On-line NIR monitoring during anaerobic treatment of municipal solid waste

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Abstract
An anaerobic digester (8 l) was fed with the organic fraction of municipal solid waste and monitored intermittently for two years with on-line near-infrared (NIR) spectroscopy and traditional chemical parameters analysed off-line. The dynamics that occurred due to changes in substrate composition (changed C:N ratio) and changes in operating conditions (overloading) could be followed using principal component analysis of the obtained NIR-spectra. In addition, process disturbances such as failed stirring and increased foaming were readily detected by the NIR-spectra. Using PLS regression the propionate concentration could be predicted in the range 0.1–3.6 g/l, RMSEP 0.53 g/l with slope 0.74 and correlation coefficient 0.85. The response on changes in the digester fluid was reproducible and could be detected within 2.5 minutes, which can be considered as real-time monitoring.

Keywords
Biogas; early warning; MSW; NIR; on-line; PCA; PLS; propionate

Background
As the implementation of anaerobic digestion has increased and the technology is becoming an important energy supplier, a greater demand for reliable biogas delivery is expected. This is especially true when the gas is used as vehicle fuel, since a distribution stop for an extended time can be very expensive. If an anaerobic digester process is disturbed it can be a question of months before the process is back to normal production of high quality biogas.

A good indicator of process failure should be correlated to the microbiological status of the process, function in real-time and it should be possible to monitor it with a reliable, robust and “easy-to-handle” instrument. Volatile fatty acids have been proposed as indicator substances (Ahring et al., 1995). Propionate seems to be a viable indicator for imbalances in the process since it readily forms in connection with process imbalances (Kaspar and Wuhrmann, 1978).

It is important to handle events such as organic overloads or toxic shocks in biogas processes as early as possible and more rapid detection techniques are needed. Near-infrared spectroscopy (NIR) is one such non-invasive analytical technique (Benson, 1996). The low reflectivity and absorptivity in the NIR-range makes it possible to analyse samples that are strongly light scattering, such as opaque liquids and slurries. In previous studies we have demonstrated the feasibility of the NIR technology (Nordberg et al., 2000; Hansson et al., 2001). This paper summarises the experience obtained during two years of operation of a laboratory-scale digester fed with municipal solid waste (MSW).

Materials and methods
Process. A mesophilic (37°C) continuously stirred tank reactor (CSTR) with 8 l active volume and 10 l total volume, was operated with a substrate consisting of the organic fraction of source sorted MSW from the municipality of Uppsala (Nordberg et al., 1999). During normal operating conditions the organic loading rate was 3 g VS l⁻¹ d⁻¹ and the hydraulic retention time was 20 days (fed once a day). The waste used during the first year (C:N ratio of 17:1) was minced and diluted with water to a VS concentration of 6%. In the second year,
protein (egg albumin) was added to obtain a lower C:N ratio (15:1) and to simulate a change in substrate composition.

Substrate overloads. In order to create system imbalances the process was overfed in a series of overloads dispersed over the years. The dynamics of the process were closely followed during the overloads and for one week after returning to normal feeding conditions by using on-line NIR and sampling of sludge and headspace for traditional analyses. The first experiment (of the first year) was administered as one day of no feeding followed by two days with a four-fold feed of substrate, thus increasing OLR and shortening HRT. The procedure is more extensively described in Hansson et al. (2001). During the second year the OLR was three-fold for two days and then six-fold for three days, with the HRT remaining at 20 d.

NIR. The NIR equipment used was a NIRsystem® 6500 from Foss Tecator with a reflectance probe inserted into the digester. During the experiments, 128 spectra were obtained every 15 min, covering 1,050 channels of 2 nm bandwidth, an action completed in less than 2.5 min. Between experiment runs spectra were obtained more intermittently. In between experiments the interval of 3 hours was used between scans.

Traditional variables. The process was analysed for the concentration of methane and carbon dioxide in the headspace and alkalinity, pH, VFA, NH₄-N and TKN in the slurry, the gas production was also registered.
Data analyses and calculation

The resulting responses in form of the NIR-spectra were studied together with chemical data using chemometric methods (multivariate analysis). The computer tool mainly used was the Camos Unscrambler©. Principal component analysis (PCA) (Wold et al., 1987) was the main tool used to analyse the information in the data matrix. PCA is a linear mathematical method that is used to find patterns in large data matrices. In short, the algorithm treats the data as vectors in a multidimensional space and tries to find the direction (vector) in which the variance is largest. These vectors are called principal component (PC) vectors and are usually numbered (PC1, PC2 . . .) in order of importance. Thereafter the algorithm makes a mathematical base-change to make the chosen PC a base-vector in the multidimensional space. By doing this it reduces the number of vectors needed to describe the variance in the matrix. The resulting PCA matrix can be plotted and studied in order to discover clusters of samples and time dependent changes.

In order to validate and explain some of the signal from the NIR, we used partial least squares (PLS) (Martens and Naes, 1989) for correlation of chemical data with NIR-spectra. PLS is a method of linear regression that, analogous to PCA, finds factors which describe a high amount of variation in both the response data and explains correlation between the response data and the process variables. These factors, often called latent variables (LV), are calculated in order of importance by maximising the covariance between the measured data and the process variables.

The concentration of acetate and propionate is highly covariant and in order to compensate for that the analysis of PLS2 was used. This method takes covariance in calculation, and compensates for some of it by using both the X and Y matrices in the calculation of the values (loadings) of the regression coefficients.

Results and discussion

The spectra sampled during the two years of reactor operation are changing over time due to the dynamics in the digester biomass and in concentration of metabolites caused by the change in operation conditions (Figure 1). The change in substrate composition between year one and two can be seen as a shift in the score position of the PCA-plot (Figure 1, the arrow 3 to 4). Disturbances such as failed stirring and foaming (Figure 1, points 2 and 6) can readily be detected by NIR. The two overload experiments showed the same pattern, i.e. the substrate overloads led to an increase in gas production and a change in the gas composition as well as a decrease of the pH and an increase in the concentration of VFA. The NIR spectra correlated well with these changes and could be used to interpret the change in process performance. The patterns in the PCA can not only be used for early warning of catastrophic events, but also for regulation of feeding. The variation in spectra at normal feed is much less than the variation above, but does clearly show dynamics which could be used for optimization of feeding (Figure 2). This could be used for speeding up the initial startup of reactors.

A PLS-regression of propionate from all experiments was made using 47 wavelengths after a treatment with multiple scatter correction and Norris second derivative. These modifications reduce the light scattering effects of particles and time dependent changes and allow the regression of propionate to be calculated using samples from all experiments. Thus, despite different substrate compositions the spectra could be combined to predict the propionate concentration (Figure 3). This indicates that the model can handle changes in composition of the substrate and digester content.

The wavelengths used (Figure 4) can be grouped in correspondence to their possible source of vibration. There are four major regions in which the correlation coefficients are distinct, a broad window between 800 to 950 nm with many wavelengths but with a low...
value of coefficients, and three narrow windows with larger coefficients around 1,050–1,100, 1,325–1,400 and around 1,700 nm. It can be noted that stray wavelengths were identified up to 1,900 nm, with high values of coefficients (1,175, 1,825, and 1,860–1,862 nm) but their influence on the model is low due to their low number. It can be noted that in the area of 800–950 nm several different types of molecular bonds produce response among which C–H, C–H2 and C–H3 are only a few. The 1,825 and 1,860 nm peaks are interesting as it is close to this range that the carboxylic bonds give response, and a removal of these resulted in a much lower correlation coefficient. At the other peaks and windows the carbon–hydrogen bond is most influential. For example the source to the

Figure 2 Variation in PCA during 24 hours (one feeding). The trajectory from 1 to 2 describes the response in the NIR spectra by one normal feeding, the time frame from equilibrium 1 to 2 is 3.5 h, i.e. the time between two samples is 15 minutes.

Figure 3 A PLS regression of measured concentration of propionate vs. predicted concentration of propionate. The samples are from three different populations and of equivalent size.
1,175 nm peak is probably a C–H\textsubscript{x} bond. The 1,325–1,400 nm window contains information of combination of C–H bonds, i.e. different patterns for different molecule structures, which makes it very interesting for predicting specific substances.

Conclusions

- NIR can be used to predict important parameters, e.g. propionate in processes where changes in sludge composition and general process environment occur.
- NIR can be used to monitor general process status over a long time (years) and changes in substrate.
- The NIR readily indicated process failures such as failed stirring and foaming.
- The combination of information showing general process status and the prediction of important parameters could be used as indicators for control strategies.
- The relative low number of wavelengths used in the prediction model indicated that an instrument using cheap and robust technology could be built.

Acknowledgements

This work has been supported by grants from The Swedish National Energy Administration (project no. P10545-2).

References


