

Jacobi, Hans Fabian; Moschner, Christian Rainer and Hartung, Eberhard

NIRS-based monitoring of important parameters of the biogas process

Major advances in the area of technical solutions for the optimal management of biogas plants have been achieved during the last few years. Despite this fact until today no technology for the online-supervision of the anaerobic process had been tested under long term conditions of practice. The aim of this study was the examination of the employment of near-infrared spectroscopy (NIRS) at a full-scale biogas plant. Therefore a plant operating since 2006 was equipped with NIRS-metrology. NIR-spectra were recorded and regular sampling for laboratory analysis of selected contents took place for 500 days. Based on the acquired data NIRS-calibrations for volatile fatty acids, acetic and propionic acid were generated. These calibrations were applied to the spectra which had been recorded continuously over the whole period of investigation. Hereby it was possible to reproduce the course of the different acids concentrations and therefore the basic potential of the employment of NIRS-technology on biogas plants could be evaluated.

Keywords

Anaerobic digestion, biogas, near infrared spectroscopy, process monitoring, volatile fatty acids

Abstract

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■ To date the optimal supervision of the biogas process is more essential than ever. Despite this fact, supervision is almost exclusively conducted non-continuously and usually not in-time by wet chemical analysis – mainly of the fatty acids. In the literature few investigations can be found dealing with online-supervision of the volatile fatty acids as leading parameters. These include their gas-chromatographical detection from the gas phase or from filtrated slurry as well as laboratory trials regarding the application of NIRS ([1]-[7]).

Material and Methods

Biogas plant The examined biogas plant consists of one primary (F) and two secondary fermenters (N1, N2) and a repository. It is operated at thermophilic conditions (F, N1) and is fed with maize silage as the sole substrate. During the period of investigation the average feeding rates were in the ranges of 4.0-5.5 and 0.9-1.6 kg oTS / (m³*d) for F and N1, respectively. On average daily about 6% of the F-volume were recirculated from N1 to F. During feeding of the plant slurry is pumped alongside a silage-input-system and thus silage is carried into the fermenter together with the slurry stream.

Near infrared spectroscopy. A NIR-measuring head was in-

serted into an upstream section of the central pipe system and was connected to a Polytec 1720 NIR-spectrometer (Polytec, Waldbronn, Germany; range: 845-1650 nm). The measuring head observed the slurry through a sapphire window. A tungsten-halogen bulb was integrated into the measuring head and its light was focused onto a $\sim 2,5 \text{ cm}^2$ -measurement spot of the passing slurry. Reflected light was focused onto a fiber optic cable and from there led to the spectrometer. Slurry was pumped at six (F) and twelve (N1) feedings during which $\sim 11 \%$ of each fermenters volume passed the measuring head every day. Single spectra were recorded and averaged during 10 s of every minute. Thereby daily $\sim 60 \text{ m}^3$ of slurry were observed spectroscopically, which for a penetration depth of 1 mm equals a daily sampling volume of 60 l. The entire optical setup was referenced weekly using a standard reflection sample (aluminum oxide ceramic, obtained from Polytec, Waldbronn, Germany).

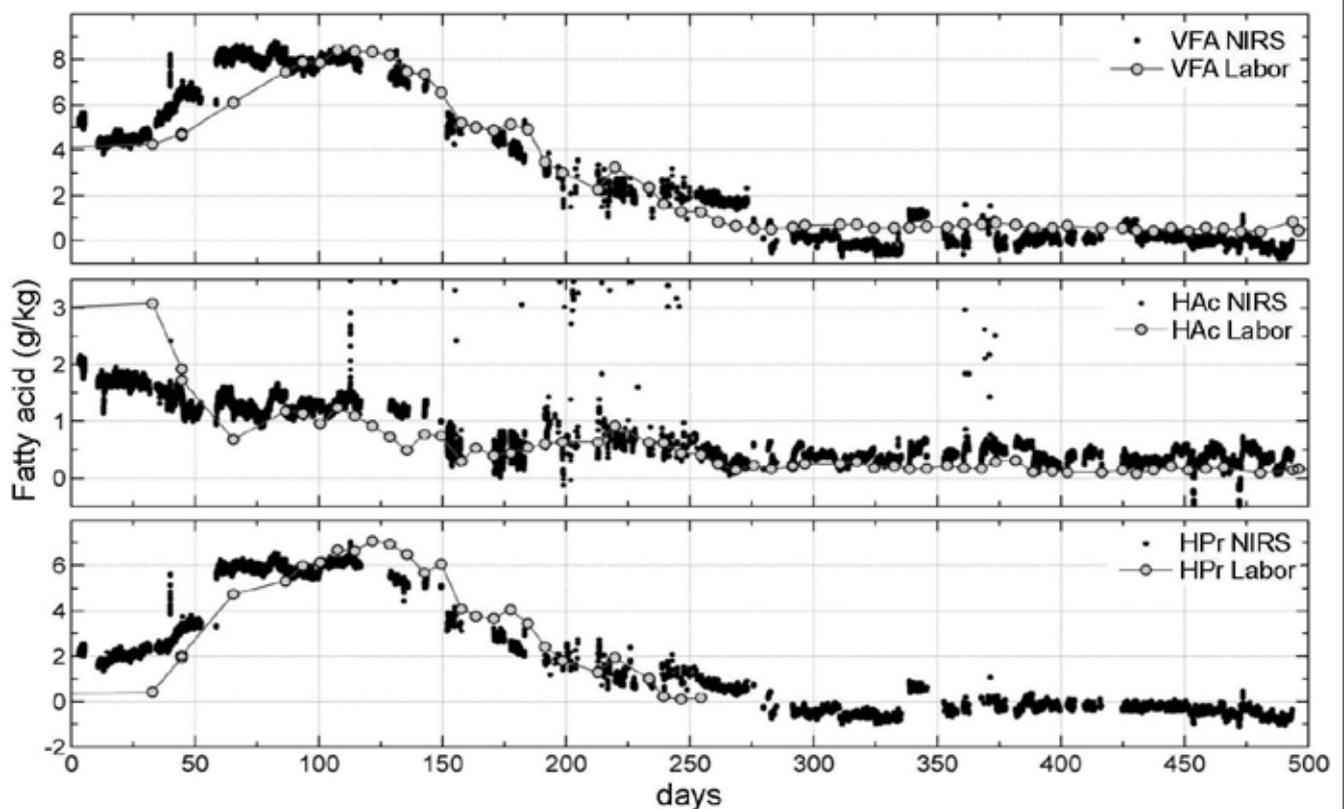
Reference sampling and chemical analysis. During the whole period of investigation weekly samples were taken from F and N1. An accredited laboratory analyzed the samples by titration and ion- or gas-chromatography, respectively, for vo-

latile fatty acids (VFA) as well as acetic (HAc) and propionic acid (HPr) down to a detection limit of 0.05 g/kg of fresh matter (FM).

Data acquisition. The control unit of the biogas plant collects all information about destination, time and duration of each feeding event as well as the pumped slurry volume. Together with the values from the reference sample analysis and the NIR-spectra these data were transferred into the PSQL-database developed by TENIRS GmbH, Kiel. The data were thus available for specific extraction for calibration development and time-series calculation (see below).

Multivariate data analysis. Analysis of chemical and spectroscopic data for the calculation of NIRS-models was performed with The Unscrambler® software (version 9.6, Camo, Norway). For this purpose all spectra recorded within 90 s before and 180 s after a sampling event were extracted, averaged and assigned to the corresponding sample. Partial least square regression (PLS) [8] was applied for calibration development and validated by full cross validation. Propionic acid values below the detection limit were interpreted as 0 g/kg and included in

Fig. 1



Ex-post NIRS-timeseries of volatile fatty acids; FOS = volatile fatty acids, HAc = acetic acid, HPr = propionic acid; large circles = values of laboratory reference analysis, small dots = calculated concentrations from NIRS spectra; laboratory values HPr after day 250 below detection limit (0,05 g/kg liquid manure)

the calibration.

Time-series. All spectra for N1 that were collected within pumping intervals were extracted from the database. Ex-post time-series were calculated by applying the developed NIRS-calibrations onto the extracted spectra. An additional filter using the deviation-value supplied by the software was applied onto the resulting concentration values. Values with a deviation exceeding a threshold were eliminated from the set. Deviation thresholds were chosen from evaluation of the data and set at 2 g/kg for

VFA and HPr and 1.6 g/kg for HAC. The deviation is similar to the confidence interval and is calculated from characteristics of the actual spectrum and the applied calibration model. It allows an identification of outliers and invalid spectra ([8], [9]).

Results and Discussion

Process behavior. The period of investigation lasted for 500 days. During this period the plant underwent different process stages with differing acid levels. Initially very high values of HPr, partially risen values of HAC and accompanying high values of VFA were observed. Concentrations decreased during the trial and leveled off at stable low values. Thereby the values for HPr very frequently fell below the detection limit (0,05g/kg FM) (**Fig. 1**).

Calibration results (NIRS). The PLS-models calculated for VFA, HAC and HPr were based on spectra and reference analysis values of F and N1. Validation results of the models achieved in this investigation are presented together with data from comparable studies in Table 1. The validation results of the VFA calibration are comparable to results from other studies. While the HPr-model yields similar results, the HAC-model is not as reliable, compared to the published data (Table 1). Judging these results it has to be taken into consideration that this study was - opposing to all other studies - carried out under in situ conditions. Therefore the experimental conditions - especially regarding the temperatures of the room, the slurry and the measuring heads - were not kept constant during the whole period. This potentially had a (negative) impact on the accuracy of the determined calibrations, because NIRS is very sensitive to changes in temperature [9].

NIRS-based ex-post time-series. The developed calibration models were applied to the continuously recorded NIR-spectra in order to evaluate their application suitability. Thus from each spectrum a concentration value for each parameter (VFA, HAC, HPr) and point of time was calculated. For N1 the resulting concentration time-series, consisting of about 50.000 values, are displayed in **Fig. 1** together with the corresponding laboratory values from the reference samples.

The NIRS-based values basically follow the course of the

Table 1

Validation results of NIRS-calibrations (PLS, full cross validation) in comparison with data from literature.

	source	r ²	RMSEP	n*	range	RPD*
Volatile fatty acids	own results	0,92	0,94	140	0,31-10,20	3,52
	[4],[7]	0,84-0,90	0,20-1,59	45-80	0,05-22,30	3,1-4,3
Acetic acid	own results	0,61	0,36	138	0,07-3,08	1,60
	[4],[6],[7]	0,77-0,89	0,20-0,91	42-80	0,04-13	3,1
Propionic acid	own results	0,89	0,85	141	0,01-7,47	2,99
	[4],[5],[6],[7]	0,76-0,91	0,21	43-80	0,06-6,2	3,4

* if stated/calculable; r² = coefficient of determination; RMSEP = root mean square error of prediction; RPD = SD/RMSEP; SD = standard deviation of laboratory results; RMSEP and range in g/kg fresh matter

reference samples' concentrations. Only the values of the first 50 days for HAC are an exception (**Fig. 1**). However, the matching of predicted and measured concentrations starts together with the change of the N1-reactor temperature from 38°C to 50°C. This resulted in essential changes of the spectra and the measuring head's temperature. The temperature from then on remained at 50°C.

The courses of HPr and VFA are very similar, because HPr is a major component of VFA. Within the first 50 days the deviations between measured and predicted values for HPr and VFA are much smaller or even negligible compared to deviations from HAC. This is probably to be ascribed to the fact that besides the special measuring conditions in the case of HAC such high concentrations as during the initial period did not occur again later on. Therefore this concentration range is insufficiently represented in the calibration. Comparable data from another set recorded without these special circumstances did not show this phenomenon [10].

For technical reasons several measurement periods only yielded invalid or no spectra. Invalid spectra are caused e.g. when the pipe with the measurement equipment was not integrated into the pumping circuit during feeding and therefore empty or when the diode array cooling of the spectrometer failed. This results in gaps in the data. Furthermore frequently steps in the level of the predicted values occur together with reference values. These are to be ascribed to sampling events during which the system was gauged. These adjustments are mainly necessary to compensate ageing and the accompanying change of performance of the tungsten-halogen bulb. In the data this partially is represented as an abrupt change, because the ageing process of the past period is suddenly corrected. However, this also means that this effect can be compensated by automatic and more frequent referencing.

Conclusions and Outlook

In the presented investigation NIRS-calibrations were developed directly at a biogas plant and therefore under in situ conditions for the first time. In principle it could be demonstrated that utilizing NIRS it is possible to follow the concentration changes of

the investigated parameters with high chronological resolution. Although the generated data currently do not show the necessary accuracy for practical implementation, they undoubtedly reflect the high potential this versatile technique is bearing. Currently efforts are made in order to improve the measuring accuracy of the NIRS-system by automatic and very frequent referencing.

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Authors

Dipl. biol. H. Fabian Jacobi is PhD student, **Dr. Christian R. Moschner** is scientific coworker and assistant director and **Prof. Dr. Eberhard Hartung** is director of the Institute for Agricultural Engineering at the Christian-Albrechts-Universität zu Kiel, Max-Eyth-Str. 6, 24118 Kiel.
E-Mail: fjacobi@ilv.uni-kiel.de

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