

Examination of commercial additives for biogas production

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Abstract. The formation of biogas from biomass is a complex process with a multitude of variable process parameters. Stability of biogas production and production rate can be vastly improved by keeping these parameters close to their optimum. One possibility to achieve this is by use of additives. In Germany alone there currently are over 250 additives on the market which demonstrates the demand for optimisation of biogas plants. The effects of these additives are hardly investigated and can only be evaluated by costly, time consuming tests (e.g. continuous anaerobic digestion experiments). A new, fast and easy to handle method was developed to evaluate some of the effects of additives. To verify the method trace elements, organic acids, FOS/TAC, ions and cations were quantified. Three additives were tested: The addition of a commercial zeolite increased biogas production by 15%. Calcium carbonate increased performance by 8% after 16 days. No negative effect on biogas production could be observed for the addition of 0.03 and 0.06 g l⁻¹ of iron(III) chloride, commonly used to reduce hydrogen sulphide concentration in biogas.

Key words: biogas, additives, zeolite, iron(III) chloride, calcium carbonate.

INTRODUCTION

Biogas production is a well-established conversion technology to obtain energy from biomass. Over 14,000 plants produce 13.4 million tons oil equivalents (toe) primary energy (52.3 TWh electricity, 432.4 ktoe heat for district heating networks and 2,010 ktoe heat consumed at the plant site) in the European Union and Switzerland (EurObserv'ER, 2014). In spite of the number of plants and the years of experience a multitude of problems still occurs. This might be due to missing monitoring instruments and equipment, the plant operator's lack of knowledge or the lack of knowledge transfer from research to application. Additives promise to enhance stability or/and performance or can be used as an emergency measure to avoid collapse of the conversion process. A study conducted by Henkelmann et al. (2012) shows that there are more than 250 additives available in Germany (Germany: 7,960 biogas plants in operation). Compared with the number of biogas plants this figure demonstrates that biogas plant operators are still facing a multitude of problems and challenges.

Additives can be classified by their main ingredients and main function: Inorganic nutrient and trace element mixtures are often prepared individually for each plant to increase stability and performance by supplying the ideal concentration of trace elements for anaerobic digestion. Since ideal concentrations depend on biocenosis and feed different optima, minima and maxima have been found by research teams, effects vary

as well (Chen et al., 2008; Demirel & Scherer, 2011). pH stabilizers are used to avoid or to reduce fluctuations of the pH which is crucial for a stable process. Additives reducing the concentration of ammonia or hydrogen sulphide are also widely in use. Both substances pose a challenge for biogas purification and can lead to corrosion in the CHP. They also can inhibit anaerobic digestion at high concentrations. Anti-foaming and anti-floating-layer agents are another large group of additives that do not affect the bacteria directly but increase the performance of the digester. Few additives based on enzymes, algae and special microorganisms are on the market.

With such a multitude of different additives on the market it is nearly impossible for the plant operators to choose, especially since effects of the additives promised by the manufacturer are hardly ever verified or in some cases not verifiable at a plant scale (e.g. process stability). To verify the effects on lab scale large scale continuous digesters fed with a variety of substrates would be needed. Thus the aim of this study is to provide a simple, cheap and fast test to quantify some effects of additives.

MATERIALS AND METHODS

Examined additives

A commercially available zeolite dotted with trace elements was used in the concentration suggested by the manufacturer (3.4 g l⁻¹). Zeolites work as a buffer, ion exchanger and provide a high surface for biofilms. To determine the amount of trace elements in the zeolite 3.4 g of the zeolite were incubated in 1 l HPLC grade water at 37.5 °C for 24 h. The liquid contained 0.54 mg l⁻¹ Al, 0.18 mg l⁻¹Co, 0.26 mg l⁻¹ Cu, 3.94 mg l⁻¹ Fe, 0.44 mg l⁻¹ Mn, 0.34 mg l⁻¹ Ni, 6 mg l⁻¹ Na, 10 mg l⁻¹ K, 23 mg l⁻¹ Mg and 84 mg l⁻¹ Ca (determined as described below).

Calcium carbonate (99%, particle size 1 µm, Carl Roth) was used to differentiate the effects of the zeolite. It works as a buffer at pH 6.2 to 8.3 and could be added in excess (10 g l⁻¹) due to its low solubility to simulate the surface provided by zeolite.

Iron(III) chloride (98%, Merck) is often used to reduce the concentration of H₂S in biogas and is commercially available under many brand names from different manufacturers. Concentrations were calculated according to the sulphur contained in the samples: 30 mg l⁻¹ was the amount needed to bind all sulphur in the substrate. Additionally a concentration of 60 mg l⁻¹ was tested to evaluate any possible inhibition.

Substrate used for biogas tests

Unseparated material from the main digester (a 1,000 m³ horizontal digester) from a biogas plant in Upper Austria was used in this study. The substrate was stored for less than 24 h at 37.5 °C before being used. The plant was running stable during, before and after the material was taken. The main digester was fed with 80% maize silage and 20% grass silage without any additives. Dry matter (DM) content was stable at 7.19–7.43% while ash content slightly changed from 24.98% DM for the first batch to 25.95% DM for the second batch.

The biogas plant was part of an intensive monitoring program from November 2012 to August 2013 (weekly samples from main digester): 12–14.5 t (mean 13.11 t) of maize and grass silage were fed daily resulting in 135–175 m³h⁻¹ (mean 159.38 m³ h⁻¹) biogas (45–55.9% methane; mean 49.15%). DM content of the main digester ranged from 6.4 to 11% (mean 8.71%) and ash content varied between 28.98 and 18.89% DM (mean 21.96%). pH value was between 7.03 and 8.57 (mean 7.57) and FOS/TAC between 0.208 and 1.154 (mean 0.459). Acetic acid concentration varied between 0 and 1.152 g l⁻¹ (mean 0.24 g l⁻¹). Ca²⁺ concentration ranged from 72 to 468 mg l⁻¹ (mean 196.95 mg l⁻¹) and Fe from 13.5 to 52.7 mg l⁻¹ (mean 40.09 mg l⁻¹).

Biogas batch test

Biogas production was determined gravimetrically using 1 l plastic bottles with fermentation locks. This gravimetric method is common to determine the ethanol production during fermentation and has been established and validated for the determination of biogas potentials in the labs of the University of Applied Sciences. For standard biogas potential batch tests the separated digester material (after 10 days at 37.5 °C to reduce its gas production) would only be used as inoculum. To this inoculum a defined amount of biomass would then be added to determine its biogas potential. In this study the unseparated material of the main digester was used as both the inoculum and the substrate to simulate a biogas plant.

500 ml of the unseparated main digester content was filled into each bottle, incubated at 37.5 °C ± 0.5 in a climate chamber for 16 days and the weight was determined daily (AND GX-4000, accuracy ± 0.01 g) after shaking the bottle. Each batch consisted of 57 bottles: 18 with substrate taken from the main digester (blank), 18 for each of the two additives tested in one batch and 3 filled with water (water blank) to estimate the mass loss by evaporation. Every second day 6 bottles (2 each) were stopped and the content analysed.

Dry matter and organic dry matter

To determine the dry matter the sample was homogenized, put into crucibles (12 g per crucible; n = 3), oven dried at 40 °C for 24 h and then dried at 105 °C for 24 h. Ash content was determined by heating the crucibles to 550 °C for 24 h. Mass of the crucibles was determined using an analytical scale (Kern 770, accuracy ±0.00001 g).

FOS/TAC

The ratio of free organic acids (measured in acetic acid equivalents) to the total inorganic carbonate was determined according to the method published by Nordmann (1977). 50 ml of the sample was centrifuged at a rotational speed of 3,500 min⁻¹ for 15 min, 10 g of the supernatant was then diluted to 50 g with HPLC grade water and used for titration. Amount of sulphuric acid (96%, Carl Roth, c = 0.05 mol l⁻¹) needed to reach pH 4.4 (FOS) and 5.0 (TAC) was determined using a Mettler Toledo Graphix DL50.

Free organic acids and sugars

1 ml of the supernatant from FOS/TAC determination was diluted to 2 ml with eluent (sulphuric acid, 96%, Carl Roth, $c = 5 \text{ mmol l}^{-1}$) and analysed for free organic acids and sugars using an Agilent Technologies 1200 Series HPLC with a Varian Metacarb 87 H column (300*7.8 mm).

Anions and cations

Concentration of Ca^{2+} , Cl^- , K^+ , Mg^{2+} , Na^+ , NH_4^+ , PO_4^{3-} and SO_4^{2-} was determined by IC using a Dionex ICS 1000 with ASRS/CSRS suppressors. 5 ml of the sample was diluted to 20 ml with HPLC grade water and then centrifuged at a rotational speed of $3,800 \text{ min}^{-1}$ for 15 min. The supernatant was filtered (fluted filter Macherey-Nagel 615 1/4) and then diluted 1:10 (anions) and 1:25 (cations) respectively. For anions an IonPac AS12A (4*250 mm) column with an IonPac AG12A (4*50 mm) guard and a carbonate buffer eluent (sodium carbonate, Carl Roth, 99.5%, $c = 8 \text{ mmol l}^{-1}$, sodium hydrogen carbonate, Carl Roth, $c = 1 \text{ mmol l}^{-1}$) was used. For cations an IonPac CS12A (4*250 mm) column with an IonPac CG12A (4*50 mm) guard and methanesulfonic acid (99% Merck, $c = 20 \text{ mmol l}^{-1}$) as mobile phase was used.

Trace elements

Trace elements (Al, Cu, Fe, Mn, Mo, Ni, Pb and Zn) were quantified by ICP-OES: 2.5 ml of the sample were diluted to 25 ml with HPLC grade water and 0.1 ml of trace element free nitric acid (65%, Carl Roth) was added. The supernatant (after centrifugation at a rotational speed of $3,800 \text{ min}^{-1}$ for 15 min) was filtered (fluted filter Macherey-Nagel 615 1/4) and analysed with a Horiba Jobin Yvon Ultima 2.

Data for trace elements, cations and anions is only shown where significant changes or differences were detected.

RESULTS AND DISCUSSION

Zeolite and calcium carbonate (batch 1)

An incubation time of 16 days was selected to be able to evaluate the kinetics of anaerobic digestion. Biogas production increased from $8.29 \pm 0.07 \text{ g l}^{-1}$ (blank) to $8.94 \pm 0.22 \text{ g l}^{-1}$ (increase by 8%) when calcium carbonate was added and to $9.53 \pm 0.36 \text{ g l}^{-1}$ (increase by 15%) with the addition of zeolite (see Fig. 1). These results are well within the range of values found in literature: Montalvo et al. (2006) for instance have shown an increase by 11–30% when digesting swine waste with zeolites for 10–30 days in continuous digesters.

Higher increase of biogas production (by up to 110%) has been shown for the digestion of pig and poultry manure: increase of biogas production by 109.75% (batch, 44 days, 10 g l^{-1} zeolite, $36 \text{ }^\circ\text{C}$) for the codigestion of poultry and pig manure (Kougias et al., 2013), increase by 10–66% for the digestion of pig waste (batch, 15 days, $4\text{--}10 \text{ g l}^{-1}$ natural zeolite, $55 \text{ }^\circ\text{C}$, high and low organic matter content) (Kotsopoulos et al., 2008).

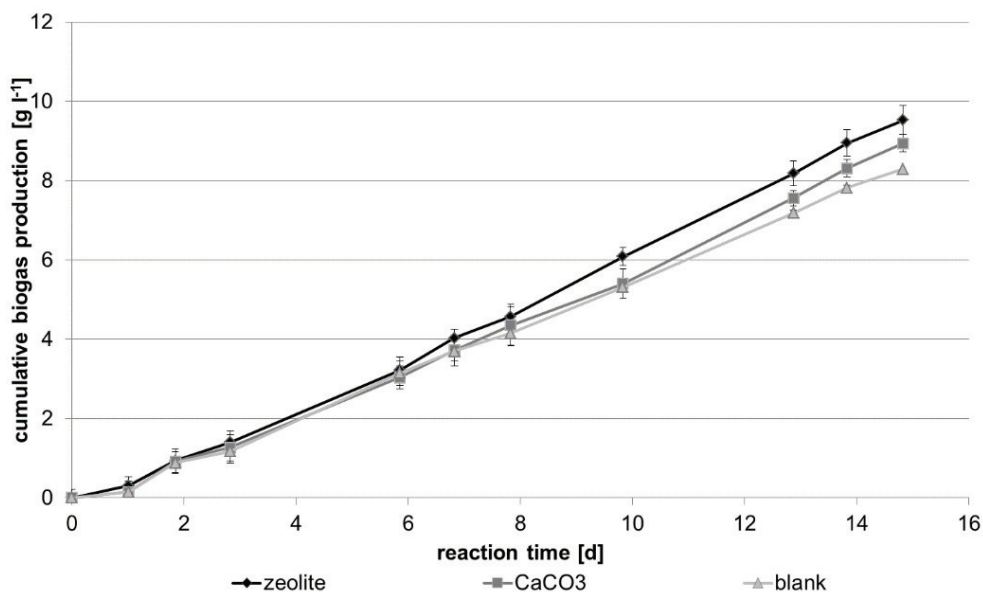


Figure 1. Cumulative biogas production for batch 1 (additives: zeolite and calcium carbonate).

Biogas results clearly show that the positive effects of zeolite exceed those of a simple buffer (calcium carbonate). The effects of zeolite as a promoter and substrate for biofilms of methanogenic archaea have been extensively studied (Milan et al., 2001, Montalvo et al., 2005, Weiß et al., 2010). It can be reasoned that the trace elements in the zeolite have a positive effect, but since the concentration is rather low (see subchapter Additives) the more likely reason is that zeolite act better as a buffer, promote biofilms and increases availability of acids and micro nutrients.

pH decreased in the first 6 days of the batch run, which is due to strong activity of hydrolysis bacteria (see Fig. 2). pH decrease is more intensive for the samples containing additives but since biogas production in this time frame is not decreased compared to the blank samples and lowest pH reached is 7.47 inhibition of methanogenesis is unlikely. pH is lower for samples containing additives during the complete batch run, which indicates a higher degradation rate of biomass. FOS/TAC confirm the strong hydrolysis in the first 6 days and indicate furthermore that degradation rate for zeolite is higher than for blank. The in comparison to zeolite and blank low value for calcium carbonate is due to the higher TAC (total inorganic carbonate) value and should be considered irrelevant for these samples.

Conversion of organic acids to acetic acid was fastest for the samples with zeolite added (see Fig. 3). Methan production rate from acetic acid was highest for zeolite and calcium carbonate while the concentration of acetic acids was stable in the blank samples between day 3 and 8 which can be an indicator for an inhibition especially since biogas production for zeolite was higher than for blank between day 6 and 8. Acetic acid concentrations are a further indicator that higher biogas yields and higher biomass throughput can be achieved by adding additives.

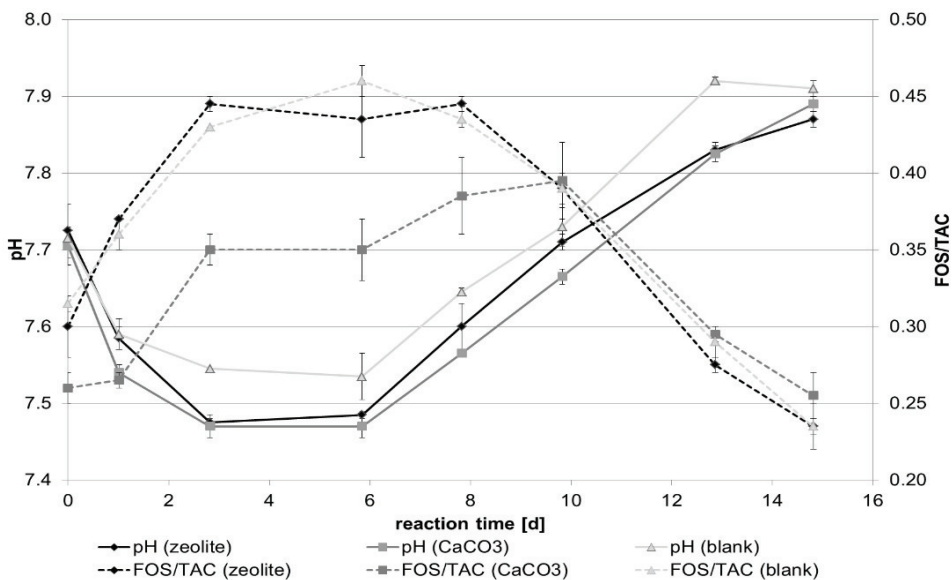


Figure 2. pH and FOS/TAC values for batch 1 (additives: zeolite and calcium carbonate).

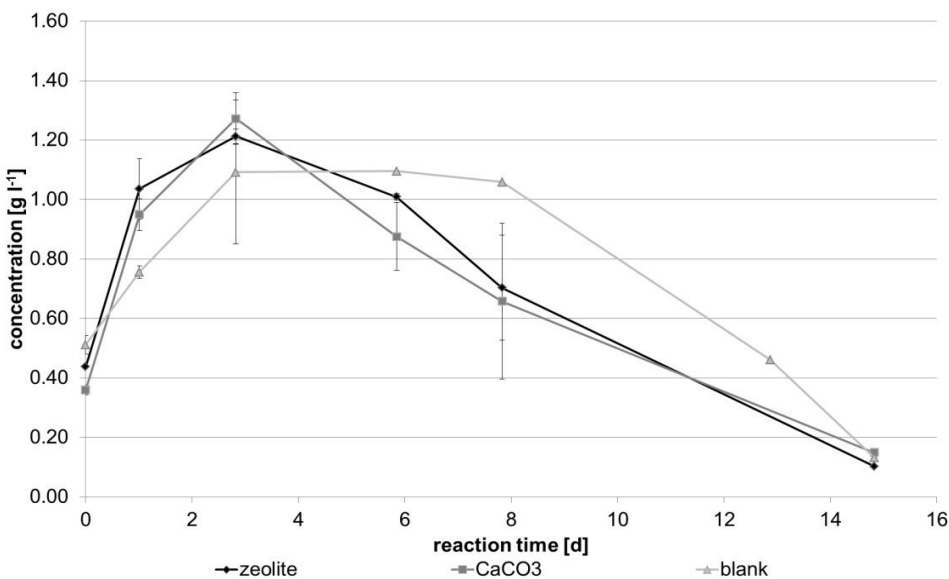


Figure 3. Concentration of acetic acid for batch 1 (additives: zeolite and calcium carbonate).

The importance and effects of trace elements have been studied extensively for numerous feedstocks on both an industrial and lab scale: Vintiloiu et al. (2012) identified concentration of Ni, Mo and S to be significant for the concentration of organic acids. Fe, Co and Na concentrations were shown to interact not directly with the concentration of organic acids but were involved in the interactions between those factors that had significant effects. Ni, Mo, S, Co and Na concentrations did not vary between blank and

additives in this test (data not shown), but iron levels were significantly higher for zeolite than for the other variations (see Fig. 4). Iron has been shown to have positive effects on methanogenic activity (Demirel & Scherer, 2011, Karlsson et al., 2012). Mn concentration is rarely studied in research, but is a cofactor for enzymes especially for hydrolysis. Concentration of Mn decreased during day 1 to 8, where hydrolysis activity was shown to be at its maximum. Concentration of heavy metals for all variations was below the detection limit. Ammonia concentration was constant between 1.3 and 1.4 g l⁻¹ for all variations. None of the trace elements, anions and cations examined in this study were above or even close to a concentration, where inhibition has been reported, but concentration of nearly all trace elements was highest for zeolite, while calcium carbonate did not always have a positive effect on trace element availability (e.g. Fe). This cannot be explained by the trace elements contained in the zeolite (see subchapter Additives), but by its ability for ion exchange.

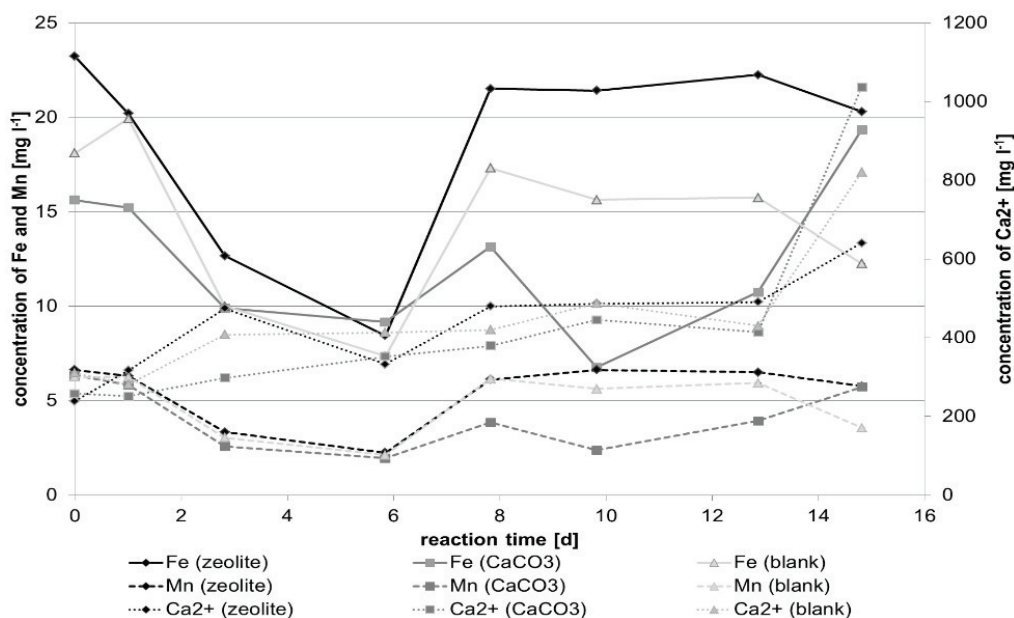


Figure 4. Concentration of iron, manganese and calcium for batch 1 (additives: zeolite and calcium carbonate).

Iron(III) chloride (batch 2)

The addition of iron(III) chloride did not result in a significant change in biogas production (see fig. 5): The blank samples produced an average of 11.06 ± 0.26 g l⁻¹ biogas, addition of 0.03 g l⁻¹ FeCl₃ led to 10.89 ± 0.37 g l⁻¹ being produced and the highest biogas production (11.25 ± 0.08 g l⁻¹) was determined when 0.06 g l⁻¹ FeCl₃ was added. Studies on the anaerobic digestion of activated sludge show a biogas reduction by 0 (Mamais et al., 1994) to 30% (Ofverstrom et al., 2011) with FeCl₃ doses at least 10 times higher. So the results of this study are within the expected range.

Biogas production increased by 2.77 g l⁻¹ compared to batch 1 for the blank samples. This might be due to changes in feed quality and composition.

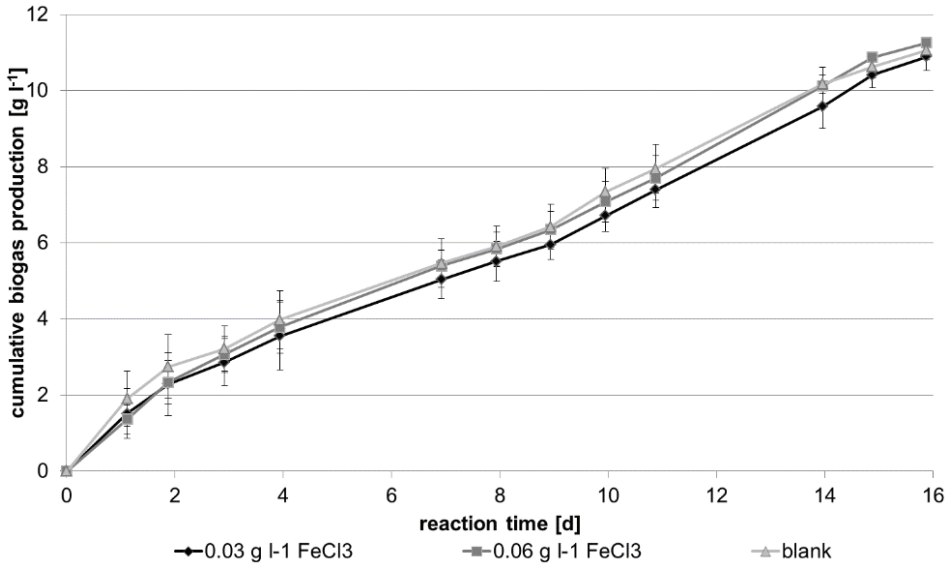


Figure 5. Cumulative biogas production for batch 2 (additive: iron(III) chloride).

Addition of FeCl₃ led to a slightly lower pH for days 4 to 16 and a higher pH on day 2 (see Fig. 6). FeCO₃ precipitation, as discussed by Mamais et al. (1994) and Ofverstrom et al. (2011), could be one reason for the lower pH. It would also explain the lower FOS/TAC values for 0.06 g l⁻¹ FeCl₃. Addition of iron(III) chloride led to an less stable pH and FOS/TAC curve with higher minima and maxima than for the blank samples.

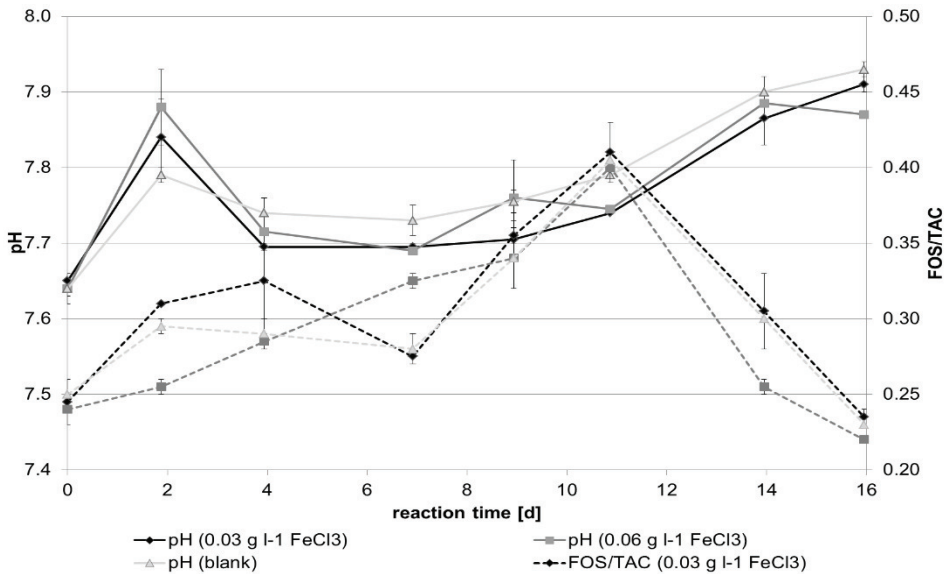


Figure 6. pH and FOS/TAC value for batch 2 (additive: iron(III) chloride).

Concentration of acetic acid was significantly higher (maximum at $1.3 \pm 0.1 \text{ g l}^{-1}$ on day 11, minimum at 0.2 on day 0) for $0.03 \text{ g l}^{-1} \text{ FeCl}_3$ than for blank and $0.06 \text{ g l}^{-1} \text{ FeCl}_3$ (maximum at $0.9 \pm 0.1 \text{ g l}^{-1}$ on day 11, minimum at 0.08 on day 0). The higher concentrations for $0.03 \text{ g l}^{-1} \text{ FeCl}_3$ could be an indicator for a slight inhibition of methanogenesis and explain the slightly lower biogas production.

SO_4^{2-} concentration decreased over time for all variations (formation of H_2S and $\text{Fe}_2(\text{SO}_4)_3$) with an unexpected peak on day 9: blank and $0.03 \text{ g l}^{-1} \text{ FeCl}_3$ samples reached a concentration of $8.6 \pm 0.4 \text{ mg l}^{-1}$ while the concentration for $0.06 \text{ g l}^{-1} \text{ FeCl}_3$ was 19% lower. On day 9 FOS/TAC was at its maximum, Fe and Mn concentrations were at their minima (see Fig. 7) and biogas production was slightly lower, which indicates high hydrolytic activity. The data suggests that addition of $0.06 \text{ g l}^{-1} \text{ FeCl}_3$ significantly reduced the concentration of SO_4^{2-} and therefore the concentration of H_2S in the biogas. Cl⁻ concentration was up to 18% higher (blank: $245\text{--}358 \text{ mg l}^{-1}$) for those samples with FeCl_3 .

Concentrations of Mn and PO_4^{3-} did not vary between the variations, but Fe concentrations were slightly higher for those samples containing FeCl_3 . Compared to batch 1 concentration of Ca^{2+} were rather frantic during batch 2 which is also reflected in a more fluctuating FOS/TAC and pH curve.

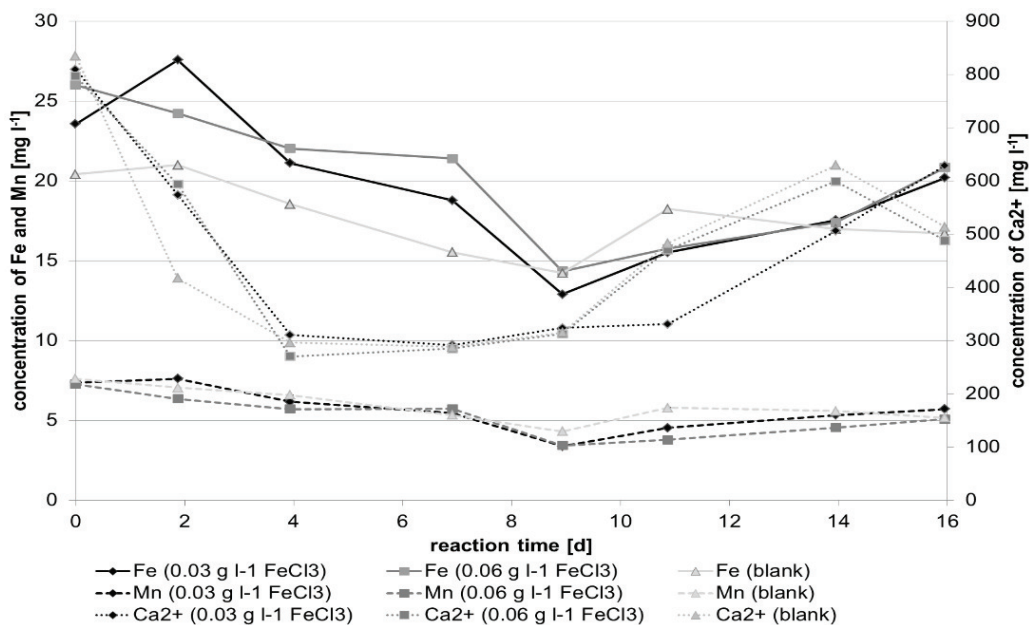


Figure 7. Concentration of iron, manganese and calcium for batch 2 (additive: iron(III) chloride).

CONCLUSIONS

The addition of a zeolite (with trace elements) significantly increased biogas production while CaCO_3 slightly increased it. Since biogas composition was not analysed it cannot be evaluated if the addition of FeCl_3 reduced the concentration of H_2S ,

but results point in that direction. No negative effect of FeCl_3 on biogas production was found, but it can be argued that it had negative effects on pH stability.

Results are within the range of findings of other researchers using more complex and expensive biogas test systems (e.g. continuous digesters). An inexpensive test system (plastic bottles, fermentation locks, a scale, and a room with constant temperature) that could be used on site was established. To evaluate the full scale of the effects and promises of commercial additives long term continuous digestion experiments would have to be carried out. The method presented allows biogas plant operators a fast and cost-effective evaluation of an additive.

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