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Sulphur binding in biogas plants using ferric salts

Almost all biogas utilization methods aim for a preferably low hydrogen sulphide content of the biogas, to avoid corrosive damages to the biogas plant components. The studies presented here show that in the biogas process hydrogen sulphide can be released not only during the conversion of organic bonded sulphur, but also through the conversion of elemental sulphur, which was previously formed during the biological desulphurisation. In the second section of the experiment, through the insertion of iron salts in the fermentation substrate, it was possible to clearly reduce the hydrogen sulphide content of the biogas by basic stoichiometric dosage. Iron sulphate however was proved to be inappropriate.

Keywords
Biogas, ferric salts, hydrogen sulphide, sulphur, sulphur precipitation

Abstract
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Biogas contains up to 1 % hydrogen sulphide (H_2S). Substrates such as liquid manure and cofermentation products (e.g. oilseed rape cake), increased use of which can be expected following the 2009 EEG Amendment, contribute to increased H_2S concentration in biogas. High sulphur content in fermentation substrate inhibits the biogas process directly, but also indirectly through precipitation of essential trace elements. Additionally, high concentrations of hydrogen sulphide in biogas through biological desulphurisation in the fermenter lead to the creation of sulphurous and sulphuric acids that can cause corrosion within gas-transporting components [1; 2].

Currently, reduction of H_2S concentration in biogas takes place mainly through biological desulphurisation directly in the fermenter. The disadvantage of this method is that, firstly, a large amount of atmospheric nitrogen is then present in the biogas. This is undesirable for subsequent preparation of the biogas to natural gas quality. Secondly, excessive introduction of oxygen can lead to formation of corrosive sulphurous acid. On the other hand, introduction of insufficient amounts of oxygen would result in insufficient reduction of biogas hydrogen sulphide content that in turn can lead to corrosion damage in central heat production plants. A further problem involves the biological reduction of hydrogen sulphide which takes place as a rule in the fermenter gas compartment. The sulphur deposits formed there break off from time to time, dropping from the fermenter cover into the substrate.

In the investigations presented here the first point to clarify is which sulphur sources contribute to the formation of the hydrogen sulphide. The subject of the second question is whether iron sulphate, iron hydroxide or iron chloride are equally suitable for the bonding of the hydrogen sulphide.

Material und methods

The investigations were conducted in laboratory fermenters with net volumes of 27 litres. A chemosensor from Awite Bioenergie GmbH (measurement scale from 0–1 500 ppm) was used for measuring hydrogen sulphide content. The quality and amount of gas was recorded once daily with the gas collected in gastight sacks from the company Tesseraux. Biogas yield was measured with an EL-FLOW mass throughflow instrument from Bronkhorst High-Tech B.V. For technical reasons the gas quality was not recorded between days 19 and 25 during the second part of the experiment.

The investigations were conducted in the thermophilic range at 50 °C. Applied as inoculum into a maize substrate was fermentation substrate from an agricultural biogas plant fed with mainly maize silage and liquid manure from cattle. The organic loading rate was 3 kg organic dry matter per cubic metre and day (kg oDM/(m^3 • d)). The inoculum was introduced to give a 40-day dwell time.

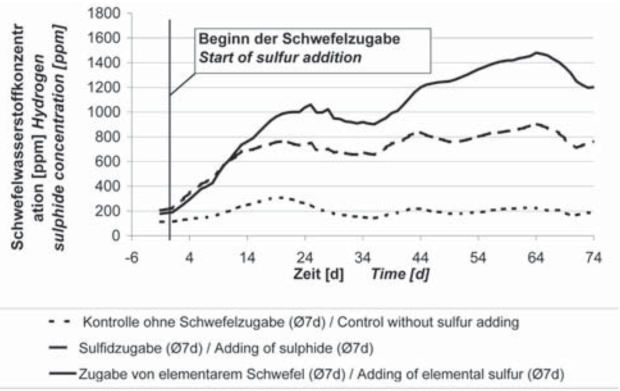
For clarification of the question whether elemental sulphur falling from the fermenter cover into the substrate can convert to hydrogen sulphide, basic sulphur was added daily to the fermentation substrate in the first part of the experiment. A variant without further sulphur addition served as control as well as a variant in which sulphur was added in the form of sodium sulphate. The addition of the sulphur was so calculated that by complete conversion of the sulphur into hydrogen sulphate it would lead to an increase in the hydrogen sulphide concentration of the biogas of around 1 100 ppm. Under the selected experiment parameters this represented approximately 3.12 g/ (m^3 • d) sulphur. Hereby was assumed that the created hydrogen sulphide transferred completely in the gas phase. The initial amount of hydrogen sulphide in the biogas created from the inoculum and the maize silage was around 200 ppm giving a maximum expected concentration of 1 300 ppm.

In the second section of the experiment the efficiency of different iron compounds in bonding sulphur was investigated. Once again the fermentation substrate from the previously mentioned biogas plant supplied the inoculum. The other process parameters also remained the same. The hydrogen sulphide content of the biogas was increased through addition of sodium sulphate. The initial hydrogen sulphide concentration was 350 ppm, the target without ferric salt inclusion at 1 100 ppm. Introduced as ferric salts were iron (III) sulphate, iron (III) chloride, iron (II) chloride and iron hydroxide.

Results

To be investigated in the first part of the experiment was which sulphur compounds in the input substrate contributed to hydrogen sulphide formation. The control variants featuring only the inoculum and the maize silage showed a stable hydrogen sulphide content in the biogas of approx. 200 ppm (**figure 1**) during the entire experiment. In the variants where additional elemental sulphur or sodium sulphide was added the hydrogen sulphide concentration in the resulting biogas increased markedly. 14 days after the initial inclusion H_2S concentration reached approx. 700 ppm. Whereas the hydrogen sulphide concentration of the variant with added sodium sulphide subsequently stabilised at a level of approx. 800 ppm, the hydrogen sulphide concentrations where elemental sulphur was added rose as high as 1 000 to 1 400 ppm.

Fig. 1



Hydrogen sulphide concentration of the biogas in the control variant and after the addition of elemental sulphur and sulphide. Laboratory flow experiment, thermophilic fermentation of corn silage and inoculum, HRT 40 d

A second set of trials was aimed at investigating whether all ferric salts were equally suitable for reducing hydrogen sulphide content. The amounts of added ferric compounds were calculated to enable complete reduction of the maximum hydrogen sulphide concentration.

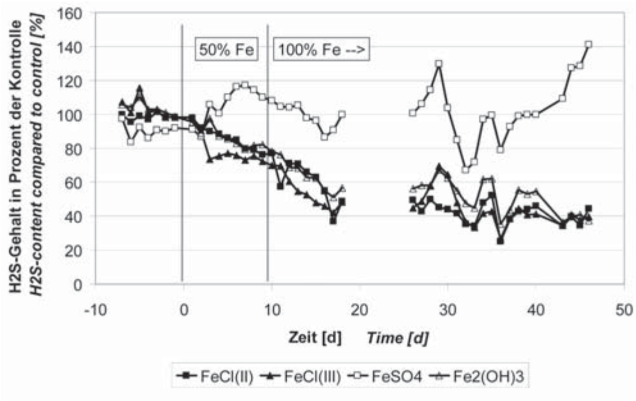
Within the experiments no appreciable differences could be determined between the divalent and trivalent ferric salts, nor between the chlorides and the hydroxide (**figure 2**). There was possibly a somewhat more rapid reduction of the H_2S content in the case of the iron (III) chloride variant. A 60 % reduction of hydrogen sulphide content was achieved with the stoichiometric equal addition of iron in the case of the chlorides and the hydroxide compared with control. Through addition of the divalent iron sulphate no noticeable reduction in hydrogen sulphide concentration could be determined. An influence of the sulphur and iron addition on methane content and yield could be determined in neither of the two conducted experiments.

Conclusions

It could be shown in the first experiment section that even elemental sulphur in the fermentation substrate of biogas plants is further reduced and therefore can serve as initial material for hydrogen sulphide formation. With that, the long-term efficacy of the biological desulphurisation needs to be discussed. Within the experiments where the amount of sulphur was the same, the addition of elemental sulphur instead of sulphide actually resulted in the highest H_2S value being measured in the biogas.

In the second section of the experiments it could be demonstrated that iron sulphate in the investigated concentra-

Fig. 2



Relative hydrogensulfide content in biogas during addition of different ferric salts compared to control. Laboratory flow-through trial, thermophilic digestion of maize silage and inoculum, HRT 40d

tions is unsuitable for the desulphurisation of biogas thus confirming earlier investigations in the state institute [3]. With all investigated variants an overstoichiometric iron introduction was required for complete hydrogen sulphide reduction. The theoretically higher sulphur binding capacity of the trivalent ferric salts could not be demonstrated within the experiment.

Literature

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