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Electronic Nose Technology for Reactor State and Biogas Quality Assessment in Anaerobic Digestion

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INTRODUCTION

The anaerobic digestion (AD) process (syn. biomethanation) has a high potential to contribute to sustainable energy production because it is one of the most advanced options available to convert especially wet biomass into multipurpose fuels (CH_4 and H_2), valuable products to serve the green chemistry/biorefinery sectors, and fertilizers readily available to agriculture. Nevertheless, a major limitation to further development of the sector is the difficulty to keep the anaerobic flora of the digesters in optimal conditions of activity. Numerous methods have been assessed to properly monitor the process but none appears to be ideal [1].

Electronic noses (e-noses) have been documented as potential tools to be employed in the AD domain, especially for process monitoring [1]. E-noses could also be used for biogas quality assessment and for safety purposes (biogas leak detection, biogas combustion, etc.) These instruments obviously present a potential in AD field but have also clear limitations. A previous work by Adam et al. [2] demonstrated that an e-nose could detect different disturbances in lab-scale reactors with an exclusive focus on the gas phase of reactors.

AIMS of the STUDY

This work presents the application of an e-nose evaluated on a pilot-scale continuously stirred tank reactor (CSTR) for two purposes: i) process stability monitoring and, ii) biogas quality assessment (methane and hydrogen sulphide content). Both purposes are essential factors for the economical viability of biogas plants. An important aspect of this work is that one instrument, an e-nose composed of 6 metal oxide semiconductor (MOx) gas sensors, was tested to reach both purposes.

MATERIAL AND METHODS

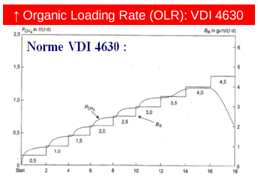
Lab-scale continuous reactors: Overfeeding campaigns

- 4 continuously stirred tank reactors (CSTR) 100l
- mesophilic temperature range (37°C)

•**Inoculum:** sludge from the anaerobic digester of a waste water treatment plant (mesophilic conditions).

•**Substrate:** dried sugar beet pulps.

↑ Organic Loading Rate (OLR): VDI 4630



E-nose and classical process state indicators: continuous data collection

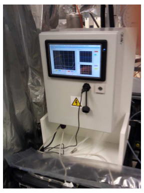
Parameters in the digestate:

Parameter	Measurement method	Measurement Frequency
pH	Saturated calomel electrode	day^{-1}
Total solids (TS)	Gravimetry (VDI 4630)	$week^{-1}$
Volatile solids (VS)	Gravimetry (VDI 4630)	$week^{-1}$
Total alkalinity (TA)	Volumetric (BiogasPro, Germany)	$week^{-1}$
Ammoniac Nitrogen (NH_4-N)	Volumetric (BiogasPro, Germany)	$week^{-1}$

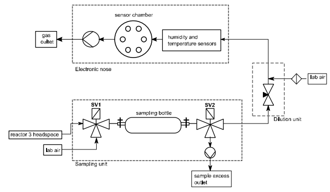
Parameters in the biogas:

Parameter	Units	Measurement method	Measurement Frequency
Biogas specific production	l/h	drum-type wet gas meter	$hour^{-1}$
CH_4 concentration	% (Volume)	Non Dispersive Infra-Red Sensor (NDIR)	$(2\ hours)^{-1}$
CO_2 concentration	% (Volume)	NDIR	$(2\ hours)^{-1}$
H_2 concentration	ppm (Volume)	Metal Oxide Semi-conductor (MOx) with molecular sieve	$(2\ hours)^{-1}$
H_2S concentration	ppm (Volume)	Electro-Chemical Sensor (ECS)	$(2\ hours)^{-1}$

E-nose configuration and measurements (on reactor n°3)



- •Array of six commercial MOx sensors
- •Sensor chamber maintained at 50°C
- •Every hour:
  - 1 min gas sampling
  - 9 min sensor exposure to diluted biogas
  - 50 min purge with clean air
- •Dilution ratio of 1:25 for biogas:air mixture
- •Data recorded every 30 s



Data analysis and Model development

1) process control

Steps:

1) Acquisition of the stable response (µS) for each sensor
2) Normalize data
3) Standardize Data
4) PCA Model training using 30 first days

5) Normalize and standardize new observation
6) Select PC number
7) Calculate T^2 and Q^2
8) If T^2 and Q^2 < control limit: update mean, standard deviation and correlation matrix
9) Return to step five

2) gas quality

20 min sensor response x 2 records/min x 6 sensors = vector of 240 data/observation

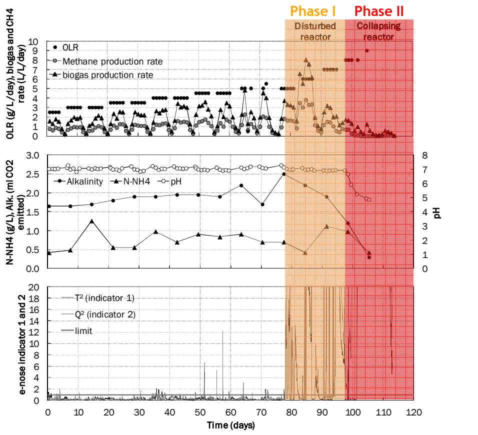
Model: Kernel PLS (using PLS toolbox, R 3.1.1. software)

Model training:
Data set of the 30 first days (300 observations)

Model testing:
10 fold cross-validation
Test set: 138 data (day 31 to 60)
finally: testing on the complete data set (day1 to 110)

RESULTS and DISCUSSION

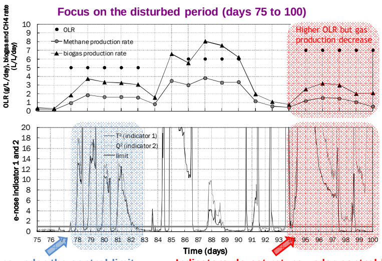
1) Process stability monitoring



Phase I: disturbed (process day 78 to 98)
- •Alkalinity sharp drop
- •Stable pH
- •H_2S concentration sharp increase
- •CO_2 concentration increase
- •Low biogas quality
- •High biogas production

Phase II: reactor collapse (after 98 days)
- •alkalinity sharp drop
- •pH decrease
- •H_2S emissions
- •Extremely low biogas production

Focus on the disturbed period (days 75 to 100)

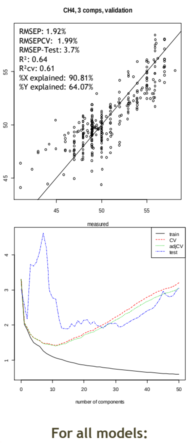


Indicators return under the control limit: process can be still recovered

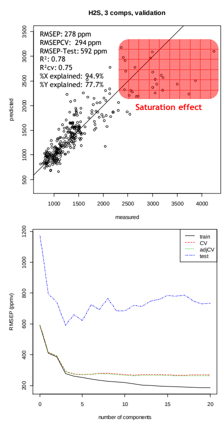
Indicators do not return under control limit: collapsing reactor

2) Biogas quality prediction

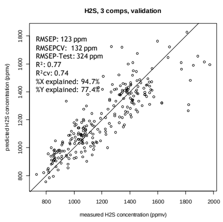
Methane content prediction



H_2S content prediction



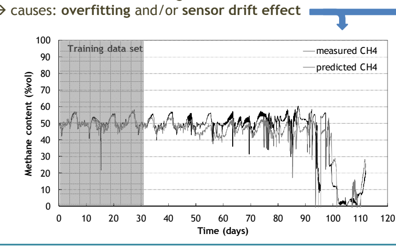
H_2S content prediction (model trained with <2000 ppm H_2S data

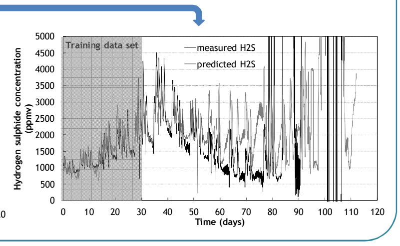


CH_4 prediction model:
- cross-validation RMSEP is good (1.99%) whereas test set presents a much higher RMSEP (3.7%) → **overfitting?**

H_2S prediction models:
- 1st model trained with all H_2S concentrations of the training data set give a RMSEP of 278 ppm whereas mean value of H_2S concentration in the training set was 1425 ppm
- 2st model trained with $[H_2S]$ lower than 2000 ppm gave RMSEPCV of 132 ppm, which is much better than the first model.

For all models:
- Test set RMSEP was much higher than cross-validation RMSEP → causes: **overfitting** and/or **sensor drift effect**





CONCLUSIONS

- The MOx-based e-nose appears as an ***interesting tool for AD process monitoring***. The study showed that it was possible to quickly detect out-of-control situations (related to both biological dysfunctions and measurement system failure) using only gas phase parameters to build the model. The e-nose could be used for rapid detection of disrupting AD process. By the e-nose advice, subsequent analytical measures should be employed to determine the cause of the process disruption.
- The same MOx-based e-nose could be utilized for a rough screening of CH_4 and H_2S concentration in the raw biogas. Even though, quality of the prediction of H_2S and CH_4 content is low. In addition, it seems that model quality was affected by the sensor drift. Though, quality of prediction degrades over time. Data pre-treatment should be investigated to compensate sensor drift effects.

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http://www.ecobiogaz.eu/

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