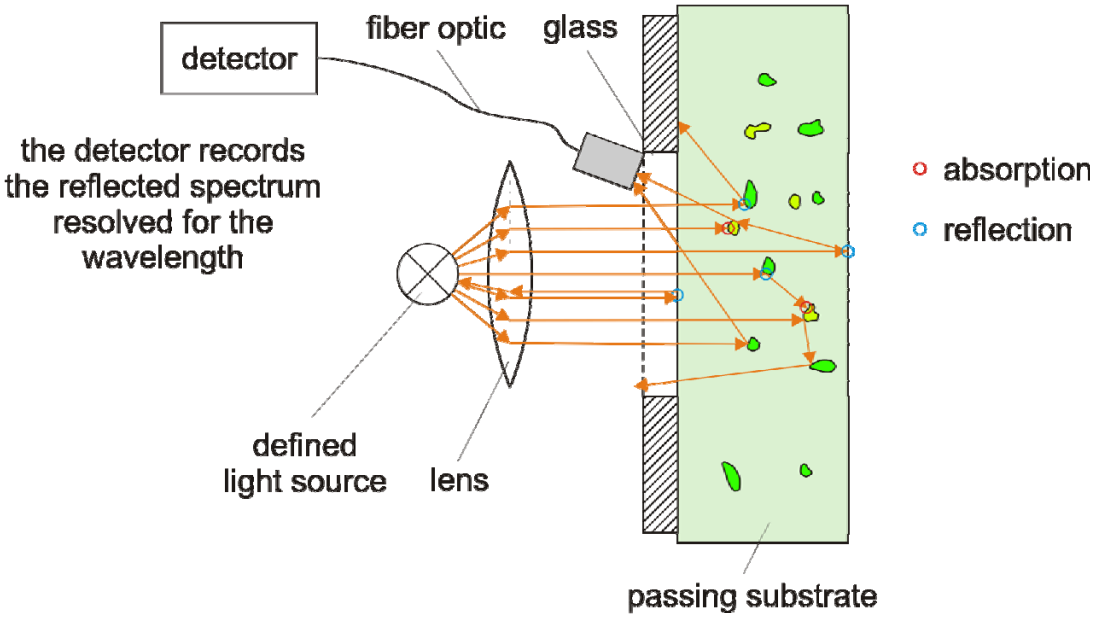

Figure 4: Measuring principle of NIRS (drawn after [6])

The following list presents the parameters that are relevant for the process control and can be analysed by NIRS.

4.1. Dry substances (DS)

Dry matter constitutes from the components (inorganic) ash and (organic) volatile substances (VS). Based on the assumption that the ash content is equally low and steady the DS content is a measure for the organic content of a substrate, and thus the theoretical gas yield and the organic loading rate. Although it is clear that the DS content is only an approximation compared to the direct measurement of the VS content it is still the predominantly determined parameter in substrates due to its relatively fast and simple measurement method: a sample is weighted twice, before and after drying at >100°C. At temperature > 100°C, though, many organic compounds vaporise. In silages that are rich in volatile small chain fatty acids or alcohols, this can results in misleadingly low results. It was suggested to measure all readily volatile substance (not to be confused with the normal VS like cellulose, starch etc.) are analysed separately and by means of their degree of volatility added to the DS content [7]. This correction results in the variants “DS n” for the normal measurement and “DS corr” for the corrected DS content. In this study the VFAs acetic acid, propionic acid and butyric acid, lactic acid and ethanol were analysed for and used for correction.

4.2. Volatile Substances (VS)

The VS content is determined by first measuring the DS content, combustion of the dry matter at 600°C and weighing to determine the ash content. VS is thus the difference between DS minus ash. This way the VS is subject to the same error as the DS content if a sample contains highly volatile substances that evaporate in the first drying step. The correct VS content is thus “DS corr” minus the ash content.

Some organics like lignin itself or lignin encrusted cellulose can not be degraded anaerobically. To determine the degradable part of the VS, Weißbach suggested the analysis of the fibre content as a measure for non degradable organics and to calculate the fermentable VS (FVS) [8]. His experiments showed that the FVS is suitable for the accurate calculation of the methane potential of a substrate.

4.3. Chemical Oxygen Demand (COD)

The COD is a measure for the chemically bound energy that can be released by oxidation irrespective of the type of its constituents. In any case one kg of COD always equals 0,35 Nm^3 of methane if digested completely. This way the analysis of COD allows for an energy balance of substrates to biomethane and digestate, as well as a measure for the biological activity within the digesters and a control to the FVS analyses.

4.4. Acetic, propionic and butyric acid

The small chain fatty acids are not only important for the correction of DS and VS but they are also a measure for the activity of acidogenic bacteria compared to methanogenic bacteria, and help to gauge the equilibrium of microbial activities. Since acetic acid is a regular product of methanisation, concentrations in the range of a few gram per kilogram are in order. Propionic and even more butyric acid, though, accumulate during process overloads and are a sign of a process malfunction.

4.5. Volatile fatty acids (VFA) and total alkaline capacity (TAC)

Determined by titration with sulphuric acid, TAC is a measure for the buffer capacity down to pH 5.0. VFA is actually a measure for the buffer capacity between pH 5.0 and 4.4; since most VFAs have their pKa value at 4.8 the results corresponds well with the sum of VFAs. The quotient VFA/TAC is popular as an easy to determine measure for the state of the AD process: low values caused by a low VFA and/or high TAC are positive for the operation and high values correspondingly negative.

4.6. Total nitrogen (tot-N) and ammonia nitrogen (NH4-N)

Nitrogen is an essential nutrient and should be checked for sufficiently high concentrations. In biomass nitrogen occurs predominantly as organically bound nitrogen. During digestion organic nitrogen is converted to ammonia. Both organic nitrogen and ammonia can serve as nutrient but ammonia is also inhibitory at high concentrations and/or pH values. Inside the digestate total N and NH4-N are important for the calculation of the fertilising potential.

4.7. Phosphorous and Potassium

Determined as P2O5 and K2O these elements are essential nutrients for both plants and bacteria. Thus they need to be checked in the substrate and digesters for the bacterial activity and in the digestate for the calculation of the fertilising potential.

NIRS can reliably determine only parameters with a concentration > 1 g/kg. The analysis of micro nutrients like iron and trace elements like cobalt would be good to have but is not possible at the moment.

5. MEASURING PRINCIPLE OF THE ULTRASONIC GAS FLOW METER

The metering of raw biogas in an industrial sized plant is challenging due to high flow rates, low pressures, high CO_2 and H_2S concentrations, and the complete saturation with water vapour which constricts the selection of accurate meters. The ultrasonic meter was developed by the company SICK especially for raw biogas. For initial calibration the calibration gas pipe system was built to be identical to that of the Schwandorf plant to achieve a maximum of accuracy. Figure 5 shows the measuring principle, figure 6 shows a cross section.

The FLOWSIC600 operates by measuring the propagation delay of an ultrasonic pulse. The standard 4-path meter is equipped with four pairs of identical ultrasonic transducers. The transducer pairs are integrated in a meter body and arranged opposite one another at a defined angle to the flow axis, thereby forming a direct measuring path.
The ultrasonic pulses cross the meter body from transducer to transducer. With no gas flowing, the pulses are emitted with the same speed (speed of sound) in both directions. When a gas is flowing through the meter body, the pulse in the direction of the gas flow is faster, while the pulse flowing against the flow is slower. This means that the transit time is shorter in the direction of flow (t_{AB}) and longer against the direction of flow (t_{BA}).
The ultrasonic transducers operate alternately as a transmitter and receiver. Each transducer is a piezo-ceramic element that is coupled with a diaphragm. To transmit signals, an alternating current is applied to the piezo-ceramic element so that it vibrates mechanically (piezoelectric effect). These vibrations are then transferred through the diaphragm to the gas. The vibrations are propagated as acoustic waves in the gas and strike the diaphragm on the opposite transducer after a propagation time that depends on the speed of sound and on the gas velocity. The waves are transferred to the piezo-ceramic element in the form of mechanical vibrations. They are then converted into an electrical signal by the inverse piezoelectric effect and used for further signal analysis.
The signals are then processed to calculate the transit times of the acoustic signals through the flowing medium. The measured values can then be calculated from the transit time thus determined.

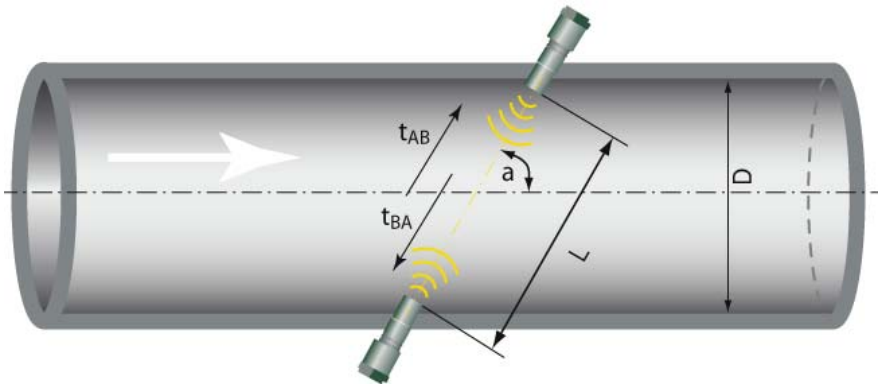

Figure 5: FLOWSIC600 measuring principle

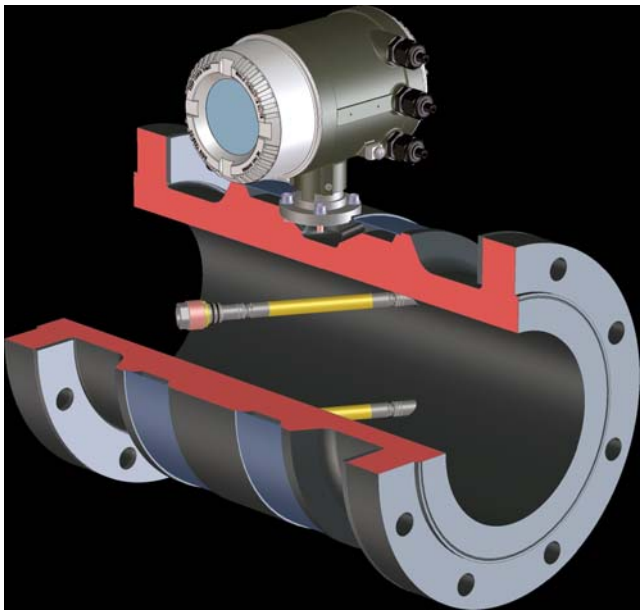

Figure 6: Cross section of the FLOWSIC600 Bio

5.1. Determination of the gas velocity

In the status “Measurement”, the FLOWSIC600 determines the gas velocity on each path 10 times per second. One measuring cycle consists of a velocity measurement per path, the integration of the operating volume, several internal procedures and the update of the measured output channels. This cycle takes about 100 ms. A 4-path-system makes 40 measurements per second.
A full analysis of the ultrasonic signals makes it possible to determine the point of time of signal reception, and thus the delay to the point of time of signal transmission. The signal propagation times in the flowing gas, t_{AB} and t_{BA}, are determined on the basis of this transit time.

Sound transit time in the direction of flow t_{AB}:

$$t_{AB} = \frac{L}{c + v_{Path} * \cos a}$$

Sound transit time against the direction of flow t_{AB}:

$$t_{AB} = \frac{L}{c - v_{Path} * \cos a}$$

L: Measuring path length
v_{Path}: path velocity
c: Speed of sound
a: Angle between the longitudinal axis of the meter body and the path

5.2. Characteristics of the FLOWSIC600 Bio

For the development of the FLOWSIC600 Bio the particularities of raw biogas were observed. Compared to flow meters that require an authority approved calibration e.g. the flow meter in the grid injection unit, the raw biogas flow measurement can operate with a lower level of accuracy. This way a

two-pathway ultrasonic flow meter was developed. The gas pipes in biogas plants such as in Schwandorf are often made of thermoplastic PE that have a low cost despite a high pressure stability and robustness. Therefore the flow meter was built with PE100. Explosion prevention requirements resulted in a special surface coating. Precipitation on the surfaces were reduced by an anti-sticking effect.
The design of the acoustic pathways made the flow meter tolerant towards vapour within the gas phase and prevents the formation of structure-borne sound bridges of fluids on the sensors. The sensors are made of corrosion-resistant titanium in a way that prevents the direct contact of the piezo-ceramic element and the biogas. This way the system is designed to have a high reliability at low maintenance costs. The accuracy of +/- 1% suffices the set requirements.
Figure 7 shows the ultrasonic flow meter after the primary digester 1.

Figure 7: Installation of an ultrasonic gas meter in the Schwandorf plant

6. RESULTS AND DISCUSSION

6.1. Modelling for NIRS

A first series of mathematical models to were developed on the base of the respective chemical reference analyses. After uploading of these models onto the NIRS central processing unit the spectra were converted into values for the analysed parameters. Figure 8 shows exemplarily the results of the VS_{corr} analysis over a period of 20 minutes within the central substrate allocator unit. Within this period five media from three process stages were pumped through. The media from the first digestion stage had the highest concentration of organics with 75-85 g/kg. In the second stage of digestion the organics were further degraded and the concentration decreased to 60-70 g/kg. After removal of fibres from the digestate (after the third stage of digestion) the concentration dropped to 40 g/kg. The scatter of the values in especially the media from the first digestion stage was due to the high content of fibres; each time a bundle of fibres was passing the sensor head it detected a temporarily high concentration of organics. With a progressing digestion of the fibres and ultimately their separation the degree of scattering decreased.

This is a fine example of the inhomogeneity of the medium and consequently the difficulty of taking representative samples for laboratory analyses. Only the averaging of a high number of values from continuous measurements will give representative results.

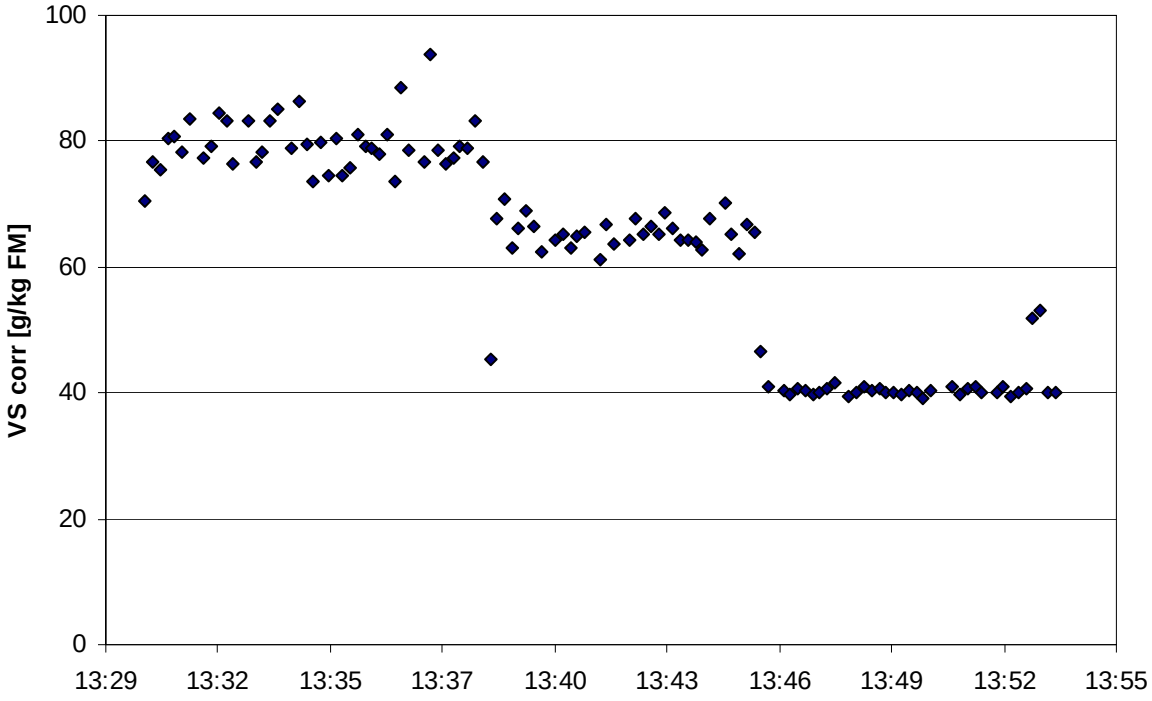

Figure 8: Volatile substances (VS_{corr}) in the central substrate allocator unit. The media were switched every 4-7 minutes starting with primary digester 1.1 (until 13:34), primary digester 1.2 (until 13:38), secondary digester 1.1 (until 13:42), secondary digester 1.2 (until 13:46), liquid phase after separation of digestate from tertiary digester line 1 (until 13:53).

The NIRS results were compared with the respective laboratory analyses to calculate the accuracy of NIRS. The accuracy was defined as the mean deviation per parameter and medium tested. Figure 9 shows the results for those parameters with a mean deviation below 15%. The key parameters organic content (VS_{corr}) and energy content (COD) ranged between 2 and 7% and were thus better than most laboratory test that exhibited deviations of up to 10% in an interlaboratory test.
The accuracy of NIRS depends highly on the concentration of the parameter tested. At concentrations higher than 1 g/kg the mean deviations were on average 8%, or at 5% if excluding VFAs and ethanol. At concentrations below 1 g/kg like propionic and butyric acid and iron the deviation is 30% and more at present. Since several parameters were in this project analysed by NIRS for the first time the number of chemical reference analyses is low. The increasing number of references and the ongoing development of the mathematical models aims at a reduction of the deviation and bettering of the accuracy.

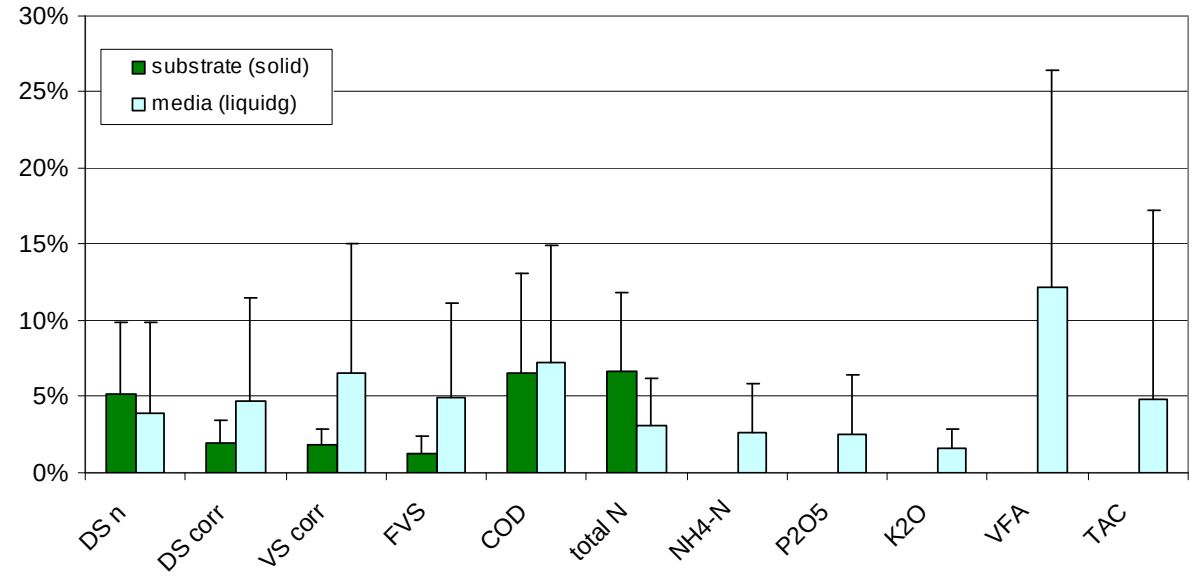

Figure 9: Mean deviation of NIRS results compared to their chemical references ($n_{substrate}$ = 10, n_{media} = 29).

6.2. Volumetric flow measurements of raw biogas

Figure 10 shows the normalised volumetric flows after the secondary digesters 1 and 2 and in the collecting pipe exemplarily for a period of 9 days. It shows that the volumetric flows after both secondary digesters was almost identical. This can be contributed to the identical feeding regime and to the potential of pressure balancing in the tertiary digester (see Figure 3). The gas pipes coming from the secondary digesters were combined in the collection pipe. Therefore the flow meter in the collecting pipe was expected to measure the sum of both precursor streams. In fact the sum of both streams from the secondary digesters was 901,137 Nm³ for the observed period of 30 days, and the 914,957 Nm³ in the collection pipe. The deviation was thus at 1.5% and near the level of accuracy given by the manufacturer (1%).

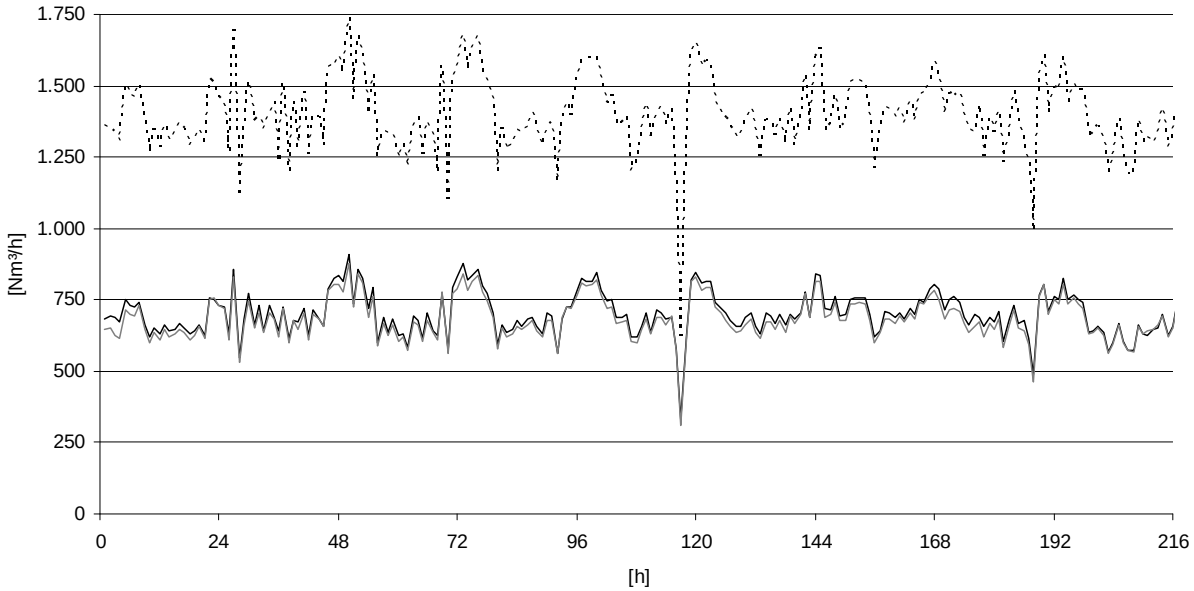

Figure 10: Normalised volumetric flow of raw biogas after secondary digester 1 (black line), after secondary digester 2 (grey line) and in the collection pipe (dotted line).

7. SUMMARY AND OUTLOOK

The installation of a near infrared spectrometer enabled the concurrent and continuous measurement of here 17 parameters in four stages of the AD process with a good degree of accuracy for key process parameters. The measurement of the volumetric flow of raw biogas by ultrasonic flow meters allowed the accurate compilation of biogas production in the different stages of the AD process. Taken together with the previously installed measurement technologies this enables an in industrial scale biogas plants unprecedented level of accuracy for the balancing of substrate and gas flows as well as an in-depth understanding of the microbial processes.
In the next stage of this project the microbial processes will be studied and modelled. These models will be used for an optimisation of the process control.

ACKNOWLEDGEMENT

The authors thank Schmack Biogas GmbH for their substantial support in the realisation of this project.

REFERENCES

1. FNR, *Leitfaden Biogas - Von der Gewinnung zur Nutzung*. 2010, Fachagentur Nachwachsende Rohstoffe e. V.: Gülzow.
2. FNR, *Biogas-Messprogramm II*, in *61 Biogasanlagen im Vergleich*. 2009, Fachagentur Nachwachsende Rohstoffe e.V.: Gülzow.
3. Vetter, A. and K. Arnold, *Klima- und Umwelteffekte von Biomethan: Anlagentechnik und Substratauswahl*, in *Wuppertal Papers*. 2010, Wuppertal Institut für Klima, Umwelt, Energie GmbH: Wuppertal.
4. Batstone, D.J., et al., *Anaerobic Digestion Model No. 1*. 2002, London: IWA Publishing.
5. Holm-Nielsen, J.B., et al., *Transflexive embedded near infrared monitoring for key process intermediates in anaerobic digestion/biogas production.* Journal of Near Infrared Spectroscopy, 2007. **15**(2): p. 123-135.
6. Andree, H., *Online Prozesskontrolle an Biogasanlagen*. 2009, TENIRS: Kiel.
7. Weißbach, F. and C. Strubelt, *Die Korrektur des Trockensubstanzgehaltes von Maissilagen als Substrat für Biogasanlagen.* Landtechnik, 2008(2): p. 2-4.
8. Weißbach, F., *Die Bewertung von nachwachsenden Rohstoffen für die Biogasgewinnung. Teil I: Das Gasbildungspotenzial der fermentierbaren Nährstoffe.* Pflanzenbauwissenschaften, 2009. **13**(2): p. 72-85.