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Early warning indicators for process failure due to organic overloading by rapeseed oil in one-stage continuously stirred tank reactor, sewage sludge and waste digesters

A. Kleyböcker [a], M. Liebrich [a], W. Verstraete [b], M. Kraume [c], H. Würdemann [a,*]

[a] Microbial GeoEngineering, Helmholtz Centre Potsdam, GFZ German Research Centre for Geosciences, 14473 Potsdam, Germany
[b] LabMET, Coupure Links 653, 9000 Ghent, Belgium
[c] Chair of Chemical and Process Engineering, Technische Universität Berlin, 10623 Berlin, Germany

HIGHLIGHTS

- ▶ Early warning indicators (EWIs) for over-acidification.
- ▶ EWI-VFA/Ca: concentration ratio of volatile fatty acids to calcium.
- ▶ EWI-PO_4/Ca: concentration ratio of phosphate to calcium.
- ▶ EWI-PO_4: concentration of phosphate.

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ABSTRACT

Early warning indicators for process failures were investigated to develop a reliable method to increase the production efficiency of biogas plants. Organic overloads by the excessive addition of rapeseed oil were used to provoke the decrease in the gas production rate. Besides typical monitoring parameters, as pH, methane and hydrogen contents, biogas production rate and concentrations of fatty acids; carbon dioxide content, concentrations of calcium and phosphate were monitored. The concentration ratio of volatile fatty acids to calcium acted as an early warning indicator (EWI-VFA/Ca). The EWI-VFA/Ca always clearly and reliably indicated a process imbalance by exhibiting a 2- to 3-fold increase 3–7 days before the process failure occurred. At this time, it was still possible to take countermeasures successfully. Furthermore, increases in phosphate concentration and in the concentration ratio of phosphate to calcium also indicated a process failure, in some cases, even earlier than the EWI-VFA/Ca.

1. Introduction

Biogas formation is a complex process that depends on a large number of interactive factors. Despite many decades of research, many aspects are not completely understood. Therefore, full-scale biogas reactors are still regarded as “black boxes” and are often operated at suboptimal organic loading rates (OLRs) to prevent process failures. Hence, one-stage continuously stirred tank reactors in commercial waste treatment plants are typically operated at OLRs of 1–4.5 kg VS m^{-3} d^{-1} (Bischofsberger et al., 2005; Ahmad et al., 2011; FNR, 2005). Developing a comprehensive understanding of this process is the key to optimize the reliability of the plant performance and the economy. It will help to increase the eco-balance of the entire process, because the failure risks will be decreased considerably.

Process failures, such as the excess accumulation of fatty acids, can be provoked by organic overloads as well as by different inhibitors (e.g. heavy metals, sulfides, ammonia and other toxic substances) (Pender et al., 2004; Tada et al., 2005; Chen et al., 2008; Braun et al., 1981; Karakashev et al., 2005). When an inhibitor exceeds its critical concentration, typically the methanogens are inhibited first. This results in an accumulation of acetic acid, an increase in the hydrogen partial pressure and a decrease in the methane content. If the hydrogen partial pressure exceeds 0.1 mbar

Abbreviations: CaO, calcium oxide; Ca, calcium; EWI, early warning indicator; LCFA, long chain fatty acid; OLR, organic loading rate; PAO, phosphate accumulating organism; PO_4, phosphate; VFA, volatile fatty acids; VS, volatile solids.

* Corresponding author. Tel.: +49 331 288 1516; fax: +49 331 288 1450.
E-mail addresses: Anne.Kleyboecker@gfz-potsdam.de (A. Kleyböcker), Liebri@gfz-potsdam.de (M. Liebrich), Willy.Verstraete@UGent.be (W. Verstraete), Matthias.Kraume@tu-berlin.de (M. Kraume), Wuerdemann@gfz-potsdam.de (H. Würdemann).

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(Harper and Pohland, 1986), then acetogenic bacteria are inhibited which leads to an accumulation of propionic acid. Propionic acid further inhibits the methanogens. Due to the inhibition of both acetogenesis and methanogenesis, the products of the hydrolysis and acidogenesis (e.g. long and short chain fatty acids) begin accumulating. Hence, the pH and the gas production rate decrease further. This process failure will subsequently be called "over-acidification" in this article.

Process monitoring parameters, such as the biogas production rate and the gas composition, are measured at 60–70% of all full-scale biogas plants in Germany. By the time the parameters indicate a process failure, it is often too late to stabilize the process efficiently (Schüsseler, 2008). In full-scale plants, the fatty acid concentration is primarily monitored after a process failure, while the hydrogen partial pressure is not monitored at all. A survey of 400 full-scale biogas plants in Germany revealed that the redox potential was determined in the reactor only in two biogas plants (Weiland, 2008).

In several studies, various parameters (e.g. the redox potential, the volatile fatty acid (VFA) concentration, the hydrogen partial pressure and the ratio of volatile fatty acids to the total amount of inorganic carbon (determined by titration and referred to as the FOS/TAC value)) have been investigated in search of a suitable early warning indicator for process failure due to the accumulation of VFAs (Allman et al., 2007; Boe, 2006; Chynoweth et al., 1994; Pind et al., 2003; Prechtel et al., 2006; Rieger and Weiland, 2006). In each case, either the parameters were not suitable as an early warning indicator or they required uniform conditions in the substrate matrix and feed to allow for a reliable interpretation. Because the substrate matrix of most waste digesters varies widely in its composition, the methane content is quite variable due to fluctuations in the energy content of the substrate mix, thereby making it difficult to detect a decrease in the methane yield due to an imminent process failure.

The aim of this work was to develop universal early warning indicators (EWIs) that are reliable, easy to measure and allow sufficient time to undertake the appropriate countermeasures successfully.

In previous experiments, the addition of calcium by the supply of CaO contributed significantly to the recovery of a biogas formation process after an excess accumulation of fatty acids, and this concept was identified as an efficient measure to stabilize the biogas formation processes (Kleyböcker et al., 2012). The calcium formed insoluble salts with long chain fatty acids (LCFAs), and the amount of phosphate that was very likely released from the phosphate accumulating organisms (PAOs) during the VFA uptake after their accumulation. The precipitates aggregated with the microorganisms. These aggregates provided more favorable conditions for the acetogenesis and the methanogenesis. In addition, LCFAs seemed to adsorb on the surface. Thus, the fatty acid concentration decreased significantly, and the biogas formation process recovered. From this concept, it follows that the decrease in calcium concentration may indicate the beginning of a process failure due to the accumulation of VFAs and the subsequent calcium precipitation with phosphates and LCFAs. Taking into account the nature of VFAs as process indicators, the ratio of VFAs to dissolved calcium was chosen to investigate its applicability as an EWI. Furthermore, the phosphate concentration was monitored because the amount of phosphate released by the PAOs during the accumulation of fatty acids may also serve as an EWI.

2. Methods

Altogether, nine experiments (OA1–OA9) were conducted to provoke process failures and to study the process recoveries. The OLR was increased until the VFA concentration increased and the biogas production rate decreased. In experiments OA7–OA9, CaO was added to prevent the biogas formation process from a threatening failure.

2.1. Laboratory-scale biogas digesters

Each reactor contained 23 L of sludge (Fig. A1 in Kleyböcker et al., 2012). The reactors were maintained at 50 °C by a thermostat (Thermo Haake B7, Phoenix II) connected to a heating coil that was placed around the reactor. The sludge was mixed pneumatically using biogas at a flow rate of 150 L h^{-1} each day for 15 min before the samples were withdrawn and 15 min after the substrate was introduced. For the biogas recirculation, a KNF N86KTE membrane vacuum pump was used. For substrates, sewage sludge and rapeseed oil were used and were charged manually every day. The sewage sludge consisted of excess and primary sludge from a wastewater management plant applying EBPR (enhanced biological phosphorus removal). Rapeseed oil was chosen as a co-substrate due to its high LCFA contents, such as oleic acid (52–67%), linoleic acid (16–25%) and linolenic acid (6–15%), and because LCFAs are frequently found in actual wastewaters (Komatsu et al., 1991). The OLR depended on the state of each experiment. While the amount of rapeseed oil varied between 0 and 9 kg VS m^{-3} d^{-1}, the daily sewage sludge load was nearly constant, with rates between 1.0 and 1.2 kg VS m^{-3} d^{-1}. The hydraulic residence time was between 20 and 23 days, depending on the OLR. The volume of the produced biogas was measured with a gas meter (Ritter TG05/5).

For the analysis of the digested sludge, samples were withdrawn at the reactor outlet. The biogas samples were withdrawn from a bypass of the gas pipe between the gas outlet and the gas wash bottle.

2.2. Wet chemical and gas analyses

The temperature and pH were measured in the digested sludge samples with a WTW pH 340i, using a Sen Tix 41 pH electrode.

For the total solids (TSs) and volatile solids (VSs) analyses, the samples were dried at 105 °C in a drying chamber (Memmert) for 24 h and then burned at 550 °C (Nabertherm Controller B170). The sample weights were determined by a Sartorius CP220S-OCE weighing machine. The TS and VS were analyzed according to the German guideline DIN 38409-1.

The concentrations of VFAs (LCK 365), phosphate (LCK 350) and calcium (LCK 327) in solution were determined photometrically (Hach-Lange DR2800) after the samples had been centrifuged twice at 10,000 rpm for 10 min (Eppendorf Centrifuge 5804).

The phosphate concentration was not monitored from the beginning of this study because it was found to be an important parameter only after most of the experiments had already been conducted. Therefore, the phosphate concentration was only determined punctually in certain retained reference samples.

The volatile short chain fatty acid ($C_2H_4O_2$ to $C_5H_{10}O_2$) concentrations were determined by ion chromatography (IC) equipped with an AS11-HC column (DIONEX ICS 3000, CA, USA). Sodium hydroxide was used as the eluent. The gas composition was analyzed by gas chromatography (GC) (SRI 8610C; SRI Instruments, Torrance, USA). The GC was equipped with a thermal conductivity detector, a silica gel column and a 13× mole sieve column (SRI, USA) using argon as the carrier gas. The measured gas components were hydrogen, oxygen, nitrogen, methane and carbon dioxide.