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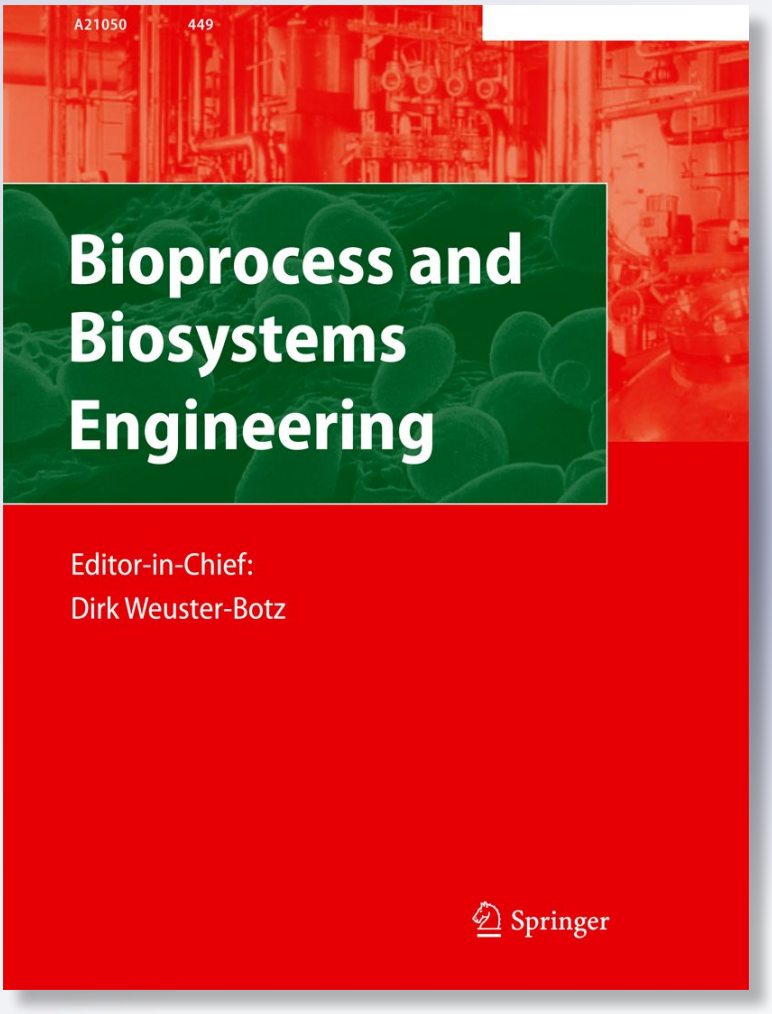

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ORIGINAL PAPER

Evaluation of an electronic nose for the early detection of organic overload of anaerobic digesters

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Abstract This study aimed at analysing the utilization of an electronic nose (e-nose) to serve as a specific monitoring tool for anaerobic digestion process, especially for detecting organic overload. An array of non specific metal oxide semiconductor gas sensors were used to detect process faults due to organic overload events in twelve 1.8-L anaerobic semi-continuous reactors. Three different load strategies were followed: (1) a cautious organic load (1.3 gVS L^{-1} day^{-1}); (2) an increasing load strategy (1.3–5.3 gVS L^{-1} day^{-1}) and (3) a cautious organic load with load pulses of up to 12 gVS L^{-1} day^{-1}. A first monitoring campaign was conducted with three different substrates: sucrose, maize oil and a mix of sucrose/oil during 60 days. The second campaign was run with dry sugar beet pulp for 45 days. Hotelling's T^2 value and upper control limit to a reference set of digesters fed with a cautious OLR (1.3 gVS L^{-1} day^{-1}) was used as indirect state variable of the reactors. Overload situations were identified by the e-nose apparatus with Hotelling's T^2 values at least four times higher in magnitude than the upper control limit of 23.7. These results confirmed that the e-nose technology appeared promising for online detection of process imbalances in the domain of anaerobic digestion.

Keywords Anaerobic digestion · Process monitoring · Electronic nose · Multivariate data analysis · Hotelling's T^2 test

Introduction

The increasing awareness in renewable and local energy resulted in the development of favorable policies to green energy and led to the development of biogas technology, especially farm biogas plants [1]. Anaerobic digestion (AD) is the process of decomposition of organic matter by a microbial consortium in an oxygen-free environment. It can be applied to a wide range of feedstocks to produce biogas [2]. Agricultural biogas plants are small-to-medium scale plants defined by the use of agricultural waste such as animal effluent and energy crops to produce biogas, which is converted into electricity and/or heat. The greatest shortfall in biogas production in the agricultural field is the lack of reliable sensory equipment to monitor key process parameters and appropriate control systems to ensure that the process continually operates at optimal performance [2]. Process imbalances in on-farm biogas plants are usually attributed to organic overloading as well as introduction of toxic substances into the reactor [3]. For this reason, on-farm reactors are not loaded at maximum capacity and it causes a non optimal profit for the biogas plant operator.

Individual volatile fatty acids (VFA) are considered, in the domain of anaerobic digestion, as the most relevant state variables for process monitoring, but their online analysis in anaerobic reactors is not obvious and only few

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systems such as NIR [4–7] or online gas chromatography [8–10] have been tested for their estimation in the anaerobic sludge. For agricultural AD plants, robustness and simplicity must necessarily be part of the process analyzer design [11].

The so-called "electronic nose" (e-nose) or "gas sensor array" is a biologically inspired system composed of an array of non-specific gas sensors [12]. When sensor responses are put together, they form a pattern, which is typical of the gas mixture presented to the array, like a signature [13]. In this way, the responses of the sensors produce patterns characteristic of each chemical mixture exposed to the sensor array. By presenting many different chemicals to the sensor array, a database of patterns 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 [12].

If only few attempts for the monitoring of AD process with e-noses have been made, applications of the e-nose for fermentation monitoring are more numerous. Cimander et al. [14, 15] could successfully monitor both pre cultivations, recombinant-tryptophan producing *Escherichia coli* strain and yoghurt fermentation. For the recombinant *E. coli* precultivation monitoring [14], the e-nose could give an assessment of the quality of the pre-culture and predict the time of phosphate limitation and the tryptophan yield coefficient of the subsequent fed-batch cultivations. Lidén et al. [16] monitored an ethanol batch cultivation with the yeast *Saccharomyces cerevisiae* with an e-nose and could predict the ethanol concentration with a root mean square error of 4.6 %. A real-time expert system with a multi-analyzer including two e-noses developed by Bachinger and Mandenius [17] could help for the control of recombinant *E. coli* cultivations, reducing the batch-to-batch variations and reducing process variability at the real-scale level. Hence, e-nose have been successfully applied both for bioprocess monitoring and quality assessment in the domain of the fermentation processes [18]. Already in 2000, the e-nose technology was applied to the monitoring of the anaerobic digestion process [19]. Indeed, e-nose technology is a potential solution to deliver fast information about reactor status to biogas plant operators as this technology is functional for online process monitoring [12, 20]. An attempt to monitor pure culture of methanogenic bacteria with an e-nose has already been realized by Brandgård et al. [21], which could estimate methanogens growth. Nordberg et al. [19] could also provide a good prediction of methane content in biogas and acetate concentration in the sludge using an e-nose on an 81-L completely stirred reactor exposed to pulse glucose overloads.

The aim of this work was to determine if an e-nose is adequate to identify the process state of anaerobic mini-reactors using a complex microbial consortium such as in real AD plants, and if it could provide an early warning of anaerobic digestion process faults, especially in the case of organic overload, using Hotelling's T^2 test. Influence of AD substrates on the e-nose response is also investigated, as they potentially interfere with the composition of the digesters gas phase.

Materials and methods

Anaerobic digester campaigns

The experiments were conducted with 12 semi-continuous anaerobic reactors of 1.8 L operational capacity (Nalgene heavy duty bottles and filling/venting closures, Nalgene Labware, Rochester, NY, USA) and monitored with a homemade electronic nose system applied directly on the gas phase. Concomitantly, the biogas composition was determined with specific gas sensors.

The digesters were inoculated with an anaerobic sludge [2.48 ± 0.01 % total solids, 53.1 ± 0.2 % volatile solids (VS)] from a waste water treatment plant (Schifflange, Luxembourg). Each digester was filled with 1.5 kg of anaerobic sludge. The digestion was realized in the mesophilic range at 38 °C. Digesters were fed using pickup tubing attached to the filling/venting closure of the bottle by which the substrate was directly introduced into the anaerobic sludge with a 5-mL syringe. Homogenization of the digestate was achieved by manual shaking every day after injecting the substrate. The biogas was collected in gas bags (Tecobag®, Tesseraux GmbH, Bürstadt, Germany) attached to the filling/venting closure.

Two feeding campaigns of the anaerobic semi-continuous digesters were implemented. During the first campaign, the digesters were fed with three categories of substrate over a period of 60 days. The second run was conducted using dry sugar beet pulp as substrate for the complete set of digesters for 45 days.

In the first run, mini-digesters were fed with (1) a sucrose solution (1,000 g L^{-1}); (2) a lipid (commercial maize oil); and, (3) a 1:1 maize oil and sucrose mixture. The digesters were randomly allotted to three organic load strategies: (1) a cautious organic loading rate (OLR) of 1.3 gVS L^{-1} day^{-1}; (2) an increasing load strategy from 1.3 to 5.3 gVS L^{-1} day^{-1} and (3) a cautious organic load as in (1) with a pulse overload of 10 gVS L^{-1} on day 48. Digesters were fed every working day and the feeding was stopped when the sludge acidity reached a pH lower than 6.7 (Fig. 5).

In the second run, the semi-continuous digesters were fed with dry sugar beet pulp pellets (Table 1). The pellets of 7.9 mm diameter were grinded with a mill (Cyclotec™

Table 1 Composition and specifications of the sugar beet pulp pellets

	Dry basis (%)	As fed (%)
Dry matter		90.73
Moisture		9.27
Protein	8.29	7.52
Crude fibre	16.97	15.42
Acid detergent fibre (ADF)	26.68	24.22
Total digestible nutrients (TDN)	69.40	63.04
Fat	1.09	1.00
Ash	7.56	6.86
Nitrogen free extract (NFE)	66.09	60.03
Calcium	1.00	0.91
Phosphorus	0.07	0.06
Potassium	0.56	0.51
Reducing sugars	2.60	2.39
Sucrose	8.96	8.15
Total sugars as invert (TSI)	8.23	7.43

1090, Foss, Denmark) to a 1-mm particle size before injection into the reactors. The feeding strategies were (1) pulse overloads applied on days 10, 15, 18 and 39 with a load of 2.7, 3.6, 5.3 and 6.7 gVS L^{-1} day^{-1}, respectively, (2) increasing load from 1.3 to 3.3 gVS L^{-1} day^{-1} over four distinct periods (Fig. 6) and (3) a cautious OLR of 1.3 gVS L^{-1} day^{-1}. The pH was monitored on one digester per feeding strategy.

Analytical methods

The biogas collected in the bags was analysed every day for methane, carbon dioxide, hydrogen sulphide and carbon monoxide content, using respectively, two infrared gas sensors, CH_4 0–100 % (±1 %) and CO_2 0–100 % (±1 %) (Dynament, UK) and a portable gas analyzer (Dräger X-am 5000, Dräger GmbH, Germany) equipped with electrochemical cells for H_2S (0–200 ppm) and CO (0–2,000 ppm). Methane and carbon dioxide sensors were calibrated each week with 0 and 100 % methane and carbon dioxide. Dräger X-am apparatus was recalibrated every 3 months. The remaining amount of biogas was used for the e-nose analyses. The pH of the anaerobic sludge was measured daily before feeding using colorimetric pH paper for the ranges 6.0–8.1 ± 0.3 and 5.0–7.1 ± 0.3 (Pehanon pH paper, Macherey–Nagel GmbH, Germany).

Monitoring with the e-nose

The home-made e-nose (Fig. 1) was adapted from the systems described in [22–24]. Sensors were selected according to the biogas composition. The e-nose was composed of six commercial metal oxide semiconductor gas sensors showing distinct propensity to react with the complete range of volatiles observed in biogas: methane, ammonia, hydrogen sulphide, hydrogen, alcohols, alkanes, alkenes, ketones, etc. [25, 26]. For these reasons, the following sensors were selected (Figaro Engineering Inc., Osaka, Japan): TGS 821, TGS 822, TGS 825, TGS 826, TGS 842 and TGS 2620 (Table 2). The sensors were placed in a PTFE chamber of an approximated volume of 220 mL. A homogenization chamber that received the biogas:air mixture was placed before the sensor chamber.

Biogas samples were diluted 25 times in air before analysis on the array of sensors. Dilution was required to avoid sensor saturation and to ensure the minimum 2 % oxygen concentration for optimal operation of metal oxide gas sensors [27]. To avoid biogas sample contamination, sample was sent to the gas sensor array by placing the sample bag in a tight pressurized drum at around 0.1 bar. The biogas sample was transferred to the sensor chamber at a flow of 250 NmL min^{-1} (1,013 hPa, 273 K) with 10 NmL min^{-1} biogas, 120 NmL min^{-1} dry air and 120 NmL min^{-1} humidified air to obtain of final mixture of biogas:air of 1:25 with 12 ± 2 % of water vapour at 38 °C. The sensor chamber temperature was maintained at 50 °C to avoid water condensation. Temperature and humidity sensors were placed both in the homogenization chamber and in the sensor chamber to monitor operating conditions. Steady-state response (expressed in µS) of the sensors was used for data processing. The system was purged with clean air for 5 min between each sample run.

Statistical analyses

Methane, hydrogen sulphide, carbon monoxide content and pH were compared by analysis of variance (ANOVA), considering two groups of data: cautious OLR (1.3 gVS L^{-1} day^{-1} and "risky" OLR (>4 gVS L^{-1} day^{-1}). Fisher's least significant difference (LSD) test was used for post hoc test.

Principal component analysis (PCA) was performed on the normalized and auto-scaled data signals obtained with the gas sensor array. The data were first normalized using the following equation [12, 28, 29]:

$$Y_{ij} = \frac{X_{ij}}{\sqrt{\sum_1^j X_{ij}^2}}$$

where X_{ij} is the stable conductance of the sensor j for the sample i, Y_{ij} is the normalized value of the signal for the sensor j and the sample i. Normalized data are then auto scaled first by mean centering and then by dividing by the standard deviation. A first PCA was achieved with the data from the reactors fed with a cautious OLR and aiming at

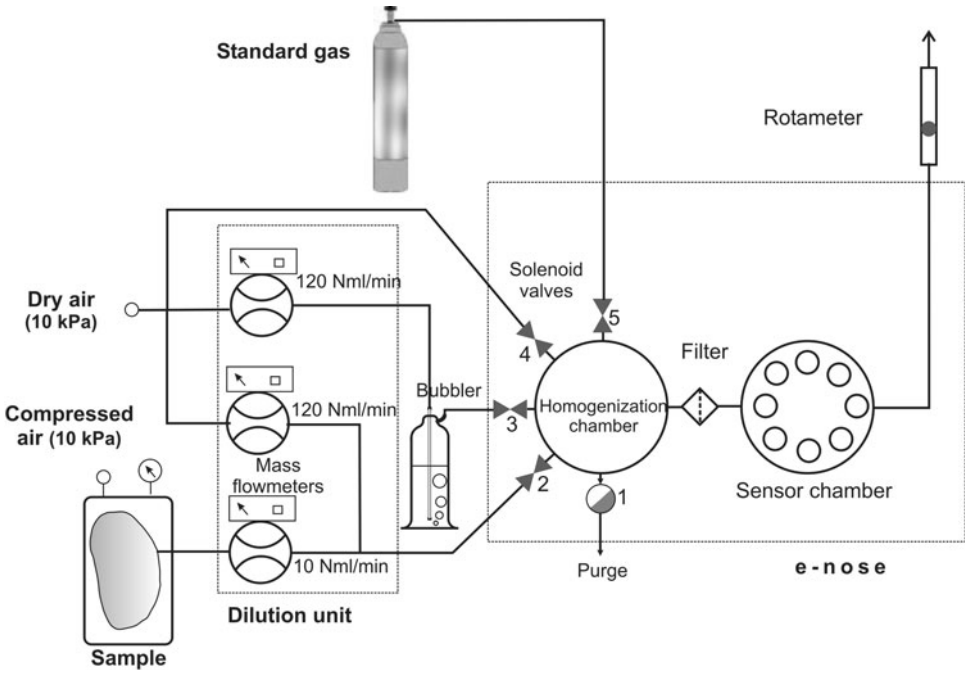

Fig. 1 Schematic representation of the biogas dilution and sensing with an electronic nose device

Table 2 Specifications of the sensors employed in the electronic nose device

Sensor[a]	Sensitivity	Range (ppm)
TGS 821	Hydrogen	50–10,000
TGS 822	Organic solvent vapours	50–5,000
TGS 825	Hydrogen sulphide	5–100
TGS 826	Ammonia	30–300
TGS 842	Methane	500–10,000
TGS 2620	Organic solvent vapours	50–5,000

[a] Figaro Engineering Inc., Osaka, Japan

assessing the influence of the substrate on the e-nose response. A second PCA was computed on the complete data set to assess the capability of the e-nose to identify early signs of process imbalances. PCA analyses and ANOVA were performed using Statistica 10® (Statsoft, France).

To ascertain the usefulness of the Hotelling's T^2 test to characterize the process status, the following procedure was followed: The e-nose response data (conductance of the six gas sensors) from four randomly selected digesters of cautious OLR (one per feeding substrate) were selected as training set (considered as stable process), and the means and variance–covariance matrix were calculated and used to determine the median and upper control limit (UCL) of the T^2 value. The training data set was first cleaned from the outliers by removing the one observation with a T^2 value above the control limit. Then, the T^2 values and the upper control limit were computed for each digester with Statistica 10® (Statsoft, France) using the means and variance–covariance matrix of the training data set cleared from outliers. Information relative to the Hotelling's T^2 test for process monitoring can be found in [30].

Results

Influence of the OLR on the gas phase composition

Means comparison with LSD test of the gas composition is shown on Fig. 2. For the cautious OLR, the pH did not show a significant difference between the substrates. The pH of the cautious OLR is significantly different from the >4 gVS L^{-1} day^{-1} OLR with oil and the sucrose:oil mixture, but not with the risky OLR using sucrose.

We observed significant differences between the digesters of cautious OLR, especially in methane and hydrogen sulphide content in the produced biogas. When comparing the two levels of OLR 1.3 versus >4 gVS L^{-1} day^{-1}, the biogas concentration in methane was the highest for maize oil, around 68 %, and it was not significantly different for the two levels of OLR. The sucrose:oil mixture showed intermediate concentration in methane but with higher concentration for the 1.3 gVS L^{-1} day^{-1} than for >4 gVS L^{-1} day^{-1} OLR. The sucrose-fed digesters showed the lowest methane concentration with a mean of approximately 52 % both for the 1.3 and >4 gVS L^{-1} day^{-1} OLR. Hydrogen sulphide and carbon monoxide concentration in biogas were significantly increasing when the OLR increased above 4 gVS L^{-1} day^{-1} compared with the cautious OLR of 1.3 gVS L^{-1} day^{-1}. For the cautious

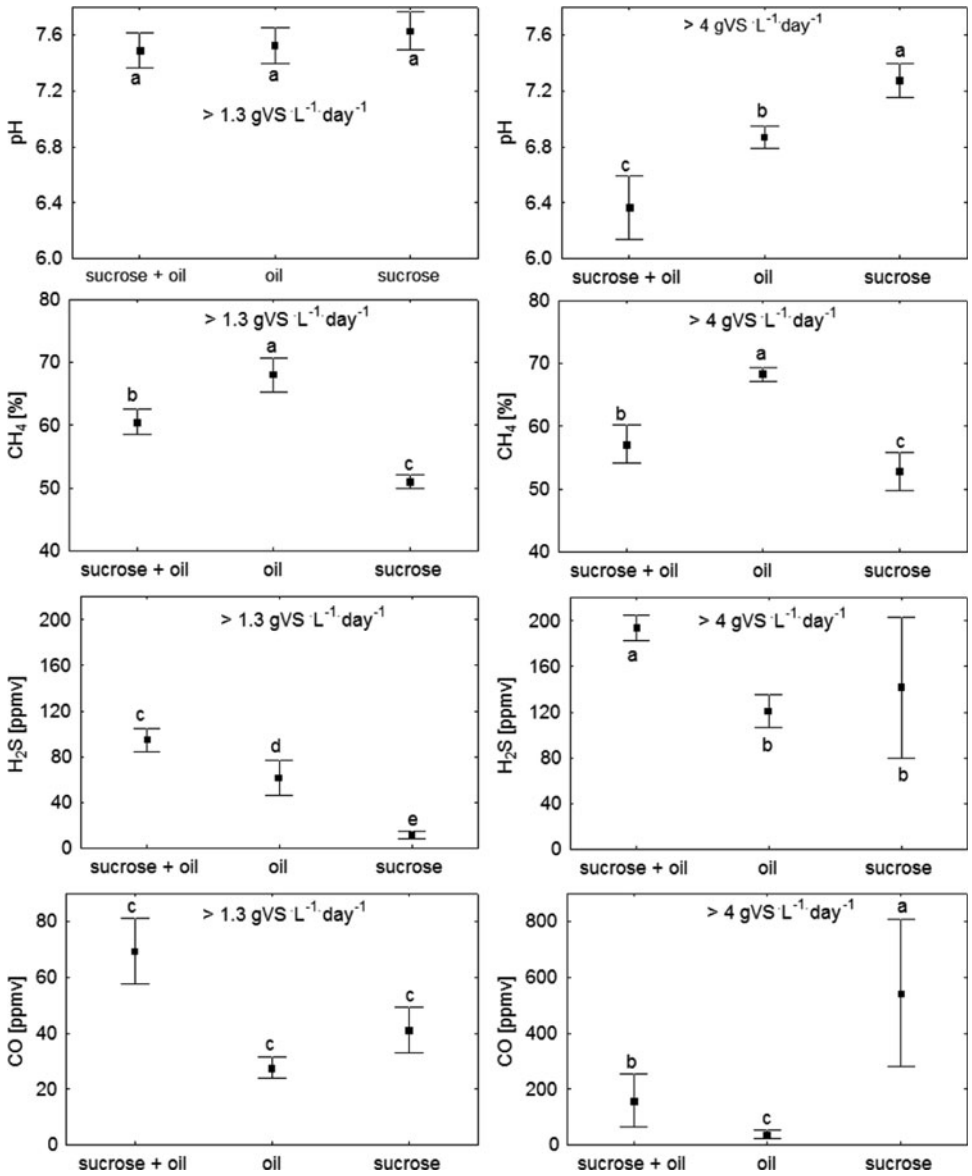

Fig. 2 Means (*squares*) and confidence intervals (*bars*) of the sludge pH and the gas phase composition for digesters fed with cautious (1.3 gVS L^{-1} day^{-1}) and risky OLR (>4 gVS L^{-1} day^{-1}). Means with the *same letter* do not differ significantly at $P \leq 0.05$

OLR, carbon monoxide did not differ significantly for the employed substrates. Hydrogen sulphide concentrations varied significantly between substrate within the cautious OLR. There were also significant differences between substrates within a same OLR for the methane content.

Gas phase monitoring with the e-nose

Influence of the substrate on the e-nose response

Results of the PCA computed on the data of digesters fed with a cautious OLR are shown in Fig. 3. The variance of the two principal components explained 93.7 % of the total variance of the cautious OLR data sublot. As observed in Fig. 3, the PCA realized for the digesters fed at the cautious organic load (1.3 gVS L^{-1} day^{-1}) highlighted four overlapping clusters. The sensor response cluster corresponding to the feeding with the dry sugar beet pulp overlapped largely with the clusters of the other feeding substrates. Clusters of the digesters fed with sucrose and maize oil appeared clearly separated. The mix of maize oil and sucrose visibly overlapped with the cluster of maize oil and dry sugar beet pulp, but not with the sucrose cluster.

Influence of the OLR on the e-nose response

PCA plot of Fig. 4 was realized with the e-nose output data of all digesters to examine the pattern of different organic loads. The variance of the two principal components explained 86.2 % of the total variance. The observations made on the digesters fed with increasing OLR strategies overlapped partly the cluster of the cautious feeding (OLR

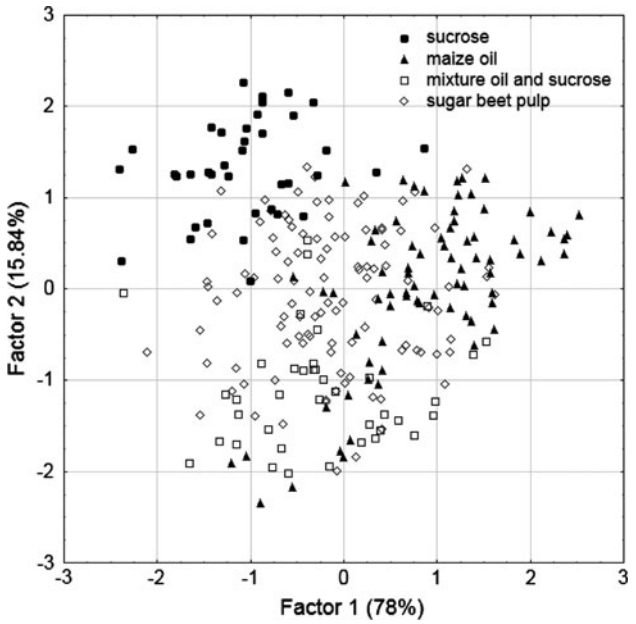

Fig. 3 Principal component analysis score plot (258 observations) of the response of the six sensors for the digesters fed with the cautious OLR (1.3 gVS L^{-1} day^{-1}) and four feeding substrates

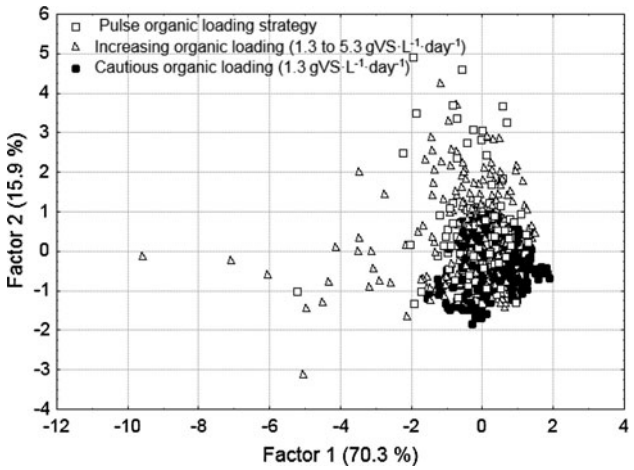

Fig. 4 Principal component analysis plot (872 observations) of the response of the six sensors for the digesters exposed to either cautious (1.3 gVS L^{-1} day^{-1}) or increasing feeding strategy (1.3–5.3 gVS L^{-1} day^{-1}) or pulse organic load, including four feeding substrates

1.3 gVS L^{-1} day^{-1} and data corresponding to the initial low feeding rate of the increasing OLR strategies) and extended in the direction of the two PCA axes. Digesters exposed to increasing OLR with sucrose extended in the direction of the factor 1, whereas digesters fed with increasing OLR with oil and the mixture oil:sucrose 1:1 extended in the direction of factor 2.

Detection of overload events with the e-nose

Hotelling's T^2 values of e-nose observations on several digesters are shown in Figs. 5 and 6 for the three employed substrates. The upper control limit value of T^2 for a stable process was determined at 23.7 and the median was 5.6. e-nose T^2 values are effectively increasing with the increasing loads, especially with sucrose (Fig. 5). In fact, the T^2 value exceeded the UCL just after the pulse organic load of 10 gVS L^{-1} and reached a value of 130.5. At the same time, the pH dropped at around a value of 6. The T^2 value receded 44.1 and then increased continuously till the end of the feeding experiment to reached a value of 331.5. With oil for feeding, the differences between increasing and cautious load were not as clear and the pH remained close to neutrality (Fig. 5). The e-nose T^2 values exceeded the UCL only for OLR above 5 gVS L^{-1} day^{-1}. The reactors fed with a mix of oil and sucrose proved to be very sensitive to the increase in organic load (Fig. 6). In fact, the pH decreased sharply when a pulse overload was applied or when the load was increased above 4.3 gVS L^{-1} day^{-1}. At the pulse load of 10 gVS L^{-1} day^{-1}, the T^2 value increased quickly above the UCL and the pH dropped.

For the oil:sucrose mixture, the e-nose T^2 value increased above the UCL when the pH decreased below 7 (Fig. 6). The T^2 values and the pH remained stable for the cautious OLR. At the pulse overload, both pH and T^2 values changed and the T^2 overcame the UCL. For the increasing OLR, the pH increased above 7 on day 32 (OLR of 2.7 gVS L^{-1} day^{-1}) and the e-nose T^2 value over passed the UCL at the same time. When the feeding was stopped, the e-nose T^2 value decreased but not below the UCL. At the same time, the pH receded to a value of 6.7.

The e-nose T^2 value decreased and increased following the loading rate of the digesters. For instance, it quickly decreased when the digester feeding was stopped and immediately increased on the following day with the restart of the feeding (Fig. 7). Changes in loading rates were rapidly detected using the e-nose output data while the methane content in the biogas and the pH remained relatively stable. Indeed, the methane content in the biogas did not seem to be strongly related to the organic load of the digesters, at least in the range used for this experiment, but appeared to vary in an erratic way, probably on a weekly basis (since the digesters were not fed during weekends), and with a relatively low amplitude. The pH variations were intentionally limited by stopping the feeding when it decreased below 6.7.

Concerning the monitoring of the semi-continuous reactors fed with dry sugar beet pulp, the sludge pH remained stable in a range extending from 7.5 to 8.1, what means that no significant disturbance of the process was achieved. Even though no significant changes in pH were observed, slight overload events and pulse overloads were

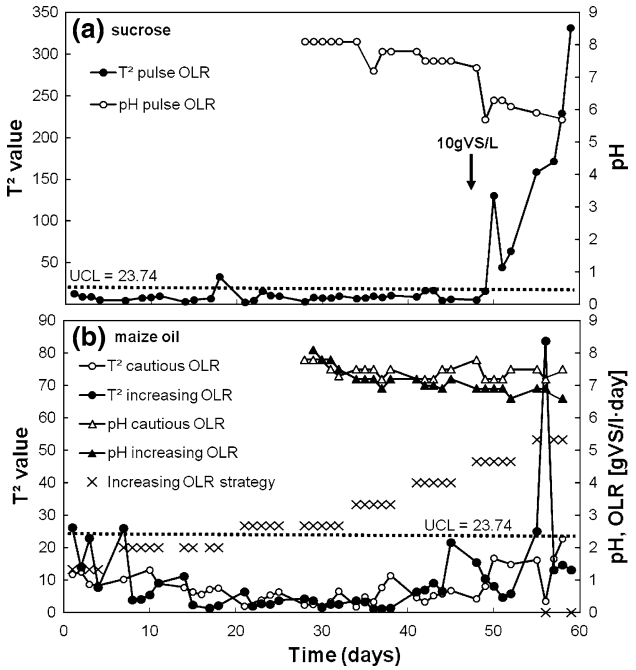

Fig. 5 Progress over time of the e-nose T^2 values, and pH of the anaerobic sludge for digesters fed with **a** sucrose and **b** maize oil. The organic loading rate (OLR) increased from 1.3 to 5.3 gVS L^{-1} day^{-1}. The upper control limit (UCL) was computed for four digesters fed with a cautious OLR of 1.3 gVS L^{-1} day^{-1}. A pulse load was applied to the cautious OLR on day 48 at a rate of 10 gVS L^{-1}

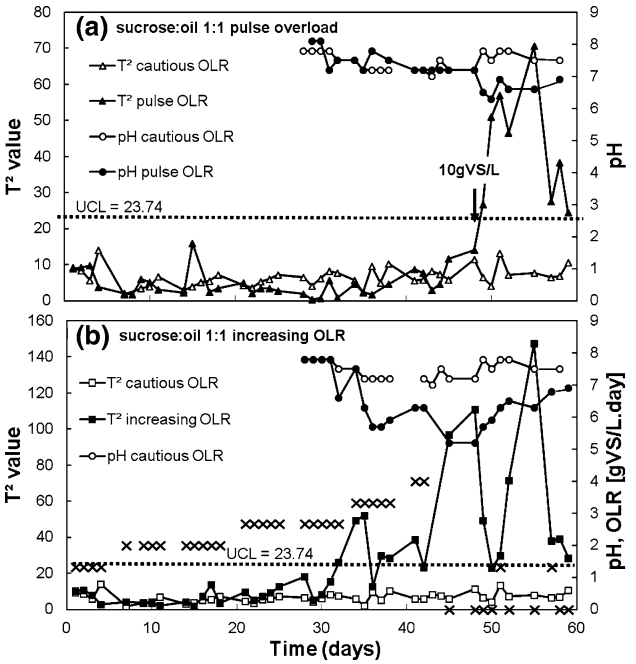

Fig. 6 Progress over time of the e-nose T^2 values, and pH of the anaerobic sludge for digesters fed with a mixture of sucrose:oil 1:1 and exposed to two disturbance strategies: **a** a pulse overload on day 48 and **b** an increasing OLR from 1.3 to 5.3 gVS L^{-1} day^{-1}. The upper control limit (UCL) was computed for four digesters exposed to a cautious OLR of 1.3 gVS L^{-1} day^{-1}

detected with the sensor array by comparing the e-nose T^2 value of the digesters exposed to a pulse load with that observed for the digesters fed with a cautious organic load (Fig. 8). The four reactors did not respond in an uniform manner. T^2 values above the UCL were only observed for the reactor A1 with a pulse of 5.3 gVS L^{-1} day^{-1} and for the reactor B6 with a pulse of 6.7 gVS L^{-1} day^{-1}. The methane content in the produced biogas remained stable (50.0 ± 3.4) along the experimental period.

Discussion

Influence of the OLR on the gas phase composition

In most cases, the pH of the sludge of the digesters significantly decreased when the organic load was above 4 gVS L^{-1} day^{-1}. The process was thus effectively disturbed by the high OLR due to the accumulation of VFA in the anaerobic sludge. However, this was not the case for the sucrose- and sugar beet pulp-fed digesters. Disturbances due to a risky OLR were thus obtained and the study focused on disturbed digesters. Methane concentration in the biogas did not vary significantly between the different organic loads when sucrose and maize oil were used as substrate. On the contrary, the methane

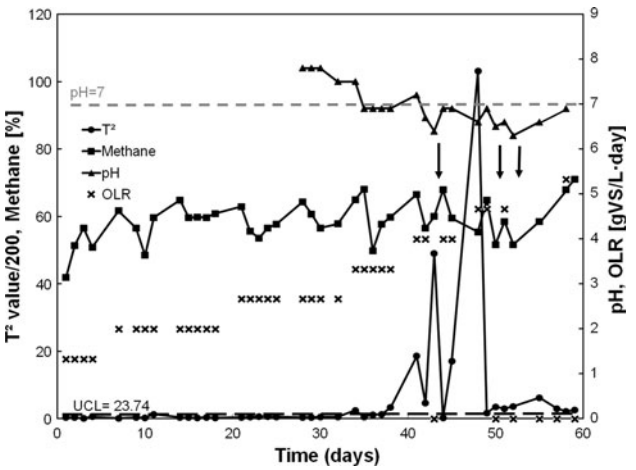

Fig. 7 Progress over time of the e-nose T^2 value, pH and methane content of a digester fed with a mixture of sucrose and maize oil (1:1) and exposed to an increasing loading rate (1.3–5.3 gVS L^{-1} day^{-1}). The upper control limit (UCL) was obtained with four digesters fed with the cautious OLR of 1.3 gVS L^{-1} day^{-1}. When the pH of the digester dropped below 6.7, the feeding was stopped for a day and these periods are indicated by *vertical arrows*

concentration in the biogas clearly depended on the nature of the substrate used for the feeding, the lipidic substrate showing the highest methane concentration in the biogas. This is in line with the estimation of the biogas production and methane content with the Symons and Buswell

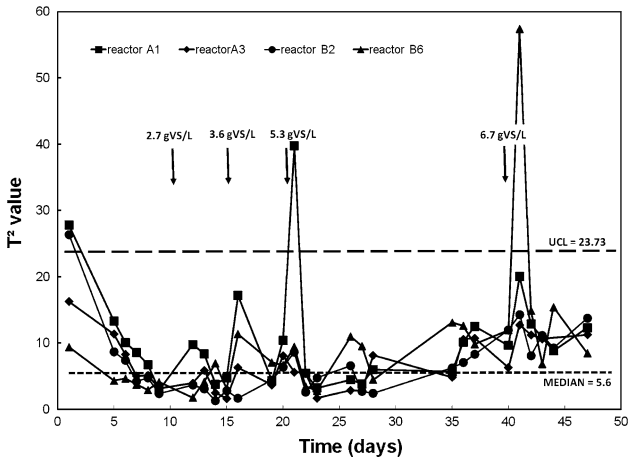

Fig. 8 Progress over time of the e-nose T^2 values observed for reactors exposed to cautious OLR interrupted by pulse organic loads with dry sugar beet pulp on days 11 (2.7 gVS L^{-1} day^{-1}), 15 (3.6 gVS L^{-1} day^{-1}), 20 (5.3 gVS L^{-1} day^{-1}) and day 40 (6.7 gVS L^{-1} day^{-1}). Median and upper control limit (UCL) were obtained for four anaerobic semi-continuous reactors fed with different substrates (sucrose, oil, sucrose:oil mixture and dry sugar beet pulp)at a cautious OLR of 1.3 gVS L^{-1} day^{-1}

equation [31] that gives higher methane content for the lipidic substrates than for the carbohydrates and proteins. In the literature, drop in the methane concentration in the biogas was reported in case of organic overload of anaerobic digesters [8, 31, 32]. In our experiments, the increased OLR had limited influence on the methane concentration. This is probably due to the fact that the feeding was stopped when the pH dropped below 6.7 and the highest OLR used (5.3 gVS L^{-1} day^{-1}) was not severe enough to cause drastic process imbalance. Carbon monoxide has already been reported as a possible state variable in anaerobic digestion process [33, 34]. We observed higher carbon monoxide and hydrogen sulphide concentrations for the high OLR (above 4 gVS L^{-1} day^{-1}) than for the cautious OLR (1.3 gVS L^{-1} day^{-1}). This showed that the process status could affect the composition of the gas phase of anaerobic digesters. In our experimental conditions, the changes in biogas composition due to increasing OLR were significant in terms of CO and H_2S but negligible in terms of CH_4.

Gas phase monitoring with the e-nose

Influence of the substrate and the OLR on the e-nose response

Methane is the main compound of biogas and all sensors of the e-nose system are sensitive to this compound. In terms of methane concentration there were little differences in the biogas composition due to the increase in OLR but the substrate nature had a strong influence on this parameter (Fig. 2). The e-nose response allowed separating sucrose and maize oil, whereas the sucrose:oil mixture and the sugar beet pulp were not clearly distinguished within the four substrates used (Fig. 3). On the other hand, the e-nose allowed segregating between cautious stable OLR and increasing ones (Fig. 4). In other words, the e-nose output data appeared more specifically influenced by the organic load of the digesters than by the substrate and the related methane concentration in the produced biogas.

Detection of overload events with the e-nose

The T^2 value appeared useful to evaluate the potential of the electronic nose system to detect disturbed anaerobic process directly on the gas phase of the reactors and indication were provided that this parameter can potentially serve as a quantitative indirect indicator of organic overload. The T^2 values remained stable for the cautious OLR for any feeding substrate without exceeding the upper control limit. The data of five anaerobic digesters with a cautious loading were used as a training set for defining a stable anaerobic digestion process and to evaluate the process disturbance intensity when increasing the OLR by using the T^2 value and its upper control limit. Thus, the median of the T^2 values of these digesters gave the stable process baseline while the control limit provided an indication of the initiation of an unstable process. The T^2 value could be used as indirect state indicator of the anaerobic process and warned off abnormal situations and transient states. Care was taken in the experimental plan to include the potential feeding substrate influence. Indeed, the training set was composed of digesters fed with different substrate and with a cautious load. e-nose observations and monitoring of the organic load using the T^2 values was as much sensitive as using the pH and better than using methane content variations as early warning indicator of process imbalance.

No disturbances were observed in some digesters, especially for the digesters fed with sugar beet pulp. The increase of organic load was certainly not sufficient to induce process imbalance with this substrate. This is confirmed by the pH that remained stable, probably related to a higher alkalinity due to the substrate composition. In fact, it is commonly admitted that the anaerobic digestion process is not affected by loads below 4 gVS L^{-1} day^{-1}. The pH of the digesters fed with the dry sugar beet pulp never decreased below 7.2. Dry sugar beet pulp is considered as a slowly degradable substrate that proves useful in cattle feeding to avoid acidosis and promote ingestion of the basal ration [35, 36]. Nevertheless, pulse overloads could be pointed out using the e-nose T^2 value while no changes were observed using the pH and the methane content. Thus, in some cases, the T^2 value derived from the e-nose

observations was more efficient than the pH to observe slight or transient process disturbances.

One of the potential disadvantages of the use of an e-nose for the monitoring of anaerobic reactors is the large diversity of feeding substrates, which can interfere on the gas sensor array signals. In fact, gaseous emissions of feeding substrates and their degradation products would be a potential drawback by interfering with the e-nose observations for the detection of disturbances. Nevertheless, it has been shown in this study that different simple substrates did not disable the detection of the high organic loadings by PCA analysis and Hotelling's T^2 test of the e-nose output data. However, the influence of much more complex and varying substrates on the e-nose signals should be further investigated. In fact, reactor substrates, which are highly complex in the case of agricultural plants could possibly interfere on the ability of the e-nose to detect disturbances of anaerobic digestion process.

Conclusions

The aim of this study was to determine the potential of the electronic nose technology for the monitoring of the anaerobic digestion process, especially to detect organic overload of the reactors. The concentration of some compounds in the gas phase changes when the OLR is pulsed and an unstable process is generated. We could demonstrate that a home-made array of gas sensors was effective for the monitoring and the detection of disturbances of the anaerobic process while using simple substrates such as sucrose and maize oil or a more complex one such as sugar beet pulps containing both carbohydrates and proteins.

The e-nose could detect organic load variations and it was also able to detect process disturbances and recovery periods. This technology appeared to be more efficient than the monitoring of methane content in the biogas for early detection organic overloads. An indirect state indicator was here derived from the calculation of the Hotelling's T^2 value. In this study, the T^2 value was shown useful to provide simplified and uncomplicated information from a complex gas sensor array and to determine a control limit for the stable process while using stable digesters as a reference set.

Focusing on the gas phase of anaerobic reactors is a quite innovative approach towards the on-line monitoring of anaerobic digesters. It should provide rapid monitoring online tools while avoiding difficult sampling from highly heterogeneous sludge with high solid content. In fact, in the liquid phase of anaerobic reactors, homogenous sampling can prove difficult and requires sample preparation that makes it complicated for online implementation. Our study confirms that the e-nose is a potential tool to be adapted for the continuous online monitoring of the anaerobic reactors. It could provide early diagnosis of process imbalances as it does not need a complex and long sample preparation. Electronic nose is a promising tool to derive a simple indirect state variable, such as the Hotelling's value, for anaerobic process monitoring while integrating the multivariability of the complex AD process.

Future work

Multivariate data analysis is adapted to multivariate processes such as anaerobic digestion and to give relevant and uncomplicated information of the process state and warn off outlier situations compared with the steady-state process [11]. However, the training data set to calculate the distance from the steady-state process must be carefully managed [11, 30]. True performance of a gas sensor array for biogas process monitoring could only be estimated by extending the present work to conditions prevailing in real agricultural situations while comparing results with VFA monitoring in the liquid phase, the latter being a well accepted method for identifying organic overload state the anaerobic process [8, 37–40]. For future experiments, an automated e-nose system that acquires automatically the biogas sample and gives real-time monitoring on hourly basis of the bioreactor status should be evaluated, allowing process control and possibly some interventions on the bioreactors.

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