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Online measurements of volatile fatty acids in renewable raw material biogas plants by NIRS

An online measurement system based on near-infrared-reflectance spectroscopy shall give information on substrate condition or the fermentation progress. Hereby, NIR sensors are calibrated according to substrate-specific parameters (volatile fatty acids, like acetic acid and propionic acid) through which the process stability in the digester can be monitored online. An appropriate positioning of the NIR-sensor is very important. Two sensors were directly installed in a 400 L digester, whereas a third sensor was placed in a bypass. For calibration of the measurement system acetate were applied to the digester to increase the acidity artificially. The developed calibration models with "support vector regression" shows the excellence of the bypass. The statistical value of the RPD (ratio of standard deviation and standard error of prediction) for acetic acid could be increased from 1.8–2.2 in the digester to 3.3 in the bypass system.

Keywords

NIRS, biogas, volatile fatty acids, multivariate data analysis, support vector regression

Abstract

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Near-infrared-reflectance spectroscopy (NIRS) is meantime applied in many different areas of agriculture and represents a rapid and non-destructive method of determining substrate-specific characteristics of samples utilising the physical-optical characteristics of the substrate. The amount of absorption, depending on the reflection of the substrate-specific contents, allows direct conclusions on the concentration of the investigated parameter. A NIRS calculation model is achieved over a statistical analysis calculated from laboratory results in combination with parallel-recorded spectra (**figure 1**).

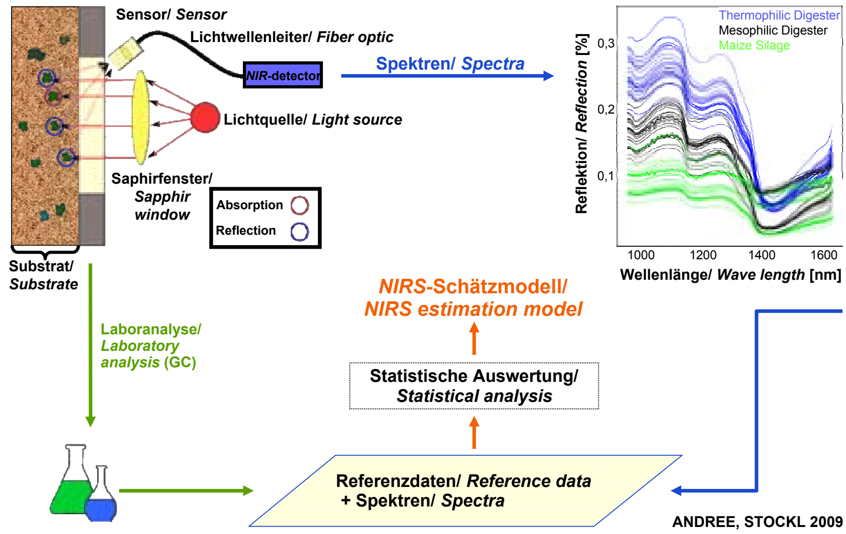
For this, content of organic fatty acids such as acetic acid, butyric acid, propionic acid and isopropionic acid, as well as valeric and isovaleric acids that correlate with the recorded spectra, are determined. With the help of a multivariate data analysis via "support vector regression" [1] calibration models are developed and tested for the various parameters. The best models were to be later used for the estimation of volatile fatty acid concentrations in unidentified samples based on the online spectra. Model reliability and precision decide upon the quality of the estimates. To achieve a good calibration model a high variation in the spectra has to be achieved. This poses the question to what extent the position of the near-infrared sensor, and the flow speed of the substrate in front of the sensor, influences the quality of the recorded spectra and the associated calibration results.

Materials and method

To determine the most suitable position for the sensor in the digester, three NIR sensors were fitted simultaneously in a thermophilic 400 litre experimental biogas digester. One sensor was separately positioned in a bypass pipeline. To achieve a uniform flow of fermentation substrate towards this sensor it was positioned in a bend on the pipeline. Because rising accumulations of gas bubbles in the pipeline system could distort the NIR sensor image, the substrate was pumped upwards in the direction of the sensor. With the eccentric screw pump moving approx. 800 l/hour this meant the total digester contents flowed twice per hour past the sensor, permitting numerous varying spectra to be recorded at this point.

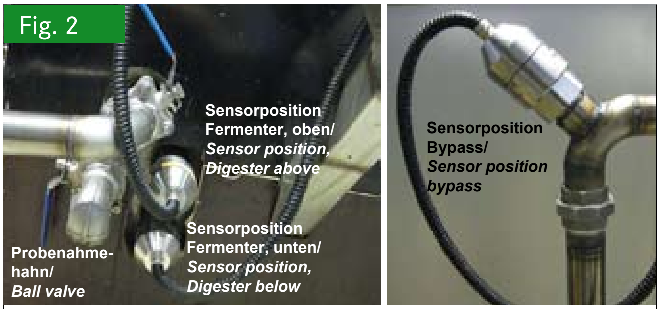
Two further sensors were positioned at the front of the digester in direct contact with the digester substrate (**figure 2**). The substrate samples were taken via sampling-tap positioned beside the front-mounted sensors. In a preliminary trial (not included here) it could be shown that the sampling location can be selected with some flexibility in this size of digester because the agitator within the digester enables an optimum homologation of the entire contents.

Fig. 1



Development of a NIRS calibration via statistical analysis with reference data and associated reflection spectra

Fig. 2



NIR sensor in a bypass, two other sensors in front of the same digester

A horizontal agitator is used for the mixing of the contents of the 400 l fermentation chamber. This is driven by an electric motor. The agitator itself comprises a number of steel rods welded onto a central shaft. A control switch allows the mixing rpm to be selected and also varied.

In the investigation depicted here the aim was to show the extent of influence on calibration result through adjustments to agitator speed compared with the influence of pumped flow through the bypass. The best position for the near-infrared-sensor can then be calculated from the results.

Experimental procedure

Into the 400 l experimental biogas digester was poured 4.8 kg (98 %) sodium acetate to achieve a target concentration of 12 g/kg acetic acid in the fermentation substrate. The fermentative degradation of the acid was documented over several days via hourly to three-hourly sampling with simultaneous recording of the spectra. During the investigation spectra were recorded in the bypass and at both sensors in front of the digester at first with running pump. At the same time the agitator ran at 30 rpm. Then the pump was switched off and spectra were further recorded at the two front-positioned sensors with the agitator still running at 30 rpm. Finally, agitator speed was increased to 60 rpm and once again the spectra recorded at the two front sensors. The recording of the spectra took place simultaneously at all three sensors over a period of three minutes. During this time it was possible to record into a databank 300 individual spectra per minute and these in turn were averaged into 6 spectra per minute. The following evaluation of the spectral data and the associated analytic regression took place with “support vector regression” (svr) on a Linux-based computer.

Results

Seven separate calibrations resulted from this experiment. These were created with “support vector machine” (svm), here explained and demonstrated in the form of a graph in **figure 3**. “Support vector machine” means machine learning, a mathematical method for identifying complex patterns. For evaluation of the results the RPD statistical figure according to Williams und Sobering [3] (**figure 4**) was applied.

The RPD presents the quotients of the laboratory value standard deviation against the standard calibration error (of the characteristic). It describes the performance of different estimating functions independently of the basic measurements. It is without unity, as is the coefficient of determination R^2, and thereby comparable over several characteristics.

The larger the RPD, the more suitable is a calibration for the forecast of the respective samples. In **figure 3** the results from the described experiments are evaluated according to various statistical figures.

The results of the seven calibrations in **figure 3** clearly show that only the calibration model from the data collected in the bypass achieves a satisfactory RPD value of 3.3. Also notable is that the operating pump appears to have had an influence on the calibration of both measurement heads at the front of the digester. With an RPD of 2.2 and 2.3 and a Range/SEP of 9

Fig. 3

	Rührwerksleistung U/ min/ *Agitator speed rpm*	Sensorposition Fermenter/ *Sensor position digester*	n	Outlier	RMSEP Vorhersagefehler/ *Prediction error*	RMSEC Modellfehler/ *Model error*	Range/ SEP Datenspanne/ Vorhersagefehler/ *Data range/ Prediction error*	RPD Standardabweichung/ Vorhersagefehler/ *Standard error/ Prediction error*
Pumpe/ *Pump*		Bypass	48	5	0.7	0.2	12	3.3
Pumpe/ *Pump*	30	Oben/ *Above* Unten/ *Below*	49	5	1.2	0.2	9	2.2
Pumpe/ *Pump*	30	Oben/ *Above* Unten/ *Below*	47	3	1.1	0.2	9	2.3
Rührwek/ *Agitator*	30	Oben/ *Above* Unten/ *Below*	47	5	1.4	0.2	7	1.8
Rührwek/ *Agitator*	30	Oben/ *Above* Unten/ *Below*	48	6	1.3	0.2	7	1.9
Rührwek/ *Agitator*	60	Oben/ *Above* Unten/ *Below*	49	6	1.2	0.2	7	2.1
Rührwek/ *Agitator*	60	Oben/ *Above* Unten/ *Below*	47	6	1.2	0.2	7	2.1

Results of seven calibration models, bypass compared with agitator (30 and 60 rpm)

Fig. 4

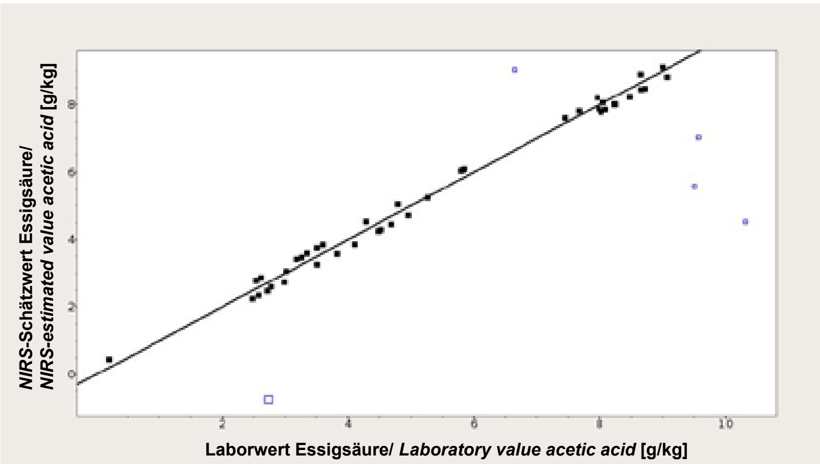
0 – 2	Nicht ausreichend/ *Not sufficient* – –
2 – 3	Für eine Orientierung teilweise geeignet/ *Partly suitable for an orientation (Screening)* –
3 – 5	Zufriedenstellend/ *Satisfactory* +
5 – 10	Gut bis sehr gut/ *Good to very good* ++
> 10	Exzellent/ *Excellent* +++

RPD forecast performance – classification according to quality

this result is better than the comparative value with switched-off pump. The increased agitator speed of 60 rpm, reflected in the RPD statistical figures of 2.1 and Range/SEP of 1.2 cannot compete with the results from the agitator at 30 rpm with pump operating. The calibration with the pump switched-off and the agitator running at only 30 rpm produces the worst results with an RPD of 1.8 and 1.9 and Range/SEP of 1.4 or 1.3. Despite a slight improvement of the statistical data with 60 rpm, only the calibration in the bypass with its throughflow of liquid, and with suitable unidentified samples, is easy to calculate.

Once again the good calibration model of the analytical reference data and the NIRS forecast value of the bypass with svr can be seen in **figure 5**.

Fig. 5



48 samples, 5 outlier, RMSEP 0,743703, RMSEC 0,224918, Range/SEP 11,913, RPD 3,304

Best calibration model: statistical evaluation of the data, bypass with pumping and agitator with 30 rpm calculated with svr

Conclusions

The good calibration model result could be improved through a higher number of samples. A robust calibration should be based on a data amount of at least 100 individual data. In the above trial the data amount comprised n = 47 to n = 49 samples. The forecast error (RMSEP) would probably reduce in line with an increase in the number of samples. Based on these results, further trials were conducted and calibration models developed whereby the sensor position in the bypass was retained. In order to cover further additional variation possibilities, two 400 l digesters, each with a sensor in the bypass, were operated simultaneously at different temperatures. Thereby, one digester ran in the mesophilic temperature range while the other, constructionally identical, digester was operated in the thermophilic range. The results of this experiment (not presented here) show definitely that very good calibration models could be developed under both temperature ranges for acetic acid, propionic acid and acetic acid equivalent. As a result, the statistical errors (RMSEP and RMSEC) were able to be drastically reduced while, at the same time, the values for Range/SEP and the RPD rose by 50–60 % in comparison with the best results of the trials here described [4]. From this it can be concluded that the acid concentrations in a digester can be recorded online and graphically presented. Process fluctuations can immediately be identified and this allows instabilities in the digester biology to be rapidly and precisely compensated for.

Despite this, it is considered an absolute necessity that further parameters be involved in the calibration such as, e.g., consistency and colour of the fermenting substrate. Still unresolved is the question whether it is possible to correctly estimate the acid contents in the digesters of several biogas plants with a single calibration model. It must also be clarified whether the models developed here from an artificial increase in acids through hydrolysis can be regarded as equal to those developed on a natural increase in acids. This question will be pursued in further work.

Literature

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