A new and straightforward biosensor to quantify volatile fatty acids in digestates

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Abstract
A new biosensor, based on the capacity of selected bacteria to specifically utilise VFAs as carbon source and producing a signal proportional to the concentration of VFAs in the digestate was developed and tested. The digestate samples to be tested did not require any preparation or solids separation.
The biosensor was tested for early detection of VFAs in anaerobic digesters at laboratory scale (5 L digesters) and the information collected was used to manually change the feed (loading rate) in the digester. The digesters monitored with the biosensor were operated in parallel with control digesters which performance was only examined using standard indicators (pH, volatile solids removal and biogas production and quality). In all cases, the biosensor was able quantify the VFAs and identify process imbalances at an early stage. Changes in feeding rates were completed according to the biosensor readings to operate digester at optimal conditions. As a result, an improved process efficiency was observed resulting in 30-50% increase in methane production and volatile solids reduction increased between 60-75%, compared to the control digesters monitored only by the standard indicators.

Keywords
Anaerobic digestion, biosensor, control of anaerobic digestion, digestate, VFAs

Introduction

The optimal conditions for anaerobic digestion (AD) have been thoroughly documented at mesophilic temperatures at 35°C and sludge retention times of ≈ 20 days in order to achieve biogas yields 1 m^3 methane gas/kg volatile solids and volatile solids (VS) reduction of around 45%. However, surveys of full-scale digesters indicate that they are very often not operated to full capacity and are recurrently subjected to adverse operational practices such as temperature fluctuations (23-38°C), inconstant feeding regimes (between 10-23 days), variable solids content on the feed (1.5-8%), changes in loading rates etc. and as a consequence the biogas yields are often lower than the optimal values and digester capacity is lost.

Anaerobic digesters are often monitored (when monitored at all) by measuring pH, VS, removal and biogas production as indicators of process performance. Changes in pH, VS, destruction or biogas production are not suitable for trouble-shooting changes in AD. This is because these parameters are at the end of a complex chain of biological reactions and their variation is already an indication of significant changes in the anaerobic biological community, sometimes even in an irreversible way. Hence pH, VS and gas monitoring can be considered a reactive form of monitoring. On the other hand, volatile fatty acids (VFA) have been widely recognized as a key parameter for understanding and controlling anaerobic processes as they are intermediate products and real time indicators of the digester stability. The application of in-situ and/or on-line instrumentation for VFAs measurement has been limited as all developed instrumentations are based on expensive equipment (gas chromatograpy, high performance liquid chromatography, Fourier transform infra-red spectrometer etc.) and require sample preparations

involving the use of filtration, membranes, chemical additions, therefore triggering extensive maintenance.

The aim of this study was to develop a biosensor that measured VFAs in complex mixtures such as fermented/digested sludge that can be used, together with the suitable control strategy, to diagnose and optimise operation in anaerobic digesters.

Results and discussion

The biosensor was based on the principle that denitrifying bacteria under anoxic conditions (nitrate rich environment without oxygen) utilise the readily available carbon (mainly in the form of volatile fatty acids) to produce carbon dioxide and nitrogen gas (eq.1).

$$5CH_3COOH + 8NO_3^- \longrightarrow 8HCO_3^- + 2CO_2 + 6H_2O + N_2, \quad (eq.1)$$

The biosensor was composed of a reaction vessel with denitrifying bacteria (sourced from surplus activated sludge from a full-scale plant) under anoxic conditions ensured by a constant stream of nitrogen gas and periodic addition of nitrate in the form of KNO_3 (Figure 1). The solution containing readily available soluble carbon as VFAs is added to the reaction vessel and the carbon dioxide produced by the bacteria measured by a sensor commercially available installed in the headspace of the reaction vessel (Figure 2).

Figure 1. Biosensor set-up.

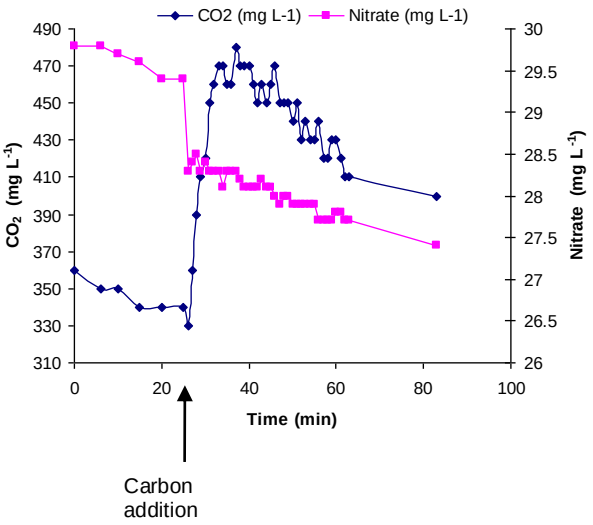

Figure 2. CO_2 production after digestate addition to the biosensor.

The biosensor could be used to estimate concentrations of VFAs of pure chemicals such us acetic

acid, mixtures of acetic acid and propionic acid, and fermented primary sludge liquors, in both batch and continuous operation (Figure 3)

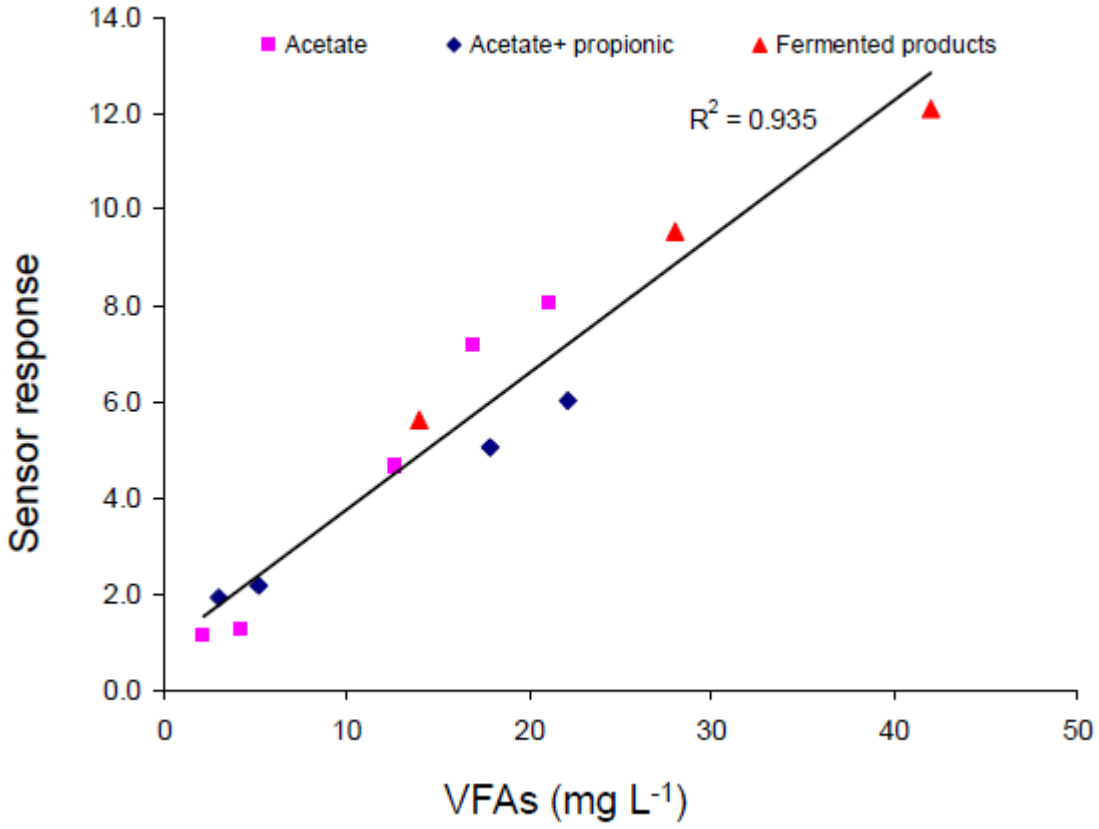

Figure 3. Biosensor linear response when different solutions of pure chemicals (acetic acid, mixtures of acetic acid and propionic acid), and fermented primary sludge liquors with varying VFAs concentrations were added to the reaction vessel. Overall this figure demonstrates that the biosensor can be used to estimate the VFAS of solutions with various degrees of complexity.

The potential of the biosensor to estimate VFAs concentration in anaerobic digesters and using that information to detect early signs of digester imbalance together with digestion biogas optimisation, was also assessed. The lab-scale results have demonstrated:

- Reproducibility of results
- Early signs of digester imbalance could be detected using the biosensor when the anaerobic digesters were subject to organic and hydraulic overloads
- Anaerobic digesters could be optimised for biogas production based on biosensor response (Figure 4 and 5).

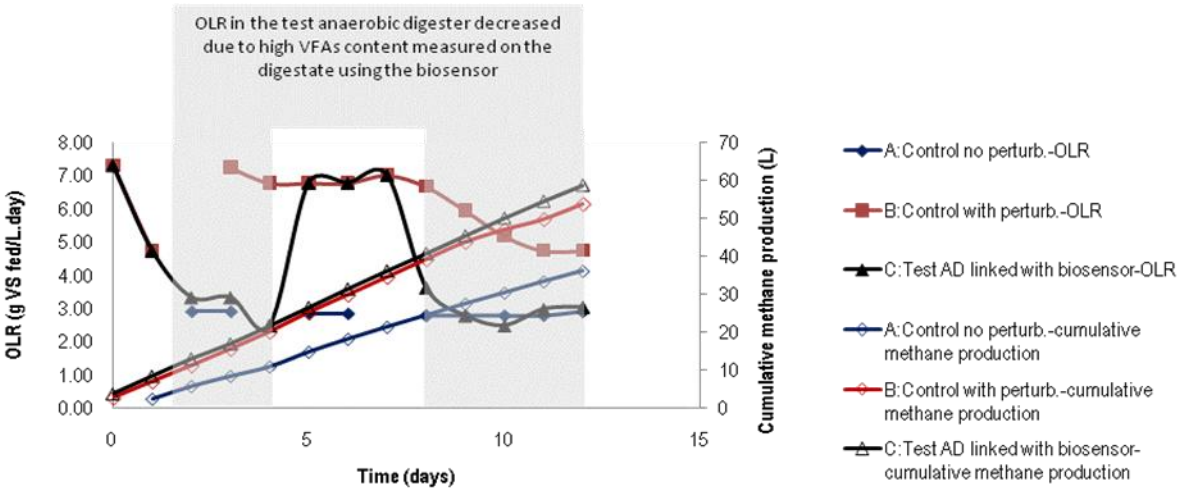

Figure 4. Three lab-scale anaerobic digesters (AD): A, B and C with 5L capacity each were operated in parallel for a period of 13 days. The organic load rate (OLR) was increased to 5-8 VS fed/L.day (variation due to sludge quality) at time 0 in digesters B and C while A was kept constant at 3 g VS fed/L.day. The ORL was adjusted to 3 g VS fed/L.day on day 3 and 8 in the digester C when the biosensor indicated high concentrations of VFAs on the digestate. Overall the methane production was 6 L higher on digester C that was optimised with the biosensor compared with digester B.

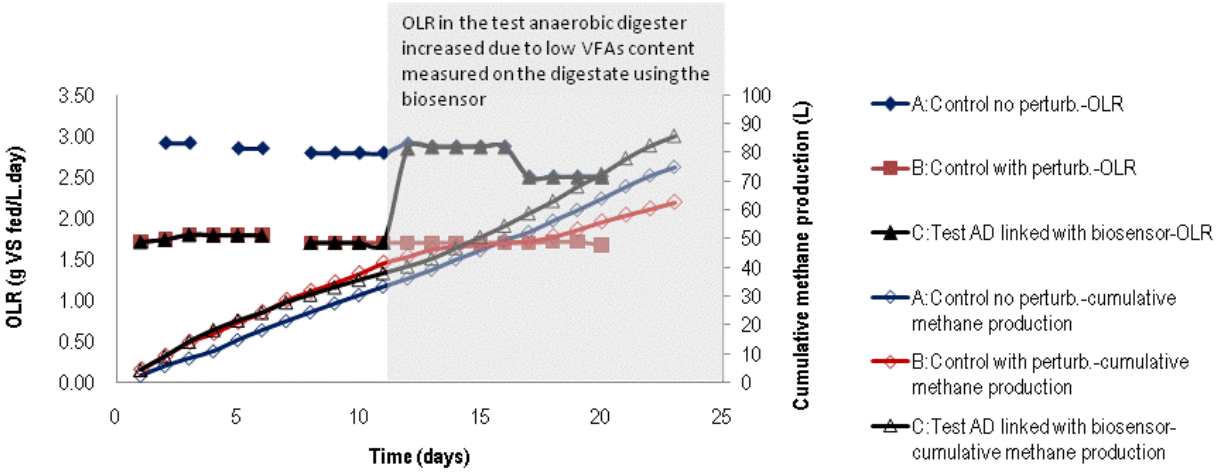

Figure 5. Three lab-scale anaerobic digesters (AD): A, B and C with 5L capacity each were operated in parallel for a period of 21 days. The organic load rate (OLR) was decreased to 1.5-2 VS fed/L.day (variation due to sludge quality) at time 0 in digesters B and C while the fed in digester A was kept constant at 3 g VS fed/L•day. The biosensor indicated low concentrations of VFAs on the digestate of Digester C after day 2. The ORL was adjusted to 3 g VS fed/L.day on day 11 in digester C. Although the biosensor indicated an imbalance much earlier (on the second day) the OLR was not changed immediately in order to verify reproducibility of VFAs measurements. Overall the methane production was 23 L higher on digester C - that was optimised with the biosensor compared with digester B.

The aim is to keep developing the biosensor to optimise the detection at low VFAs concentrations (100 mg/L), and to integrate the biosensor into a control system that can be used to regulate the digester feed.

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