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Upscaling of an electronic nose for completely stirred tank reactor stability monitoring from pilot-scale to real-scale agricultural co-digestion biogas plant

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HIGHLIGHTS

- An electronic nose could assess process state of a pilot-scale anaerobic reactor.
- The use of gas phase of an anaerobic reactor was relevant to assess process state.
- An anaerobic digestion process state indicator was obtained through PCA monitoring.

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ABSTRACT

This study investigated the use of an electronic nose for on-line anaerobic reactor state monitoring at the pilot-scale level and then upscaling to the full-scale level. E-nose indicator was compared to classical state indicators such as pH, alkalinity, volatile fatty acids concentration and to other gas phase compounds. Multivariate statistical process control method, based on principal component analysis and the Hotelling's T^2 statistics was used to derive an indicator representative of the reactor state. At the pilot-scale level, the e-nose indicator was relevant and could distinguish 3 process states: steady-state, transient and collapsing process. At the full-scale level, the e-nose indicator could provide the warning of the major disturbance whereas two slight disturbances were not detected and it gave one major false alarm. This work showed that gas phase relation with anaerobic process should be deeper investigated, as an e-nose could indicate the reactor state, focusing on the gas phase.

1. Introduction

Transfer of process monitoring instrumentation from the laboratory or pilot-scale to real-scale biogas plant is a real challenge. Many technologies have been tested up to the pilot-scale, but the working conditions encountered on biogas plants complicates the real-scale implementation (Madsen et al., 2011). On-line instrumentation for digester stability and performance monitoring is still lacking at the full-scale level, especially in agricultural biogas plant where high-tech instrumentation is not used for economical and technical reasons (calibration, maintenance, cost, etc.). An important limitation is the exposure of analytical tools and sensors to harsh and variable conditions, especially for the analyzers working on the liquid phase. Indeed, the liquid phase is heterogeneous, with high particulate and solid content, bubbles, and the formation of biofilms which deteriorate sensing material or lead to instrumentation clogging (Madsen et al., 2011; Spanjers et al., 2006). Presently, near infra-red spectroscopy (NIRS) is the main technology evaluated for on-line process monitoring at full-scale biogas plant. By the use of chemometrics techniques, NIRS applied to the liquid phase is suitable for total volatile fatty acids (TVFA), acetate and propionate monitoring at the pilot-scale level (Ward et al., 2011). At the full-scale level, Krapf et al. (2013) could use an *in situ* NIRS for an acceptable estimation of volatile solids (VS), ammonium, total inorganic carbon (TIC) and TVFA but the system needs to be further investigated to evaluate the long-term stability of the model and calibration system.

Gas phase of anaerobic reactors is a harsh environment, with corrosive and high humidity conditions in the reactor headspace. Hydrogen sulfide content in biogas is usually high (200–10,000 ppm) and in presence of 2–8% of air, is biologically oxidized either to free (solid) sulfur or (aqueous) sulfurous acid. Elementary sulfur accumulation may clog small gas sampling

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tubing. Sulfuric acid corrodes material and tubing. Foaming is another dilemma to deal with when the gas phase is sampled. Some excess foam event can take place in the anaerobic reactors and clog or damage tubing and material. For this reason, gas sampling system must be correctly realized, especially when it is implemented close to the reactor headspace. Even though, gas phase is more homogeneous than liquid phase and its sampling avoid direct contact with the high-particulate content liquid phase.

Electronic nose (e-nose) is one of the technologies based on the gas phase which can be potentially used for on-line monitoring of anaerobic reactors. Rudnitskaya and Legin (2008) realized a survey of the use of electronic noses and electronic tongues (e-tongues) (sensor arrays exposed to liquid) for the monitoring of biotechnological processes and biogas process. They concluded that e-tongues and e-noses are of particular interest for the analysis of complex liquids and gas mixtures respectively and deliver simple information of complex multi-factorial biological systems. They possess all advantages of chemical sensors systems for monitoring bioprocesses: rapid measurements, possibility of easy automation of the sensor set up and relatively simple and inexpensive instrumentation. The particular advantage of e-noses and e-tongues systems compared to discrete sensors is that they avoid traditional problems of selectivity in complex media. They also offer the possibility to perform recognition, classification and quantitative determination of components concentrations simultaneously in multicomponent media.

Not many attempts for the monitoring of anaerobic digestion (AD) process with e-noses have been made but applications of e-nose for fermentation monitoring are more numerous. For instance, e-noses were fruitfully applied in numerous bioprocesses monitoring projects (Bachinger and Mandenius, 2001; Cimander et al., 2002; Lidén et al., 1998; Mandenius, 2000; Mandenius et al., 1999). However, the low number of publications on applications of e-noses as AD process monitoring tool is presumably due to the complexity of the process and to the complex composition and diversity of the biomass employed in anaerobic digestion compared to other fermentation processes (Rudnitskaya and Legin, 2008). The e-nose technology was applied to the monitoring of the anaerobic digestion process by Nordberg et al. (2000). They could provide a good prediction of methane content in biogas and acetate concentration in the sludge using an e-nose on a 81 L completely stirred reactor exposed to pulse glucose overloads. Brandgård et al. (2001) also attempted to monitor pure culture of methanogenic bacteria with an e-nose by which he could estimate methanogens growth. Therefore, e-nose technology appears as a potential solution to deliver fast advices about reactor status to biogas plant operators as this technology is functional for online process monitoring using the gas phase (Pearce et al., 2003; Rudnitskaya and Legin, 2008).

Electronic nose is a generic term that refers to a biologically inspired system composed of an array of non-specific but complementary gas sensors. Most widely employed sensors in e-noses are metal oxide semiconductor (MOX) sensors. Other sensors are conducting polymers, acoustic/gravimetric wave etc. Currently, new technologies are also integrated in these systems such as, nanosensors, biosensors, mass spectrometer, ion mobility spectrometer, etc. (Arshak et al., 2004; Gutiérrez and Horrillo, 2014). Selection of the sensors depends on the application of the e-nose, as well on the cost and precision requirements of the instrument. When the sensor array is exposed to a gas mixture, sensor responses are put together and form a pattern, which is typical of this gas mixture (Nicolas et al., 2001). A database of patterns is built up and used to train the pattern recognition system that finally allows recognizing an unknown gas mixture. The context of e-nose application is large. In fact, e-noses have been evaluated in various research areas such as environmental monitoring, security, medical diagnosis, food industry, etc.

In a previous work, we demonstrated that an e-nose based on metal oxide semi-conductor gas sensors could detect process disturbances on lab-scale semi-continuous anaerobic reactors through multivariate statistical process control techniques (MSPC) (Adam et al., 2013). In fact, as gas sensors of the e-nose are non specific, they present a certain degree of redundancy/correlation, which allows the application of multivariate techniques. MSPC methods have already been used in the domain of AD process monitoring for the early detection of disturbances by the use of numerous process parameters data and near-infrared instrumentation data on the reactor and its feedstock (Reed et al., 2013). The work presented here uses the same approach and compares data of on-line electronic noses exposed to the headspace pilot-scale reactor and then upscaled to a full-scale agricultural reactor at Faascht (Belgium, Attert) with classical off-line process state indicators such as individual volatile fatty acids (VFA), total volatile fatty acids (TVFA), pH, the ratio VFA/total inorganic carbon (TIC), total ammonia nitrogen (TAN), volatile solids (VS) and total solids (TS).

2. Methods

2.1. Pilot-scale reactor evaluation

A mesophilic pilot-scale CSTR reactor of 100 L was monitored with the e-nose over 114 days. Day 1 corresponds to the day where the e-nose data were available (e-nose sensors needs 2 days to stabilize). Prior to the e-nose implementation, the reactor was stabilized during 97 days with low but increasing organic loading rate (OLR). The reactor was inoculated with anaerobic sludge of the wastewater treatment station of Schifflange (Luxembourg) (TS: 1.6%, VS: 55.2%TS). It was fed during working days with sugar beet pulp pellets added with water, maintaining the hydraulic retention time to approximately 40 days. After day 66, maize oil was added to the feeding mixture to decrease foam formation which was significant and could deteriorate biogas sampling lines. The German standard for fermentation test VDI 4630 (Anonymous, 2006) was followed for the experimental set-up of the pilot-scale reactor. Organic loading rate was increased every 2 weeks by step of 0.5 kgTS m^{-3} until reactor collapsed.

2.1.1. Analytical methods

Gas phase of reactors was monitored using two distinct apparatus: (i) a set of specific gas sensors for gas composition assessment and measuring methane, carbon dioxide, hydrogen and hydrogen sulfide concentration in the biogas. This multisensor array of specific sensors was connected to the digesters after the gas dryer to avoid water condensation and extend the lifespan of the sensors. Every 2 h, methane and carbon dioxide were measured with specific infrared 0–100% sensor (model TDS0054 and TDS0048, certified types, Dynament, UK). Hydrogen and hydrogen sulfide were measured respectively with a sensor ranging from 0 to 2000 ppm and an electrochemical cell (0–10,000 ppm) (model I-42, IT Dr. Gambert, GmbH, Germany). Biogas production was recorded every 2 h using a drum-type humid gas meter (model TG05, Ritter Apparatebau GmbH & Co. KG, Bochum, Germany). The biogas production rate was estimated by dividing the daily production by the reactor volume. Biogas uptake by the e-nose before the gas volume meter was considered as negligible, as the e-nose uptake corresponds to approximately 250 mL per hour.

Additionally, process state variables of the reactors were analyzed off-line. Once a day, before reactor feeding, pH was measured using a portable pH sensor (profline pH 197i with sentix®41 pH probe, WTW, Germany). Alkalinity and ammonia content were