Near-infrared-reflection spectroscopy as measuring method to determine the state of the process for automatic control of anaerobic digestion

Andrea Stockl[1*], Daniel Löffler[2], Hans Oechsner[3], Thomas Jungbluth[3],
Klaus Fischer[2], Martin Kranert[2]

(1. *State Institute of Agricultural Engineering and Bioenergy, University of Hohenheim, 70593 Stuttgart-Plieningen, Germany;*
2. *Institute for Sanitary Engineering, Water Quality and Solid Waste Management, University of Stuttgart,*
Bandtäle 2, 70569 Stuttgart, Germany;
3. *State Institute of Agricultural Engineering, Livestock System Engineering, University of Hohenheim, 70593*
Stuttgart-Plieningen, Germany)

Abstract: A recently developed control strategy for the anaerobic digestion process requires secure knowledge about the state of the process. The near infrared reflection spectroscopy (NIRS), provides the possibility to determine process parameters of the anaerobic digestion process online and directly at the digester. To investigate if the NIRS measurements can successfully be used for the characterization of the state of the process within the control strategy the control was operated on two experimental digesters. The NIR spectra were recorded during the experiments. The values of the process parameters (mainly concentrations of organic acids) obtained by NIRS differ from the values of the chemical analyses during the experiment. Nevertheless the state of the process is categorized equally on the basis of both measurement methods. It can consequently be stated that NIRS is expected to meet the requirements of the control strategy.

Keywords: near-infrared-reflection spectroscopy (NIRS), state of the process, automatic process control, anaerobic digestion, biogas
DOI: 10.3965/j.ijabe.20130602.008

Citation: Stockl A, Löffler D, Oechsner H, Jungbluth T, Fischer K, Martin Kranert. Near-infrared-reflection spectroscopy as measuring method to determine the state of the process for automatic control of anaerobic digestion. Int J Agric & Biol Eng, 2013; 6(2): 63－72.

1 Introduction

The support for the expansion of renewable energies in Germany is regulated by the Renewable Energy Source Act[1,2] which has the target of protecting limited fossil fuel resources and reducing CO_2 emissions. Through a minimum price regulation for electricity supply networks paying for electricity produced by renewable energy, it increased the incentive for investment in new plants. Before the introduction of the legislation in March 2 000 there were less than 1 000 biogas plants connected to the electricity network in Germany. Until the first amendment of the legislation in 2004 the number of new biogas plants starting operation had doubled. The first amendment especially encouraged the use of energy crops which augmented the interest in biogas production and led to further increases in the building of biogas plants[3,4]. With the second amendment in 2009 the number of biogas plants throughout Germany had already reached 4 670[5]. According to the German Agency for

---

Received date: 2013-02-06 **Accepted date:** 2013-06-12

Biographies: Daniel Löffler, PhD, Email: daniel.loeffler@iswa.uni-stuttgart.de. **Hans Oechsner,** PhD, Agricultural Scientist, Email: hans.oechsner@uni-hohenheim.de. **Thomas Jungbluth,** PhD, Professor, Email: thomas.jungbluth@uni-hohenheim.de. **Klaus Fischer,** PhD, Email: klaus.fischer@iswa.uni-stuttgart.de; Prof. Dr.-Ing. **Martin Kranert,** Email: martin.kranert@iswa.uni-stuttgart.de.

***Corresponding author: Andrea Stockl,** Ddiipl.-Ing. Agriculture; Andrea Stockl is studying for her doctorate at the University of Hohenheim, Germany; Email: andrea.stockl@uni-hohenheim.de.

Renewable Resources (FNR) further 1 100 new plants were connected to the electricity supply network in 2010 while this number is expected to continue to increase[5]. This boom of new biogas plants in the last 10 years is notably accompanied by questions about the optimal utilization of the regenerative substrates applied, as well as topics like the reliability and the efficacy of the plants become more important. Key aspects in this context are the precise monitoring and control of the anaerobic digestion process. Breakdowns in electricity production through process failures are both time and cost intensive. As a result a continuous monitoring of the biological process within the digester is required so that preventative action can be taken when necessary.

In particular online measurements of intermediate products in the anaerobic reaction chain can directly provide important information about the conditions of the process so that these parameters can consequently serve as early warning indicators. Besides better monitoring of the process these innovative measurement methods like the near infrared reflection spectroscopy (NIRS) additionally allow the development of automatic process control strategies which are based on the online availability of an increasing number of process parameters. Even though control strategies for the anaerobic digestion process on biogas plants are a tool to enable a more targeted and simplified utilization of the process while maintaining its stability no automatic process control has yet established as state of the art on biogas plants.

This article therefore aims to demonstrate that NIRS as innovative online-measuring method can be used for the monitoring of the state of the process, allowing to guide the process securely to a defined operation state by a recently developed automatic control strategy (presented in detail in the report[6]).

2 Methodology

The near infrared reflection spectroscopy is investigated as an appropriate method to monitor the process stability in digesters. The NIRS measuring system has to be calibrated on the specific parameters that indicate the process conditions. NIR spectra determined over reflected light that is irradiated on a substrate sample correlate directly to the concentrations of the specific parameters in the substrate sample.

A NIRS-calibration can be performed on all volatile fatty acids (VFA) like acetic acid, propionic acid, n-valeric acid, iso-valeric acid, n-butyric acid, iso-butyric acid and caproic acid, the sum of all mentioned VFA or the sum parameters of the volatile organic acids (VOA) and the buffer capacity (TAC) which were determined via titration. The developed NIRS-calibration model must be validated with leave one out validation or a test-set validation. After validation of the measurement system the desired concentrations of specific parameters in an unknown substrate sample can be determined online without chemical analysis of substrate samples.

Due to the development of online measurements methods like the NIRS, it is expected that the named process parameter can easily and economically be collected online. Assuming this online availability as a future state of the art, the mentioned parameters can be incorporated in the design of control strategies for the anaerobic digestion process. The Anaerobic Digestion Model No.1 (ADM1) first published by Batstone et al.[7] was used for the development, adjustment and first evaluation of appropriate control strategies. Based on the results in this virtual laboratory, promising control strategies where then transferred to laboratory-scale digesters.

To investigate the capability of NIRS to meet the requirements of the developed control strategy operational experiments were conducted on two digesters. During the experiments chemical analyses were used for the operation of the control strategy while NIR spectra were recorded analogously. To especially include conditions at the limit of process stability the operation of one digester was intentionally set-up with higher risks. The final comparison of both measuring methods provides information about the applicability of NIRS for this purpose.

3 Materials and methods

3.1 Experimental setup

The experiments were carried out on two experimental laboratory-scale biogas digesters of the biogas laboratory of the University Hohenheim. The digesters were operated at a thermophilic temperature of 52℃ (digester 1) and at a mesophilic temperature of 41℃ (digester 2). The feeding mixture consisted of 30 weight-% of cattle manure and 70 weight-% of maize silage referring on the fresh, undried material. The contents of dry matter (DM) and organic dry matter (ODM) were measured referring on the German industry standard DIN EN 12879 and DIN EN 12880[8,9]. The horizontal lying digesters comprise a total volume of 452 L. Four hundred litres of this volume are the liquid working volume, while the rest of the volume remains for the gaseous phase. The heating of the digester by a surrounding external water circulation system ensures the required and constant operation temperature. Heat losses could be avoided through a thermal insulation around the digester. The feeding occurred through a hopper. The degraded digestate was emitted through a submersible overflow at the opposite end of the feeding hopper, thus maintaining a constant fermentation volume of 400 L.

Both digesters were stirred with a horizontal motor-driven paddle stirrer. The gas volume detection at digester 1 was performed with a bellows-type gas flow meter BK-G4 of the Elster GmbH (measurement range 40 – 6 000 L/h) with previous cooling of the biogas to 10℃. The gas volume at digester 2 was mainly recorded by a drum-type gas flow meter TG 1/5 of the Dr.-Ing. Ritter Apparatebau GmbH (measurement range 2-120 L/h) after water precipitation. Subsequent to the gas meters, the amount of gas was stored in gas bags. The gas was analysed in different time intervals from an automatic gas-collection system. From these records the gas composition could be derived. The gas amounts were converted to the standard reference conditions according to the German industry standard DIN 1343, with a standard temperature of 273.15 ℃K and a standard pressure of 1013.25 hPa[10]. The gas composition was initially limited on CO_2 and methane (CH_4) summing up to 100%. During the further experiment the hydrogen concentration (H_2) was additionally included. The samples for the analysis of the process parameters were drawn through a sampling tap before the feeding. The pH value was determined by a pH electrode SenTix 21 of the WTW Wissenschaftlich Technischen Werkstätten GmbH here. Either after a freezing storage at -21℃ or directly after the sampling the samples were analysed via gas chromatography for all volatile fatty acids, including acetic acid, propionic acid, n- valeric acid, iso-valeric acid, n-butyric acid, iso-butyric acid and caproic acid. The frozen samples were defrosted in a refrigerator at 4℃ overnight. For each sample the NIR spectra were recorded as well. From most of the samples the VFA, the TAC and the ratio of the VFA to the TAC value were determined via titration with the instrument “785 DMP Titrino” of the German Metrohm GmbH & Co. KG (for more details please refer to the previous study[11-13]).

3.2 Experimental operation

In preparation for the actual control experiments the digesters were run without the control mechanism to obtain operational data and to conduct the digesters to a defined steady operational state. During this period the model (NIRS) was calibrated and could consequently be used for the adjustment of the control strategy. After this adjustment, the operational experiment of the control strategy started. During the control operation of approximately one month the daily manual feeding was realized as exact as possible at the same time of day. The new daily amount of input was determined on the basis of the daily value of the CH_4 production.

3.3 Control strategy

As described by Löffler[6], the developed control strategy consists of two hierarchical levels. The concept of different hierarchical levels is for example proposed and recommended in Expert systems in bioprocess control[14]. A time discrete Proportional-Integral controller (PI controller) uses the daily CH_4 production to adjust the amount of a fix mixture of input material to the set-point of the CH_4 production (Figure 1). Derived from reports by Lunze and Ogunnaike[15,16], the daily calculation of the amount of input (u(t)) is given in Equations (1) – (3).

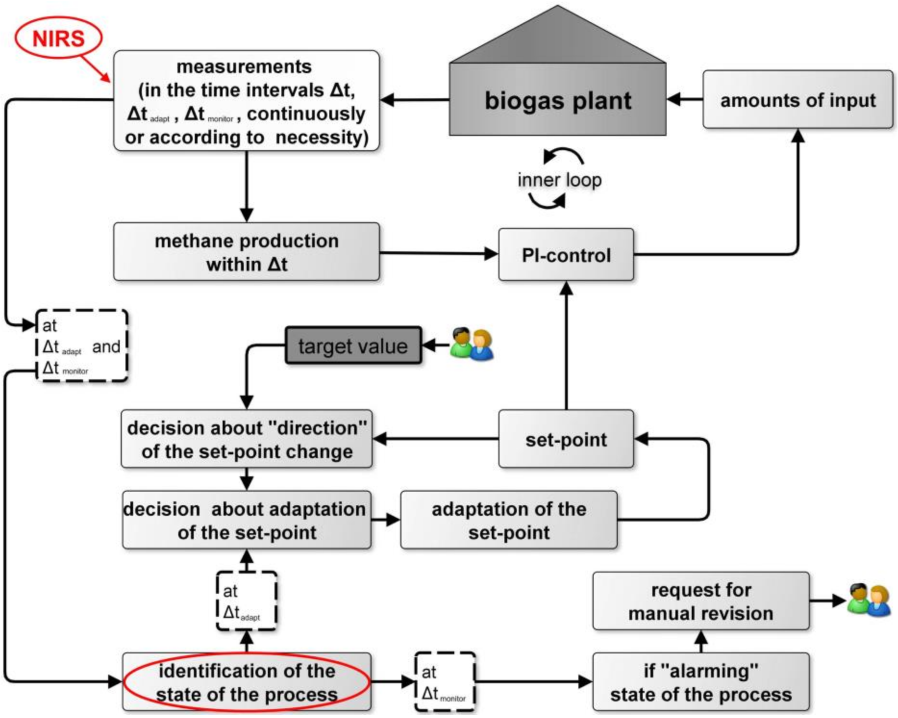

Figure 1 Schematic set-up of the control strategy taken and adapted from the reference[6], reprinted with permission from DIV Deutscher Industrieverlag GmbH

While Equation (1) accounts for both digesters, Equation (2) represents the adjustment result of the PI-control for digester 1. Equation (3) respectively shows the daily calculation of $u(t)$ for digester 2.

$$\varepsilon(t) = \text{set-point}(t) - \text{CH}_4\ \text{production}(t) \tag{1}$$

$$u(t) = 2*4.4/3*10^{-6}*\varepsilon(t)+12*4.4/3*10^{-6}*\Delta t*\Sigma^{t}_{i=1}\ \varepsilon(t) \tag{2}$$

$$u(t) = 2*6.9/3*10^{-6}*\varepsilon(t)+12*6.9/3*10^{-6}*\Delta t*\Sigma^{t}_{i=1}\ \varepsilon(t) \tag{3}$$

As explained in the report[6], the PI control as the inner loop working on a daily basis is guided and controlled by a superordinated knowledge-based part of the control system. Due to the complexity and nonlinearity of the anaerobic digestion process, the part of control strategy is needed to guarantee a secure operation of the inner loop. Within this part the identification of the state of the process constitutes the basis for the guidance of the inner loop and for subsequent reactions to states of the process which cannot be classified as "securely stable" anymore. NIRS measurements allow to online monitor process parameters indicating the state of the process.

This means the state of the process can also be identified at least daily. For the identification of the state of the process, a set of process parameters is used to categorize the state of the process as "securely stable", "acceptable", "critical" or "alarming". In case of an "alarming" state of the process, a request for manual revision by the operator is produced. The "adaptation matrix" as the decision-taking part of the control strategy is responsible to finally guide the process to the operator-defined target value of the CH_4 production. According to the state of the process and the target value, a decision about the adaptation of the set-point is taken here in fix time intervals (seven days here).

For the operation of the above mentioned digesters this part of the control strategy is executed every seven days while the step size for the set-point adaptation was adjusted to 50 L_N CH_4/d for digester 2 and with less focus on secure stability to 100 L_N CH_4/d for digester 1. The target values were set to 700 L_N CH_4/d for digester 2 and 900 L_N CH_4/d for digester 1. The organic loading rates at the beginning of the control operation were approximately 3.05 kg and 4.06 kg of organic dry matter per day and m^3 of liquid-filled digester volume for digester 2 and digester 1, respectively, which means that the feeding to digester 2 comprised 1.8 L cow manure and 4.2 kg corn silage; while digester 1 was fed with 2.4 L cow manure and 5.6 kg corn silage (for further details please refer to the previous study[6]). As the secure identification of the state of the process and therefore as well sufficient online instrumentation are identified as key elements for successful automation of biogas plants the following demonstrations focus on these aspects. Hence, the background of the two main topics here (process control and NIRS measurements) is firstly commented more in detail. As proposed in the report[6], the parameters included in the identification of the state of the process are the pH, concentrations of organic acids, their changing and their correlation among each other, the concentration of long-chain fatty acids, the ratio of the VOA to the TAC, the concentration of free ammonia nitrogen, the dry solid content in the digester and the ratio of the control deviation $\varepsilon(t)$ to the set-point.

Table 1 gives the values of the process parameters for the categorization of the state of the process which are most relevant for the demonstrations here. All values refer to the above mentioned digesters operated with an input mixture of 70 weight-% of corn silage and 30 weight-% of cow manure. In case of different operational conditions the values may have to be adapted.

Table 1 Values of the process parameters for the categorization of the state of the process for the digester operated with an input mixture of corn silage and cow manure (taken and adapted from the report [6])

Process parameter	"securely stable"	"acceptable"	"critical"	"alarming"
VFA	< 1 500 mg HAc$_{eq}$/L	1 500 – 2 500 mg HAc$_{eq}$/L	2 500 – 4 500 mg HAc$_{eq}$/L	> 4 500 mg HAc$_{eq}$/L
ΔVFA	< 200 mg HAc$_{eq}$/(L*Week)	200 – 1 000 mg HAc$_{eq}$/(L*Week)	1 000 – 1 500 mg HAc$_{eq}$/(L*Week)	> 1 500 mg HAc$_{eq}$/(L*Week)
C_{ac}	< 1 500 mg$_{ac}$/L	1 500 – 2 000 mg$_{ac}$/L	2 000 – 3 000 mg$_{ac}$/L	> 3 000 mg$_{ac}$/L
ΔC_{ac}	< 150 mg$_{ac}$/(L*Week)	150 – 400 mg$_{ac}$/(L*Week)	400 – 1 000 mg$_{ac}$/(L*Week)	> 1 000 mg$_{ac}$/(L*Week)
C_{pro}	< 200 mg$_{pro}$/L	200 – 400 mg$_{pro}$/L	400 – 1 000 mg$_{pro}$/L	> 1 000 mg$_{pro}$/L
ΔC_{pro}	< 100 mg$_{pro}$/(L*Week)	100 – 300 mg$_{pro}$/(L*Week)	300 – 500 mg$_{pro}$/(L*Week)	> 500 mg$_{pro}$/(L*Week)
Ac./Prop.	> 2.5	2.5 – 2.0	2.0 – 1.5	< 1.5
VOA/TAC	< 0.4	0.4 – 0. 5	0.5 – 0.6	> 0.6

Note: VFA: sum of the concentrations of acetic, propionic, butyric and valeric acid in equivalents of acetic acid (HAc$_{eq}$); ΔVFA: change of the concentration of VFA within L week; C_{ac}: concentration of acetic acid; ΔC_{ac}: change of the concentration of acetic acid within L week; C_{pro}: concentration of propionic acid; ΔC_{pro}: change of the concentration of propionic acid within L week; Ac./Prop.: Ratio of acetic to propionic acid (mg HAc$_{eq}$/mg HAc$_{eq}$); VOA/TAC: ratio of the sum parameters VOA to TAC, which are both obtained by titration (see above).

Each measured parameter can consequently be assigned to a categorization of the state of the process. The worst categorization obtained, finally characterizes the overall state of the process.

3.4 Measurements with NIRS

The advantages of the NIR-measurement instrumentation in general are the online availability of the measured data and the general applicability of the measuring system. The measurements were performed on undestroyed raw material resulting in faster available results. Thereby the results can be used immediately after NIRS-calibration of the system without any pre-treatment of the samples.

The NIR measurement system comprises of a diode array spectrometer with 256 photo diode elements (for more details refer to Stockl (2012)[11]). Through a 10 mm sapphire window in front of the sensor head the light of a wolfram halogen lamp shines on the digester substrate. The reflected light is directed via an optical fiber into the spectrometer where it is evaluated. The data are stored in an external database. The measuring range extends from 960 nm to 1 700 nm.

The sensor is located in a by-pass pipeline system with an integrated pump. The total digester substrate is pumped twice per hour past the sensor. Simultaneously while recording the spectra substrate samples were drawn at a sampling tap located near the pipeline system. In order to avoid losses of the intensity of the lamp the sensor head was fitted with an integrated automatic dark (0% reflection) and white alignment (100% reflection). Each reflection adjustment was performed every hour and stored as reference in the database. NIRS-calibration models were developed on different parameters with multivariate data analysis[17] and support vector machine regression[18,19].

In order to predict process parameters like the acid concentration or the VOA/TAC from the recorded NIR spectra a NIRS-calibration model is required. The NIRS-calibration model used here was developed based on a previous experimental operation of both digesters, which will briefly be described in the following. During this experimental operation shredded wheat was given to both digesters (digester 1 and digester 2) to increase the organic loading rate. In a period of twelve days both digesters were three times fed with shredded wheat. A wheat addition of each time 10 kg was realised at digester 1 (thermophilic) on the first the third and the eighth day of the experiment. Digester 2 (mesophilic) was fed on the same days but with 10, 5, and 2.5 kg of shredded wheat, respectively. Before the wheat addition both digesters were operated at an organic loading rate of 3 kg oDM/digester volume and day. During this time acid concentrations were hardly detectable.

The advantage of feeding the digesters with shredded wheat instead of maize silage is the faster increase of the acid concentrations. However, the acids are reduced just as fast. Already after two days, respectively after five days, only low acid concentrations were detectable in the digester substrate by chemical analyses. With this experiment enough data could be obtained to develop the NIRS-calibration model.

With part of the data of this previous experiment NIRS-calibration models were developed for several process parameters. The different NIRS-calibration models for VFA, the ratio VOA/TAC, acetic acid and propionic acid were consequently performed with independent data. For the development of the NIRS-calibration models, some representative samples were selected from a total amount of 166 samples. To prevent overfitting the selection of the samples was first done by a limitation of the concentration span and then by choosing a few representative samples for each concentration level. Table 2 shows the quality of the NIRS-calibration models for digester 1 in common parameters. Due to the selection of the samples outliers are not listed in Table 2.

Table 2 Statistical parameters to evaluate the quality of the different NIRS-calibration models in the thermophilic operated digester (digester 1)

	1n	2RMSECV	3RMSEC	4Range	5RER	6RPD	7C	8G
VFA	59	0.40	0.26	0.75-5.49	11.92	3.27	14.1	0.0025
C_{Ac}	80	0.33	0.23	0.58-4.82	12.91	3.11	14.1	0.0025
C_{pro}	121	0.11	0.06	0.35-1.84	16.6	4.49	30.5	0.0055
VOA/TAC	67	0.06	0.05	0.26-0.96	11.61	3.17	14.1	0.0025

Note: 1n=number of samples, 2RMSECV [g/kg]=root mean square error of prediction, 3RMSEC [g/kg]=root mean square error of calibration, 4Range [g/kg]=data spread, 5RER=ratio of data spread and standard error of prediction, 6RPD=ratio of standard deviation and standard error of prediction, 7C=penalty factor, 8G=balancing factor.

The quality of a NIRS-calibration model is expressed by the statistical parameters shown in Table 2. A low RMSECV value indicates a good quality of a NIRS-calibration model. A further criterion for assessing a model is the RER, which describes the prediction error based on the data range and is susceptible to outliers[11]. RER should be as large as possible; a value over 10 represents a dimension for a suitable calibration[20].

Williams and Sobering[20] published that the RPD value over 3 is indicative of a good NIRS-calibration and for the prediction of particular samples. Every calibration model applied in this experiment used the Gaussian radial basis function (RBF) as kernel function[19,21-23]. An important aspect, which should not be neglected, is the right choice of the best three hyperparameters ε, C and G. The value of ε is fixed at 0.1 in the system by the software and both other parameters have to be found by trial and error. The C-value is described as a penalty parameter, and the G-value, as a compensation parameter[24]. A higher C-value increases the training time for the data and reduces the prediction precision because the influence of the training errors is more strongly weighted. The G-value refers to the extent of the Gaussian function or bell curve in data distribution. There are no standard values for these two parameters. Finding the best combination of these parameters constitutes a complex task, especially because it comprises the risk of large errors. Today there are software programs that calculate the best combination of these parameters[25]. In the used software this automatic procedure was not yet implemented.

4 Results and discussion

The result of the experimental control operation on digester 2 is shown in Figure 2. As expected the CH_4 production always approaches the actual set-point within a range of fluctuation.

By the weekly adaptation of the set-point by the control strategy the process is step by step guided to the final target value of 700 L_N CH_4/d, while the state of the process remains “securely stable” until the set-point reaches the target value. The control operation on digester 2 consequently represents a normal operation course without incidents.

To prove the appropriateness of the set values of the process categorization (Table 1) and to check the limits of this procedure, the information of the process categorization was ignored during the operation of digester 1. Besides the higher loading rate already at the beginning and the higher step size of Δset-point of 100 L_N CH_4/d, this approach leads to increases of the organic loading even though it is not recommendable according to the state of the process. Analogically to Figure 2, the result of the operation of digester 1 is shown in Figure 3.

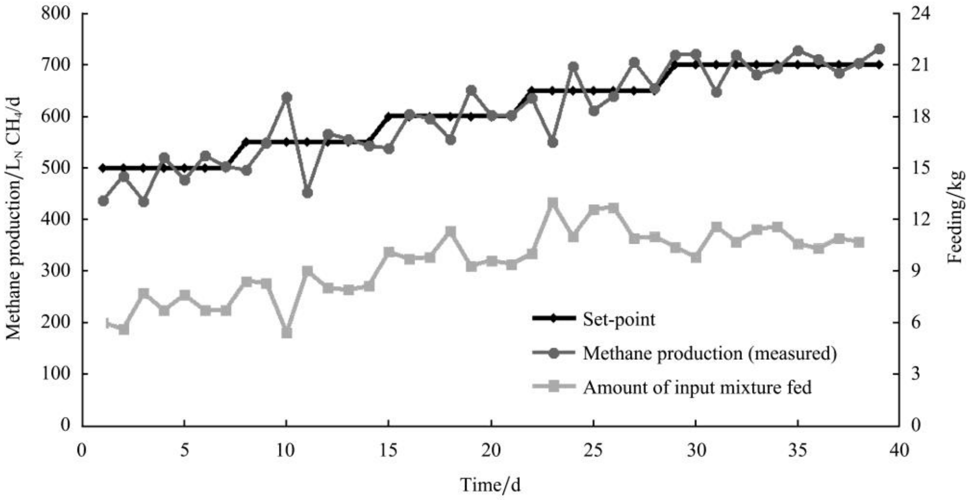

Figure 2 Experimental operation of the control strategy on digester 2 (taken and adapted from the reference [6], reprinted with permission from DIV Deutscher Industrieverlag GmbH)

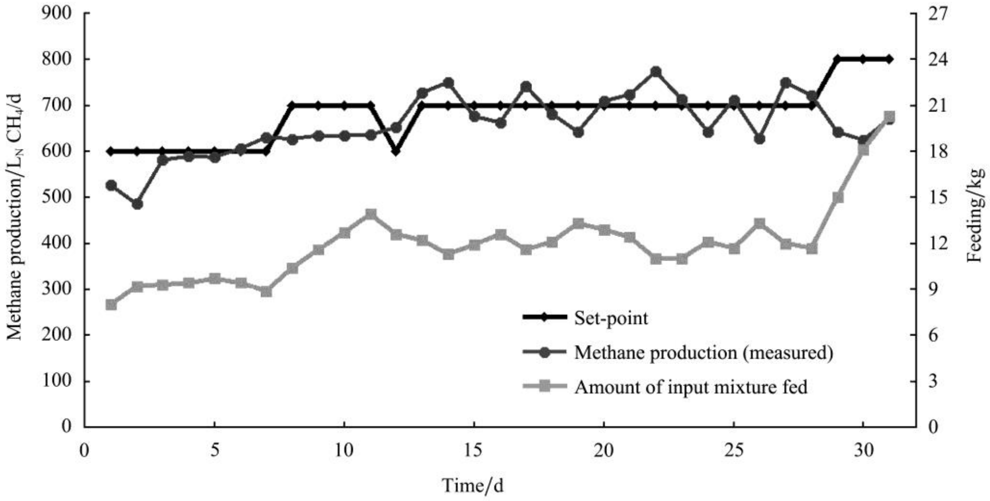

Figure 3 Experimental operation of the control strategy on digester 1 (taken and adapted from the reference [6], reprinted with permission from DIV Deutscher Industrieverlag GmbH)

As the actual set-point in the second week could not be reached even until the day 11 the set-point was reduced on the day 12 to prevent process failure. As the set-point was reached immediately after this intervention the set-point reduction was retracted on the following day. The following calculations change in comparison to an operation without this intervention but do not significantly influence statements about the identification of the state of the process.

In contrary to digester 2, the state of the process rapidly deteriorates from the initial category “acceptable”, especially due to disregarding the demands of the state of the process. This means ignoring the values given in Table 1 leads to instability of the process. Deeper analyses as in [6] suggest that closer limits within the identification procedure of the state of the process are not required to prevent process failures in this case.

Table 3 shows the weekly characterization of the state of the process and the resulting suggestions for the adaptation of the set-point except for the day 28, where no relevant changes to the previous check on the day 21 occurred. During the operation the chemical analyses from the laboratory were used for the categorization procedure. To investigate if and how the NIRS measurements can be used for this purpose as well, the NIR spectra which were recorded during the experimental operation were afterwards analysed as well, leading to analogous results also presented in Table 3.

Table 3 Characterization of the state of the process for digester 1 based on chemical analyses from the laboratory and data obtained by NIRS (adapted and extended from the reference [6])

process parameter	day 7				day 14				day 21			
	LD	PS_{LD}	NIRS	PS_{NIRS}	LD	PS_{LD}	NIRS	PS_{NIRS}	LD	PS_{LD}	NIRS	PS_{NIRS}
VFA	1589	acc.	1 892	acc.	2 595	crit.	2 081	acc.	2 664	crit.	2 488	acc.
ΔVFA	-77	stab.	-	-	1 006	crit.	189	stab.	69	stab.	407	acc.
C_{ac}	1211	stab.	1 314	stab.	1 662	acc.	1560	acc.	1 688	acc.	1 686	acc.
ΔC_{ac}	25	stab.	-	-	451	crit.	246	acc.	26	stab.	126	stab.
C_{pro}	391	acc.	-	-	948	crit.	1 100	al.	1 005	al.	1 000	al.
ΔC_{pro}	-152	stab.	-	-	557	al.	-	-	58	stab.	-100	stab.
Ac./prop.	3.82	stab.	-	-	2.16	acc.	1.75	crit.	2.07	acc.	2.08	acc.
VOA/TAC	0.403	acc.	0.44	acc.	0.523	crit.	0.47	acc.	0.564	crit.	0.54	crit.
overall PS	acceptable		acceptable		alarming		alarming		alarming		alarming	
suggested Δset-point	±0				- 100 or f. s.				- 100 or f. s.			
realized Δset-point	+ 100				±0				±0			

Note: LD: laboratory data, chemical analyses; PS: state of the process; stab.: “securely stable”; acc.: “acceptable”; crit.: “critical”; al.: “alarming”; f. s.: further steps; grey: “decisive PS for the characterization of the overall PS”; Δset-points: given in L_N CH_4/d; Units of the parameters: As above in table 1.

The NIRS measurements were performed at the same three selected time points (see Table 3, day 7, day 14 and day 21) to verify the wet chemical analysis data. NIRS values over a period of 20 min at twelve o’clock noon were summarized to a mean value. To compare the NIRS mean values with the chemical analysed values the RMSECV (shown in Table 2, not equal for each parameter) has to be included.

The limits of the deviations of the estimated values to the values of the chemical analyses given as percentages change significantly when the RMSECV is included in the evaluation. The RMSECV is not further taken into consideration here, but should not be ignored. The NIRS determination of the concentration of the VFA in comparison to the chemical analysis shows a discrepancy of 7% up to 37% in the worst case, while it ranges from 0.1% to 26% for the determination of the concentration of acetic acid. The determination of the concentration of propionic acid could not be achieved for the first date, because of missing data in the lower and the higher concentration range. However, the remaining two values show a good correlation with the chemical analysis with a discrepancy of 0.5% to 16%. The difference between the VOA/TAC values obtained with NIRS in comparison and the chemically analysed values vary between 4.3% and 29% in the worst case. Even though the differences given as percentages are high in some cases, the process categorization across all process parameters results in the same categorization of the state of the process for the three days considered in Table 3.

Consequently the operational experiment of the control strategy would have resulted in the same results with NIRS measurements.

5 Conclusions

The operational control experiments showed that the control strategy itself can be used to securely guide the anaerobic digestion process to user-defined states of the process (digester 2). The categorization of the state of the process plays a key role within this control strategy to monitor, supervise and guide the process. NIRS allows to directly determining the concentrations of organic acids or the VOA/TAC online. Taking the whole process categorization into account the obtained accuracy (discrepancies of up to 37%) is regarded as sufficient for the process categorization. Moreover the results can be improved significantly with more appropriate NIRS-calibration models. This leads to the conclusion that the NIRS measurements can replace the cost- and time-intensive chemical analyses and provide online-measurements for the presented control strategy.

Acknowledgements

The authors thank the Ministry for Rural Areas and Consumer Protection of the federal state of Baden-Württemberg (Germany) and the Baden-Württemberg Foundation gGmbH for the financial support of the project within the “research platform on bioenergy”.

Abbreviations

ADM1: Anaerobic Digestion Model No.1
DM: dry matter
NIRS: near-infrared-reflection spectroscopy
oDM: organic dry matter
PI controller: Proportional-Integral controller
RER: ratio of data spread and standard error of prediction
RMSEC: root mean square error of calibration
RMSECV: root mean square error of cross validation
RPD: ratio of standard deviation and standard error of prediction
TAC: buffer capacity determined by titration
VFA: volatile fatty acids, parameter representing the sum of the concentrations of single volatile fatty acids in equivalents of acetic acid (HAceq)
VOA: sum parameter of the volatile organic acids determined by titration

[References]

[1] Anonymous. Gesetz für den Vorrang Erneuerbarer Energien (Erneuerbare-Energien-Gesetz (EEG)) vom 25. Oktober 2008 (BGBl I S. 2074), das durch Artikel 2 Absatz 69 des Gesetzes vom 22. Dezember 2011 (BGBl I S. 3044) geändert worden ist.

[2] Anonymous. Gesetz für den Vorrang Erneuerbarer Energien (Erneuerbare-Energien-Gesetz (EEG), konsolidierte (unverbindliche) Fassung des Gesetzestextes in der ab Januar 2012 geltenden Fassung), 2011 (Grundlage: des Deutschen Bundestages vom 30. Juni. BT-Drucksache 17/6071 und Beschluss des Deutschen Bundestages vom 30.Juni (BT.Drucksache 17/6363)).

[3] Oechsner H, Lemmer A, Helffrich D. Use of verdure in agricultural biogas plants - a way to significant evaluation of turf growth. Einsatz von Gründgut in landwirtschaftlichen Biogasanlagen - Ein Weg zur sinnvollen Verwertung von Rasenaufwuchs. Rasen-Turf-Gazon, 2003a; 34(2): 46-48.

[4] Oechsner H, Lemmer A, Neuberg C. Energy crops as fermenting substrate in biogas plants. Feldfrüchte als Gärsubstrat in Biogasanlagen. Landtechnik, 2003b; 58(3): 146-147, 221.

[5] Agency of Renewable Resources (FNR). Biogas Basisdaten Deutschland (Basical data of biogas Germany). 2010, Gülzow, available at: http://www.bio-energie.de/biogas/biogasanlagen-in-deutschland/.

[6] Löffler D. Entwicklung einer Regelungsstrategie für den Anaerobprozess am Beispiel landwirtschaftlicher Biogasanlagen. Dissertation. ISBN: 978-3-8356-3352-0. In: Stuttgarter Berichte zur Abfallwirtschaft, 2012, Volume 105, Oldenbourg-Industrieverlag Munich. Dissertation, University of Stuttgart, Stuttgart.

[7] Batstone D J, Keller J, Angelidaki I, Kalyuzhnyi S V, Pavlostathis S G, Rozzi A, et al. Anaerobic digestion model no.1 (ADM1), 2002, Scientific & technical report 13, IWA Publishing, London.

[8] Charakterisierung von Schlämmen - Bestimmung des Glühverlustes der Trockenmasse, DIN EN 12879. Beuth Verlag GmbH, 2001a, (Deutsches Institut für Normung e.V. (DIN)).

[9] Charakterisierung von Schlämmen - Bestimmung des

Trockenrückstandes und des Wassergehalts, DIN EN 12880. Beuth Verlag GmbH, 2001b, (Deutsches Institut für Normung e.V. (DIN)).

[10] (DIN) German Institute for Standardization. DIN 1343-Reference conditions, normal conditions, normal volume; concepts and values. 1990, German Standard.

[11] Stockl A. Near infrared spectroscopic online monitoring of process stability in biogas plants. Engineering in Life Sciences, 2012; 12 (3): 295-305.

[12] Rieger C, Weiland P. Prozessstörungen frühzeitig erkennen. BIOGAS Journal, 2006; (4): 18-20.

[13] Lemmer A. Biogaserzeugung. In: Graf F, Bajohr S (Eds), Biogas: Erzeugung, Aufbereitung, Einspeisung, Oldenbourg, Munich, 2011, pp. 75-118.

[14] Konstantinov K B, Aarts R, Yoshida T. Expert systems in bioprocess control: Requisite features, in: Fiechter, A., (Ed), Bioprocess design and control, Advances in biochemical engineering, biotechnology, Springer, Berlin, Heidelberg, 1993, volume 48, 169-191 p.

[15] Lunze J. Regelungstechnik 1: Systemtheoretische Grundlagen, Analyse und Entwurf einschleifiger Regelungen, Springer-Lehrbuch, sixth rev. ed., Springer, Berlin, Heidelberg, 2007.

[16] Ogunnaike B A, Ray W H. Process dynamics, modeling, and control, Oxford University Press, New York, 1994.

[17] Kessler W. Multivariate Datenanalyse für die Pharma-, Bio- und Prozessanalytik (Multivariate data analysis for pharma-, bio- and process analytics). Wiley-VCH, Weinheim, 2007.

[18] Gunn S. Support vector machines for classification and regression. Technical report, Image Speech and Intelligent Systems Research Group, University of Southampton, 1998.

[19] Cristianini N, Shawe-Taylor J. An introduction to support vector machines and other kernel-based learning methods. Cambridge University Press, UK, 2000.

[20] Williams P C, Sobering D C. Comparison of commercial near infrared transmittance and reflectance instruments for analysis of whole grains and seeds. Journal of Near Infrared Spectroscopy, 1993; 1: 25-32.

[21] Schölkopf B, Smola A J. Learning with kernels. *MIT press*, Cambridge, 2002.

[22] Üstün B, Melssen W J, Buydens L M C. Facilitating the application of Support Vector Regression by using a universal Pearson VII function based kernel. Chemometrics and Intelligent Laboratory Systems, 2006; 81(1): 29-40.

[23] Üstün B, Melssen W J, Buydens L M C. Visualisation and interpretation of Support Vector Regression models. Analytica Chimica Acta, 2007; 595(1-2): 299-309.

[24] Zhao C Y, Zhang H X, Zhang X Y, Liu M C, Hu Z D, Fan B T. Application of support vector machine (SVM) for prediction toxic activity of different data sets. Toxicology, 2006; 217(2-3): 105-119.

[25] Witten F. Data Mining: Practical Machine Learning Tools and Techniques. Morgan Kaufmann Pub, 2005. Available at: http://mestrado.deinfo.uepg.br/mestrado/docs/WittenFrank.pdf.