First tests of using an electronic nose to control biogas plant efficiency

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Abstract

The demand for online monitoring and control of biogas process is increasing, since better monitoring and control system can improve process plants stability and economy. A number of parameters,such as gas production, pH, alkalinity, Volatile Fatty Acids (VFA) and H_2, in both the liquid and the gas phase have been suggested as process indicators. For different reasons these indicators do not offer enough information to build a consistent feedback control able to promptly forecast and solve plants working problems. The study proposes the use of unconventional complex sensors as a possible solution to engineer a reliable control system. Tests to analyze the biogas coming from a plant were performed using an electronic nose (Airsense PEN 2, AIRSENSE Analytics GmbH). In particular, a 108 olfactometric fingerprinting reference database obtained by different combination of VFA (acetic, propionic e butyric acids, pure or in solution with water) was initially determined. As a second step, the e-nose was tested to verify a potential difference in the analysis of gases emitted by digested manure. Statistic multivariate analysis confirm that the e-nose can distinguish the manure and digester mixed liquor aromatic emission proving the possibility of using this technology as possible base for a biogas control system.

Introduction

The increasing awareness in renewable energy and *green energy* improved the development of biogas technology, especially farm biogas plants (Holm *et al.*, 2009).

Anaerobic digestion (methane fermentation) is a biotechnological process utilizing biomasses, mainly waste, to produce valuablebiogas.

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Biogas can be produced by mesophilic and termophilic plants. During the methanogenesis process, manure, that can be added with biomasses to adjust the anaerobic digestion, is converted to mono and oligomers (aminoacids, long chain fatty acids, saccharides). The substrate fermentation leads mainly to volatile fatty acids (VFA) and acetic acid followed by gases (H_2, CO_2) which,in the last step, are transformed to methane and CO_2. In the meanwhile, the concentration of simple ions and pH varies.

According to environmental fluctuations and for changes in plant feeding, the anaerobic digestion can be altered by many factors(Ward *et al.*, 2008). For this reason a continuous digestion and plant monitoring is needed to avoid the system instability. A wide number of indicators - as volatile fatty acids evaluation (VFAs), pH, redox potential, biogas production rate, and composition - to monitor the correct anaerobic digestion are used. Among these indicators, VFA and biogas production are widely considered as the two most crucial and direct indicators of the system status (Holm *et al.*, 2008), since the increase in VFA concentration is linked tothe methanogenesis inhibition or organic overloading, and implies a risk of process upset (Hansson *et al.*, 2003).

VFAs detection can be performed through fluorescence spectroscopy (Madsen *et al.*, 2011; Pearce *et al.*, 2003), near-infrared (NIR) spectroscopy (Nicolas *et al.*, 2001), titration (Cimander *et al.*, 2002) and gas chromatography(Liden *et al.*, 1998).

Other techniques, extremely useful to detect the quality of the fermentation process status,are the biogas composition and the production rate (Holm et a, 2007; Holm *et al.*, 2008).

Because of the high complexity of biogas plants and fermentation status the interrelations of the many involved parameters remain unclear. In this frame, a wide adopted technique is to set a threshold values for some individual indicators like pH and VFA. These last ones are considered as the most relevant state variables for process monitoring, and are used to judge thereactor status on the basis of the detected values. However, once the threshold values are reached can only reveal the current reactor status, but it is actually, in most cases, too late for an effective process control.

A promising alternative approach is to use the electronic nose.

The electronic nose is a biologically inspired system composed of an array of non-specific gas sensors (Pearce *et al.*, 2003). When sensor responses are put together, they form a pattern, which is typical of the gas mixture. In this way, the sensors responses produce characteristic patterns for each chemical mixture exposed to the sensor array. By presenting many different chemicals to the sensor array, a patterns database is built up and used to train the pattern recognition system that finally allows recognizing a gas mixture. More extensive information about e-nose technology can be found in Pearce *et al.*, 2003.

The first e-nose technology use was applied to the monitoring of the anaerobic digestion process by Nordberg *et al.* 2000. More recently, the electronic nose was proposed as an innovative online monitoring to autoalert and control the system (Adam *et al.*, 2013).

The main aim of this work was to determine the correct technique to use an e-nose as a *discriminator* in anaerobic digestion status.

Indirectly, this study is leaded to investigate the e-nose technology as a new robust, simple, sensitive tool for biogas production monitoring in order to optimize the process and increase gas yield in small scale agricultural plants.

Materials and methods

In the present study, a preliminary test on the e-nose ("Airsense PEN 2", AIRSENSE Analytics GmbH) abilityto detect the biogas plant overloading was performed, analyzing both gases and manure samples collected in vials.To this purpose:

1. As a first step, the olfactometric fingerprints of VFAs (acetic, propionic and butirric acids) in purity or diluted with deionized water (around 108 combinations) were determined, in order to represent the VFAs produced during the anaerobic digestion process. The "training set" obtained in laboratory conditions represented the olfactometric fingerprints reference database of the biogas contained in the headspace of the minireactors.
2. As a second step, the e-nose was tested to verify a potential difference in theanalysis of gases emitted by digested manure (collected in nalophan bags) and by manure itself, in order to set up the proper experimental conditions.

Odor analysis

Manure samples odor were analyzed by means of a PEN 2 electronic nose (WMA Airsense, Schwerin, Germany). It consists of: a sampling unit; a sensor array made up of ten metal oxide semiconductor (MOS, see Table 1) chemical sensors; a software for data storage and multivariate statistical processing (pattern recognition system). During sampling, two hypodermic needles were inserted through the vial rubber cap into the headspace. The first needle was connected to the sampling unit, while the second was connected to a charcoal filter by means of a polytetrafluoroethylene (PTFE, Teflon) hose. Odor analysis was performed in a two step way: measurement and standby. Electro-valves, controlled by a computer program, guided the air through different circuits depending on the stage of the analysis. Irrespective of the phase, airflow in the measurement chamber was kept constant (Table 2). During the measurement phase, the sampling unit "inhaled" the volatile gases present in the vial headspace and sent them - at a constant rate (6.67 mL s^{-1}) - to the measurement chamber causing changes in sensor's conductance: this phase lasted 80 s, which was enough time for the sensor signals to reach a stable value. When a measurement was completed, a standby phase of 160 s was activated.

Table 1. Sensors of the PEN 2 electronic nose (WMA Airsense, Schwerin, Germany).

Number in array	Sensor-name	General description	Reference
1	W1C	Aromatic compounds	Toluene, 10 ppm
2	W5S	Very sensitive, broad range sensitivity, react on nitrogen oxides, very sensitive with negative signal	NO_2, 1 ppm
3	W3C	Ammonia, used as sensor for aromatic compounds	Benzene, 10 ppm
4	W6S	Mainly hydrogen, selectively (breath gases)	H_2, 100 ppb
5	W5C	Alkanes, aromatic compounds, less polar compounds	Propane, 1 ppm
6	W1S	Sensitive to methane (environment) ca. 10 ppm. Broad range, similar to No. 8	CH_3, 100 ppm
7	W1W	Reacts on sulphur compounds, H_2S 0.1 ppm. Otherwise sensitive to many terpenes and sulphur organic compounds, which are important for smell, limonene, pyrazine	H_2S, 1 ppm
8	W2S	Detects alcohols, partially aromatic compounds, broad range	CO, 100 ppm
9	W2W	Aromatics compounds, sulphur organic compounds	H_2S, 1 ppm
10	W3S	Reacts on high concentrations >100 ppm, sometime very selective (methane)	CH_3, 10 CH_3, 100 ppm

Table 2. Summary of the operating conditions of the e-nose during headspace analysis of manureodor).

Operating condition	
Transport gas	Ambient air (cleaned by charcoal filter)
Sampling rate	10 mL s^{-1}
Amount of sample/vial	6.67 mL s^{-1}
Vial volume	20 mL
Data acquisition	
Headspace generation time	1800s
Sampling time	80 s
Flushing time	160s
Total measurement time	240s

Its purpose was to clean the circuit, and the measurement chamber in particular, in order to return the sensor signals to their baselines. During this phase, clean air entered the circuit, crossing the measurement chamber first and pushing the remaining volatiles out of the circuit itself.

The ten MOS chemical sensors comprising the sensor array operated by transduction of the chemical compounds in the manure aroma into electric signals (Yuwono and Lammers, 2004). At the end of the measurement, these signals were recorded and stored, to be analyzed either by the software of the pattern recognition system or by statistical analysis software. One pattern comprises the signals from all ten sensors taken during the measurement of a sample.

The software records the variations occurring in the ratio (G/G0) between the conductance of each sensor, G (Ω-1), at each second of measurement and the reference, G0 (Ω-1), which is the conductance that the sensor shows when clean charcoal-filtered air enters the measurement chamber.

PCA and discriminant analysis

To increase the knowledge attained from the considered variables and, according to them, try to discriminate as much as differences as possible during the manure monitoring, data were submitted to principal component analysis (PCA) followed by discriminant analysis. PCA is a linear, unsupervised pattern-recognition technique very useful for analyzing, classifying, and reducing the numerical datasets dimensionality in multivariate problems (Todeschini, 1998).

Linear Discriminant Analysis (LDA) (Meloun *et al.*, 1992) is one of the mostly used classification procedure which maximizes the variance between categories and minimizes the variance within categories. The dataset was preparedusing the signals recorded during the measurement last 5 s when sensor signals were stable meaning that an equilibrium between their sensitivity and the sample manurevolatile compounds was achieved. Statistical analysiswascarried out using Scan for Windows.

Results

Building of an olfactometric "training set" based on odor emitted by mixed compounds of acetic, propionic and butirric acid. The choice to analyse VFA was linked to their capacity to be used as good indicators of digestion process: in particular,as shown in the Figure 1, during overloading or stress episodes corresponding to the rise of the partial hydrogen pressure, propionic acid is more instable than acetate and buthirrate (Boe, 2006).

Results of PCA analysis related to the analysis of gases emitted by digested manure (collected in nalophan bags) and by manure itself are reported in the following Figure 2. Items called with numbers are referred to manure samples (G1…G8) and indicates the air sampled in the minireactors headspace.This preliminary trial was conducted to test the e-nose potential performances differences to detect samples as gases emitted by manure during digestion or as manure itself.

The score plot reported in Figure 2 showed that both procedures gave good results, since either gases samples or manure samples resulted suitable in the two identification groups by the e-nose (G1, G4, G5 and G8 were symmetrically in the graphic opposed to 1, 4, 5 and 8 with respect to the second component; G2, G3, G6 andG7 were opposed to 2, 3, 6 and 7 with respect to the first component.

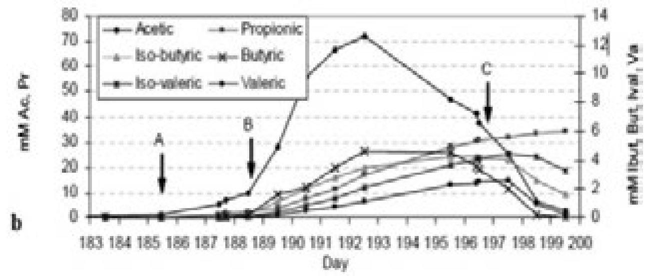

Figure 1. VFA concentration during an organic overloading (in normal conditions before "A", from "A" on adding fiber and rapeseed oil, from point "B" start adding glucose, from point "C" back to normal feed again (from Boe, 2006, *On line monitoring and control of the biogas process*).

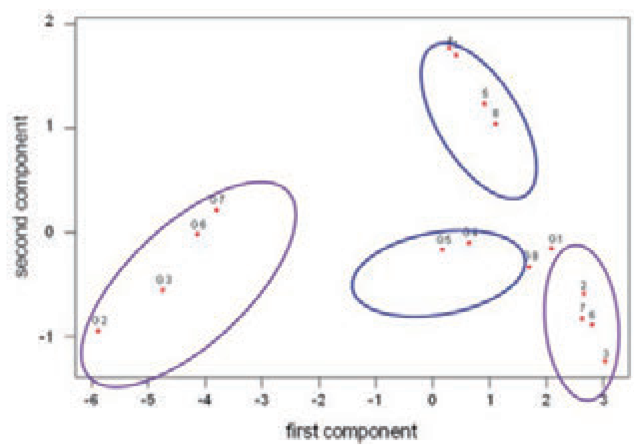

Figure 2. Score plot provided by PCA analysis. Items called with numbers are referred to manure samples (G1…G8) and indicates the air sampled in the minireactors headspace.

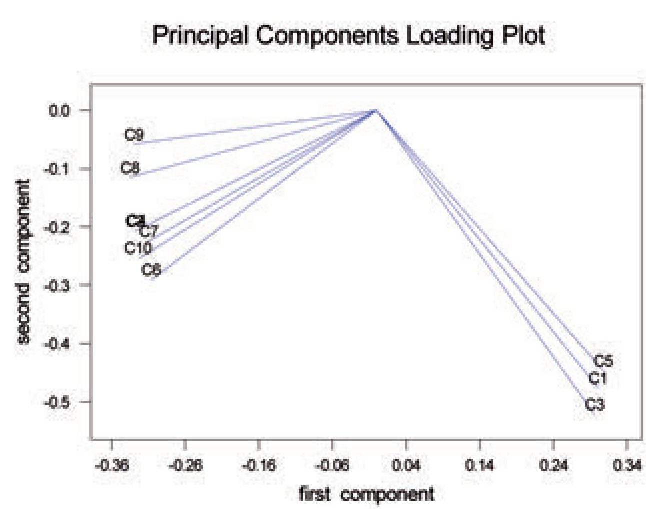

Figure 3. Loading plot provided by PCA analysis.

Conclusions

Electronic nose demonstrated its potential to detect gases emitted by manure during digestion or as manure itself. This procedure can represent a correct technique to monitor, in further studies, the biomethanation process and to discriminate overload situations of anaerobic plants.

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