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Short Communication

Near-infrared spectroscopy (NIRS) for a real time monitoring of the biogas process

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ABSTRACT

In this research project Near-infrared spectroscopy (NIRS) was applied to monitor the content of specific process parameters in anaerobic digestion. A laboratory scaled biogas digester was constantly fed every four hours with maize- and grass silage to keep a base load with an organic loading rate (OLR) of 2.5 kg oDM/m^3 * d. Daily impact loads with shredded wheat up to an OLR of 8 kg oDM/m^3 * d were added in order to generate peaks at the parameters tested. The developed calibration models are capable to show changes in process parameters like volatile fatty acids (VFA), propionic acid, total inorganic carbon (TIC) and the ratio of the volatile fatty acids to the carbonate buffer (VFA/TIC). Based on the calibration of the models for VFA and TIC, the values could be predicted with an R^2 of 0.94 and 0.97, respectively. Moreover, the residual prediction deviations were 4.0 and 6.0 for VFA and TIC, respectively.

1. Introduction

Near-infrared reflection spectroscopy (NIRS) is widely applied in agriculture, with great application to several agricultural processes such as quality control of animal feed and herbal products (De Boever et al., 1997). Moreover, NIRS systems have been successfully implemented for analyses of chemical compositions in maize silage such as neutral detergent fiber, crude protein or ash content (Cozzolino et al., 2006; Lovett et al., 2005; Jacobi et al., 2011). Recent studies investigated NIRS to assess the biochemical methane potential (BMP) of meadow grasses (Raju et al., 2011) and maize silage (Jacobi et al., 2012), or the BMP potential of a wide variety of plant biomass samples (Triolo et al., 2014; Doublet et al., 2013) and confirmed the NIRS potential use for various applications. Furthermore NIR spectrometers are used to determine chemical compounds (such as N, P and K) in organic fertilizers. Therefore, the widely applied NIRS measuring method in the biogas sector for a real time monitoring of process specific parameters (Lomborg et al., 2009; Ward, 2016) is inevitable. For certain quality parameters, the NIR-spectroscopy is a rapid, cost-effective and sufficiently precise analysis. The demand of the households for electricity and heat varies on a daily basis and is seasonal. Therefore a flexible and demand-oriented biogas production gains more and more importance to cover daily peaks in power demand. One possible approach, in addition to a flexible energy production with further combined heat and power-units (CHP-unit), is to adjust the biogas production from a biogas plant by an accurate feeding process with rapidly digestible substrates. Objective of this research project was the simulation of a flexible and demand-oriented biogas production, which helps to cover the demand for electricity during peak times. A permanent and constant maintenance of the base load generated the optimal load management of the experimental biogas plant and additional impact loads with shredded wheat should simulate the demand peaks. As a result of these high organic loading the biocenosis was overloaded under stress conditions and VFA were accumulated. Goal of this study was the collection of spectral data in order to develop prediction models for VFA concentration, carbonate buffer and other parameters.

2. Material and methods

2.1. Experimental setup

The experiments in the project were performed in a semi-continuously operated horizontal plug-flow digester with a volume of 240 liter at 39 ± 2 °C. A defined biocenosis (total mixed ration and cattle manure) was used as inoculum for the experiment (Dandikas et al., 2015). The digester was equipped with a suitable measurement window (sapphire glass) for spectral analysis of the digester content. The substrate samples were collected via a ball valve located near by the probe. The FT-NIR spectrometer (Matrix-F, Bruker Optics, Ettlingen) detects a spectral range (data in wave number) from 12.800 to 4.000 cm^{-1} (this corresponds to a wavelength range of 800–2.500 nm). Each spectrum consisted of 64 scans and was recorded using an InGaAs

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detector in diffuse reflection. A paddle agitator in the digester provided as far as possible a uniform mixing of the digester content. During experiments, an automatic feeding system developed by the Institute of Agricultural Engineering and Animal Husbandry was used to guarantee a defined and constant substrate feeding of the laboratory biogas digester. Twelve cartridges arranged in a circle with a volume of 350 mL moved the substrate (maize- and grass silage) every 4 h into the digester. The digester was fed with manure once per day, maize silage and grass silage, at the ratio of 40:30:30 in mass%, respectively. An organic loading rate of 2.5 kg oDM/$m^3 * d$ could be achieved as basic load. During the experimental phase, an additional daily single impact load (compared to a flexible feeding) was generated with shredded wheat, resulting in a temporarily increased OLR up to a total of 8 kg oDM/$m^3 * d$. The experimental period took three weeks, where shredded wheat was applied to the digester from Monday to Friday. At weekends the impact loads were omitted, only the basic load was maintained.

2.2. Statistical parameters for assessing model suitability

The recorded spectra and the associated reference data of the chemical analyses of the simultaneously withdrawn substrate samples are required to calibrate the NIR spectrometer. The reference data and the spectra were combined in a statistical evaluation to calculate the NIRS calibration models. The calibration of a model should be based on 60–120 representative samples, which cover the intended concentration range. The quality of the NIRS calibration model was defined by the following statistical parameters (Stockl and Oechsner, 2012). The coefficient of determination (R^2) should be close to one. Low values of the root mean square error of cross validation (RMSECV) indicates a high quality of a NIR-calibration model. The RPD (residual prediction deviation) is the ratio of the standard deviation of the reference values of the validation samples to the standard error of prediction. An RPD value above 3 indicates a good NIR-calibration and can be used for a rough screening of particular samples. RPD-values of 3–5 are "satisfactory", 5–10 are declared as "good to very good" and an RPD-value above 10 proves an "excellent" calibration model (Williams and Sobering, 1993). A partial least squares (PLS) regression was performed using the software package Opus (Version 7.0, Bruker Optics, Ettlingen). For all specific parameters, each calibration was automatically tested by a leave-one-out-full-cross-validation (Martens and Martens, 2001). The full cross-validation is especially suitable for reflecting possible estimation errors and is represented by the RMSECV. The average error of applying the generated models to the left-out spectra gives an almost unbiased estimate of the true error of the classification model (West-Nielsen et al., 2005). An optimisation method in Opus tested systematically various spectral regions and pretreatments, to determine the best combination for each parameter (Krapf et al., 2013b). The used pretreatments consist of standard normal variate (SNV) transformation, multiple scatter correction (MSC) and evaluation of the first derivative. The calibration models for propionic acid and the ratio of the volatile fatty acids to the total inorganic carbon are based on the first derivative, the volatile fatty acids titrated on MSC, the acetic acid on SNV and the total inorganic carbon was created with combined pretreatments of the first derivative and standard normal variate.

3. Results and discussion

The total experiment was divided into two independent, successive experimental sections with equal experimental setup. The results of the first section were needed to develop the calibration models, whereby an already existing comprehensive spectral and laboratory analysis data base (more than 500 samples out of preliminary experiments, Krapf et al., 2013a,b) was available (Table 1, Figs. 1–4 left sides). However, from the parameters of the acid range many samples were omitted, because the concentrations were close to zero. The preliminary experiments were carried out in three different digesters, where one of them was the same as in the experiment described in this study. The statistical quality parameters of the calibration models are summarized (Table 1). The coefficients of determination ranged from 0.97 to 0.85, for the total inorganic carbon and the ratio of the volatile fatty acid to the total inorganic carbon, respectively. In the literature VFA prediction models in terms of R^2 values (> 0.8) were comparably well (Holm-Nielsen et al., 2007; Jacobi et al., 2009). For a better classification the RMSECV have to refer to the concentration range of the respective parameter (RMSECV in %). The carbonate buffer (TIC) showed a low error of cross-validation (4.1%) referring to the concentration range. The highest error values were recorded for propionic and acetic acid, 7.7% and 7.5%, respectively. The RPD values have good statistical characteristics with 4.0 for the volatile fatty acid in accordance to Lomborg et al., 2009 (RPD between 2.8 and 3.6) and 6.0 for the carbonate buffer, and thus the high quality of the calibration models were confirmed. In the second experimental phase, the calibration models were used to predict the 5 parameters during the experimental period of three weeks (Table 1, Figs. 1–4 right sides). The black horizontal line, only shown in the first graphic, defines the maximum concentration used for the model calibration (Fig. 1 right side). It is not possible to extrapolate, that means that an extension does not work for the application to samples with higher concentrations than those included in the calibration model. The value of the R^2 resulted from the individual laboratory values in combination with the values of 30 min estimation by NIRS at the time of the sampling. An exclusion of the samples and spectral data above 6 g/kg propionic acid improved the R^2 from 0.78 to 0.85. The gap in the data around the 25/6/2015 is due to a change in substrate. In the time period before 25/6/2015 the biocenosis of the digester was extremely stressed, with high concentrations of acids (e.g. butyric and valeric acid) not included in the calibration model. Therefore half of the digestate was exchanged with manure to stabilize the biocenosis. The estimation of acetic acid (graphically not shown, similar to VFA) and the volatile fatty acid titrated is quite unsatisfactory in this period. In the estimation of volatile fatty acid titrated the increase of total acid with a simultaneous decrease of the carbonate buffer was precisely visualized (Figs. 3, 4 right side). The correlation between the estimated and measured values was high with a correlation coefficient of 0.96 (VFA) and 0.93 (TIC). The suspension of the impact load during the weekend, with the recovery of the biocenosis was clearly visible in the period around 5/7/2015. The ratio of the VFA to the carbonate buffer showed in the calibration model an unsatisfactory $R^2 = 0.85$ and RPD-value of 3.0. Despite these insufficient quality parameters of the calibration model mostly the estimation was very good with an R^2 of 0.96. In the period around the 5/7/2015 the estimation by NIRS compared to the reference values of the laboratory didn't fit so well, but the change of tendency was clearly visible.

Table 1
Statistical parameters to evaluate the quality of the different NIRS calibration models.

	[1]R^2	[2]n	[3]RMSECV	[4]RPD	[5]Range	[6]RMSECV in%
Propionic acid	0.91	162	0.43	3.4	0.2–11.4	7.7
Acetic acid	0.91	159	0.84	3.3	0.2–5.8	7.5
Volatile fatty $acid_{titrated}$ (VFA)	0.94	172	0.96	4.0	0.5–17.3	5.7
Total inorganic carbon (TIC)	0.97	167	0.71	6.0	3.7–20.7	4.1
VFA/TIC	0.85	515	0.27	3.0	0.1–4.3	6.5

[1]R^2 = coefficient of determination, [2]n = number of samples, [3]RMSECV [$g * L^{-1}$] = root mean square error of cross validation, [4]RPD = ratio of standard deviation and standard error of prediction, [5]Range [$g * L^{-1}$] = data spread, [6]RMSECV in % = root mean square error referred to the Range.