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Counteracting foaming caused by lipids or proteins in biogas reactors using rapeseed oil or oleic acid as antifoaming agents

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ABSTRACT

Foaming is one of the major operational problems in biogas plants, and dealing with foaming incidents is still based on empirical practices. Various types of antifoams are used arbitrarily to combat foaming in biogas plants, but without any scientific support this action can lead to serious deterioration of the methanogenic process. Many commercial antifoams are derivatives of fatty acids or oils. However, it is well known that lipids can induce foaming in manure based biogas plants. This study aimed to elucidate the effect of rapeseed oil and oleic acid on foam reduction and process performance in biogas reactors fed with protein or lipid rich substrates. The results showed that both antifoams efficiently suppressed foaming. Moreover rapeseed oil resulted in stimulation of the biogas production. Finally, it was reckoned that the chemical structure of lipids, and more specifically their carboxylic ends, is responsible for their foam promoting or foam counteracting behaviour. Thus, it was concluded that the fatty acids and oils could suppress foaming, while salt of fatty acids could generate foam.

1. Introduction

Nowadays, increasingly more biogas plant operators raise the necessity in finding efficient and cost effective antifoaming solutions for the biogas plants in order to avoid the dramatic consequences of foaming incidents (Barber, 2005; Ganidi et al., 2009). Foaming occurs intermittently in the biogas plants, lasting from one to three weeks, resulting commonly in 30–50% biogas production loss and typically occurs up to three times per year (Kougias et al., 2014a). The causes of foaming in biogas reactors have been previously investigated, identifying the feedstock composition, the organic overload, and the presence of specific microorganisms as the main causes for foam formation (Dalmau et al., 2010; Kougias et al., 2014c; Moeller et al., 2015). The generated foam in biogas plants is termed as metastable, which means that theoretically might persist "indefinitely" if it is absolutely protected from external disturbances (Vardar-Sukan, 1998). Therefore, an efficient antifoaming action should be applied in order to destabilise the formed foam.

The most commonly applied solution to suppress foaming in biotechnological processes is the addition of antifoams. Antifoams are defined as surface active chemical substances that, when dispersed in the foaming media, will destroy the foam by causing bubble coalescence (Junker, 2007). Several

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chemical antifoams are available in the market with varying degrees of foam destruction effectiveness (Moeller et al., 2012).

The antifoam efficiency is depending on many parameters and it is well known that a certain antifoaming agent may not be suitable for every application (Routledge and Bill, 2012). In a recent study, it was reported that the usage of commercial antifoams did not have any successful effect on combating foaming in a mesophilic two-stage biogas plant in Germany (Moeller and Görsch, 2015). One important parameter defining the suitability of the chemicals to be used as antifoaming agents, especially for biological process, is their toxicity. A clear example is the use of tributylphosphate (TBP). TBP is polar oil that showed excellent antifoam efficiency in various processes (Privitera et al., 2014). However, when TBP was applied in anaerobic digestion systems for biogas production, fatal inhibition of methanogenesis was recorded both in batch and continuous feeding reactors (Kougias et al., 2014b). This indicates that the chemical composition of the antifoams is important in order to avoid negative impacts and deterioration of the process. However, the specific chemical composition of the antifoams is usually not provided by the suppliers, but only their general description, and thus, several compounds should be tested in order to select the most efficient one for each specific application.

According to the manufacturers, many marketable types of antifoams, suitable for bioprocesses, are derivative of fatty acids or oils. However, it has been previously found that lipids can induce foaming in manure based biogas plants (Kougias et al., 2013a). Therefore, this contradicting behaviour of lipids to act as foam promoters or suppressors needs to be further investigated.

Another important issue that should be taken into consideration is the cost of antifoams application, which depends on both the price of the chemical and the required dosage. Moreover, the efficiency of antifoaming agents is directly linked with the applied dosage. It has been previously documented that each antifoaming agent pose its own optimal concentration that has to be added in the foaming media, below which has reduced efficiency, and above which it may act as foam stabilizer (Karakashev and Grozdanova, 2012). Nevertheless, according to the antifoam product specifications from manufacturers, an indicative typical dosage of commercial antifoams suggested for bioprocesses is 0.1% v/v (Kougias et al., 2013b).

In practice, antifoams are applied in two different ways in full-scale biogas plants; either by mixing the antifoam with the substrate in the pre-storage tank before feeding, or by spraying the antifoam directly on top of the liquid/foam surface inside the reactors. The biogas plant operators should select an antifoaming solution based on its price, response time, biodegradability and environmental impact since the digester effluent is normally applied as fertilizer on farmland (Kougias et al., 2013b).

The effect of four different antifoaming agents on foam suppression and process performance in overloaded reactors had been investigated in our previous study (Kougias et al., 2014b). It was found that rapeseed oil, oleic and octanoic efficiently suppressed foaming caused by carbohydrate overload in biogas reactors. Moreover, they were found able to suppress foaming in biogas reactors treating lipid or protein rich manure substrates (Kougias et al., 2015). In the present work we extensively further investigated the effect of two antifoams on foam suppression and process performance in reactors fed with lipid- or protein-rich substrates. The chosen antifoams were rapeseed oil and oleic acid, which had shown the strongest antifoaming potential in our previous investigation. The aim of this study was to evaluate the suitability of these antifoams for suppressing foam that was caused by lipids or proteins. It was especially important in the case of lipids, as they can both cause and counteract foaming, and therefore it is important to elucidate which is the active mechanism for foaming and antifoaming effect. The effect of the antifoaming agents on the biomethanation process was investigated both in batch assays and in continuous reactor operations. The research was performed under thermophilic temperature, as this is the typical operating condition for most of the biogas plants in Denmark. It should be noted that lipids in the form of free fatty acid (oleic acid) and natural oil (rapeseed oil) were applied as antifoams, while lipid in the salt form (Na-Oleate) was used as foam promoter. This was based on the hypothesis that lipid (Oleate) can act as foam promoter when added as fatty acid salt (Na-Oleate, which is basically a soap), while acting as antifoam when added in the form of fatty acid (oleic acid), due to the difference in the carboxylic ends in their chemical structure. Therefore, an additional aim was to elucidate the reason for the opposite behaviour of these lipid compounds.

2. Materials and methods

2.1. *Feedstock characteristics and preparation*

The inoculum used in the experiment was digested manure obtained from a thermophilic anaerobic reactor of Snertinge biogas plant, Denmark. The feedstock was dairy cattle manure supplemented with lipids or proteins. The cattle manure was stored at −20 °C and thawed at 4 °C for 2–3 days before use. The characteristics of the raw cattle manure are presented in Table 1. The raw cattle manure was mixed with Na-Oleate (≥99%, Sigma–Aldrich) at a concentration of 12 g/L, or 9 g/L gelatine (Fluka Chemika), to be used as a representative of the lipid- or protein-rich substrates, respectively. The concentrations of Na-Oleate and gelatine used in this study were based on our previous study, in order to ensure persistent formation of foam (Kougias et al., 2013a).

Table 1 – Cattle manure characteristics.

Parameter	Unit	Values
pH	–	7.3 ± 0.04
Total solids (TS)	g/L	61.6 ± 0.4
Volatile solids (VS)	g/L	48.1 ± 0.4
Total Kjeldahl Nitrogen (TKN)	g-N/L	2.87 ± 0.18
Ammonium Nitrogen (NH_4^+)	g-N/L	1.74 ± 0.13
Total Volatile fatty acids (VFA)	g/L	7.77 ± 0.53
Acetate	g/L	5.44 ± 0.4
Propionate	g/L	1.39 ± 0.09
Iso-butyrate	g/L	0.12 ± 0.01
Butyrate	g/L	0.55 ± 0.02
Iso-valerate	g/L	0.18 ± 0.01
Valerate	g/L	0.06 ± 0.00
n-hexanoate	g/L	0.02 ± 0.00