

Use of Biogas in Fuel Cells - Current R&D

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Abstract: Fuel cells are a promising alternative to conventional combined heat and power units for biogas plants. Up to now more than ten fuel cells (SOFC, PEMFC, MCFC, PAFC) fuelled with biogas or a similar gas were tested worldwide in lab and in pilot scale. One of the major problems is the irregular and changing composition of biogas. In addition to the main components, methane and carbon dioxide, it contains various harmful trace compounds such as hydrogen sulphide (H_2S) and other volatile sulphur compound (VSC). Because of their high reactivity, some of these trace gas compounds limit fuel cell performance and cause operational problems. In order to guarantee adequate durability and reliability of the fuel cell system, potential contaminants have to be identified. Biogas from different commercial biogas plants and laboratory fermenters fed with various substrates was analysed, using gas chromatography and mass spectrometry (GC-MS). Besides hydrogen sulphide also carbonyl sulphide (COS), methanethiol (MeSH), ethanethiol (EtSH), dimethyl sulphide (DMS) and carbon disulphide (CS_2) were detected and quantified and correlations could be found between the fermentation and substrate type and the amount of these trace gases in biogas. In selected cases the chronological sequence of these compounds were measured during the entire digestion process.

Keywords: Fuel cell, biogas, PEM, H_2S , VSC.

1. Introduction

Fuel cells (FC) offer promising options to generate electricity with high efficiency and low environmental pollution. In the near future fuel cells will be primarily used as off-grid batteries and for decentralized power generation in homes, farms and small business. In general fuel cells are fuelled with hydrogen mainly produced from fossil fuels, particularly natural gas. Out of the big range of biofuels the biogas seems to be most suitable because it has a high percentage of bound hydrogen and it is easy to produce, also in small scale without noise and harmful emissions, which may be important for many applications. In the recent past there were several efforts proving the applicability of biogas in principle. However, the high price and the insufficient durability of the tested FC systems prevent to exceed the stage of research and development (R&D).

Furthermore, there are three important interrelated open-end questions, namely which is the most suitable FC type for biogas, what is the content of harmful FC damaging trace gas compounds and are there any connections between this content and the type of substrates and fermenters (digesters). The last two questions are an object of current research at ATB Potsdam-Bornim (Leibniz Institute for Agricultural Engineering).

2. State-of-the-art

The principle of the fuel cell was discovered by the German scientist Christian Friedrich Schönbein in 1838. It is an electrochemical process that converts a source fuel into an electric current through reactions between this fuel (e.g. hydrogen) and an oxidant (e.g. oxygen from air), triggered in the presence of a

catalyst. Up to now several FC types were developed which are characterized by the electrolyte and the fuel. For the use of biogas are particularly interesting the Phosphoric Acid FC (PAFC), the Molten Carbonate FC (MCFC), the Solid Oxide FC (SOFC) and the Proton Exchange Membrane FC (PEMFC). These types were primarily developed for hydrogen (H_2), thus they need the conversion of biogas to hydrogen, called reforming which - depending on the FC type - may be an internal or an external process (Table 1).

Up to now more than ten fuel cell systems from 25 W_{el} to 250 kW_{el} were worldwide tested with biogas, landfill or waste water gas in lab and in pilot scale [1-7] (Figure 1). Although many investigations are focused on the SOFC it is still unclear which type is most suited for biogas. This depends not only on the



Figure 1. PEM fuel cell test stand for biogas at ATB (1 kW_{el})

Table 1. Main characteristics of fuel cell systems suitably for biogas [8-10].

Item	PAFC System	MCFC System	SOFC System	PEMFC System
Operating temperature	180-220°C	600-660°C	500-1000°C	70-200°C
Energy source	H_2 , NG, Biogas	NG, Coal- and Biogas	NG, Coal- and Biogas	H_2 , NG, MeOH (Biogas)
Hydrogen production	External reforming	Internal reform.	Internal reform.	External reforming
Catalyst poisons	CO (%), S	S, Halogens	S, Halogens	CO (ppm), S
Gas processing	Desulphurization, CO-Conversion	Desulphurization, Dehalogenization	Desulphurization, Dehalogenization	Desulphurization, CO-Conversion
System efficiency	NG: 36-40%	NG: 44-52%	NG: 35-56% (without turbine)	NG: 30-40% , H_2 : 45-60%
Start-up duration	NG: hours	NG: approx. 10 h	NG: approx. 10 h	NG: hours, H_2 : ms
Experiences	Commercial since 10 years	Commercial	Field trials	Start of commercialization
Cost target	1000 - 1250 €/kW _{el}	1250 - 1500 €/kW _{el}	1000 -1500 €/kW _{el}	500 - 1500 €/kW _{el}

H_2 : Hydrogen, NG: Natural gas, MeOH: Methanol, CO: Carbon monoxide, S: Sulphur

costs, efficiency, experience and temperature but particularly also on the tolerance of the fuel cell related to harmful gas compounds, the so-called contaminants or catalyst poisons.

Biogas contains 48-75% methane (CH₄), 25-50% carbon dioxide (CO₂), 0-4.3% oxygen (O₂), 0-16% nitrogen (N₂), 0-1% ammonia (NH₃), 0-6,000 ppm hydrogen sulphide (H₂S), 0.1-5 ppm carbonyl sulphide (COS) etc. [2-3]. With exception of methane, all the other compounds are more or less harmful to reformer and/or fuel cell and decrease the efficiency and/or the durability of the system.

In every FC system the sulphur compounds are harmful in particular. Therefore a great deal of research has been focused on hydrogen sulphide. H₂S is a very effective contaminant because very low concentration levels reduce the fuel cell performance dramatically [14-17]. However, only little information has been published on the other volatile sulphur compounds (VSC) [12-24].

3. Experimental

3.1 Experimental program

Biogas of two groups of fermenters was studied: 1st of continuous fermenters, which dominate in practise, and 2nd of batch fermenters. The biogas of the first group was obtained from seven laboratory fermenters (60-120 l) of various stages and temperatures (L1-L7) as well as from three commercial agricultural biogas plants of different types (1,250-2,650 m³; 300-500 kW_{el}) located in North East Germany (P1-P3). Different typical biogas crops and/or agricultural manures were used as substrates. The biogas samples were taken directly from the digesters and the post-digestion tanks. In order to complete the measurements, the gas composition of a mashing tank (P3) was also analyzed (Table 2).

The biogas of the second group of fermenters, of the batch fermenters, was sampled several times during the 31 days lasting tests (B1 and B2). At the beginning of the tests, gas analyses were carried out in intervals of 1 to 3 days. After two-week duration, the intervals extended due to receding gas production. The tests were made in accordance with the guideline VDI 4630 in 2 l-fermentation vessels [11]. A semi-continuously operated two-stage solid-state reactor (120 l) with bioleaching was also analyzed (BLA). Bioleaching is a special fermentation process in which the liquid phase (percolate) periodically passes through a solid substrate (Table 3).

3.2 Gas analysis

The biogas was collected in 20-l PETP sample bags from Tesseraux (Bürstadt) which were connected to the gas-sampling valve. The samples were injected in splitless mode and the temperature was increased from 50 to 220°C. These gas samples were analyzed using gas chromatography and mass spectrometry (GC-MS). The GC-MS analysis was performed with an Agilent 6890 GC system coupled with an Agilent 5975 mass spectrometer. The analyses were separated and detected with a 60 m DB1 column (dimethyl polysiloxane, 0.53 mm ID, 5 µm film thickness, Agilent, USA) followed by mass spectrometry. The mass spectrometer (MS) facilitated the identification of unknown trace compounds. In full scan mode, all masses between 2 u and 300 u were monitored and ionisation was carried out in the electron impact (EI) mode. Helium was used as carrier gas (Figure 2).

The following trace gases with the indicated detection limits were analysed: hydrogen sulphide (H₂S; 1 ppm), carbonyl sulphide (COS; 1ppm), methanethiol also known as methyl mercaptan (MeSH or CH₃SH; 2 ppm), ethanethiol (EtSH or CH₃CH₂SH; 9 ppm), dimethyl sulphide (DMS or (CH₃)₂S; 10 ppm) and carbon disulphide (CS₂; 500 ppb). The calibration parameters were established for H₂S and the other VSC samples at various concentration levels. All VSCs were obtained in a gas cylinder containing 30 ppm of each compound in nitrogen and were diluted from 30 ppm to 500 ppb for calibration. H₂S was purchased in a separate cylinder containing 300 ppm in 60% methane and 40% carbon dioxide mixture and was diluted to 1 ppm. The whole analytical procedure has been described in detail by Ellner et al. [18].



Figure 2. GC-MS system for identification and quantification of trace gas compounds.

Table 2. Sample characteristics of the analyses of continuous fermenters.

Test	Substrate	Process	Sample no.	Sampling at
L1	100% maize silage	single-stage, LF, mesophile	2	digester
L2	100% maize silage	single-stage, LF, thermophile	2	digester
L3	50% maize silage 50% cattle manure	single-stage, LF, mesophile	4	digester
L4	50% maize silage 50% pig manure	single-stage, LF, mesophile	13	digester
L5	100% rye silage	two-stage, SF with BL, mesophile	3	anaerobic filter, hydrolysis reactor
L6	100% rye silage	two-stage, SF with BL, mesophile	1	anaerobic filter, hydrolysis reactor
L7	100% rye silage	two-stage, SF with BL, thermophile / mesophile	3	anaerobic filter, hydrolysis reactor
P1	81% cattle manure 13,5% maize silage 3% grass silage 2,5% rye and barley grain	two-stage, LF, mesophile	3	digester
P2	41,3% cattle manure 58,7% maize silage	three-stage, LF, mesophile	3	post-digestion tank
P3	72,3% cattle manure 26,8% maize silage 0,9% rye grain	three-stage, LF, mesophile	2	digester,
			2	post-digestion tank, mashing tank
			2	

LF: liquid state fermentation SF: solid state fermentation BL: bioleaching (semi-continuous)

Table 3. Sample characteristics of the fermentation progress analyses.

Test	Substrate	Process	Sample no.	Sampling at
B1	100% rye silage	single-stage, LF, mesophile	9	digester
B2	100% rye silage	single-stage, LF, thermophile	12	digester
BLA	100 % rye silage	two-stage, SF with BL, thermophile/mesophile	10 10	anaerobic filter, hydrolysis reactor

LF: liquid state fermentation SF: solid state fermentation BL: bioleaching (semi-continuous)

Table 4. Volatile sulphur compounds in biogas from continuous laboratory fermenters.

Test	H ₂ S (ppm)	CS ₂ (ppm)	DMS (ppm)	EtSH (ppm)	MeSH (ppm)	COS (ppm)
L1	79 – 223	n.d.	n.d.	n.d.	n.d.	n.d.
L2	234 – 236	n.d.	n.d.	n.d.	<2 – 7	n.d.
L3	694 – 915	n.d.	n.d.	n.d.	n.d.	<1 – 3
L4	1200 – 2309	n.d.	n.d.	n.d.	n.d.	<1 – 3
L5	662 – 2589	n.d.	53	8	<2 – 396	<1 – 3
L5.H	684	n.d.	12	n.d.	53	8
L6	830 – 1931	n.d.	<10 – 71	n.d.	<2 – 177	<1 – 3
L6.H	843	n.d.	53	n.d.	180	7
L7	580 – 1336	n.d.	<10 – 23	n.d.	9 – 22	n.d.
L7.H	816	n.d.	11	n.d.	53	8

H: Hydrolysis reactor n.d.: not detected

Table 5. Volatile sulphur compounds in biogas from commercial plants.

Test	H ₂ S (ppm)	CS ₂ (ppm)	DMS (ppm)	EtSH (ppm)	MeSH (ppm)	COS (ppm)
P1.D	68-334	<0.5-4.0	n.d.	n.d.	n.d.	n.d.
P1.P	48-219	<0.5-3.0	n.d.	n.d.	<2-7	<1-2
P2.D	68-88	<0.5-0.6	<10-11	n.d.	n.d.	n.d.
P2.P	42-56	n.d.	<10-11	n.d.	n.d.	n.d.
P3.D	350-525	n.d.	n.d.	n.d.	n.d.	<1-2
P3.P	343-534	n.d.	n.d.	n.d.	<2-6	n.d.
P3.M	450-2576	n.d.	n.d.	n.d.	<2-7	4-8

D: Digester P: Post digestion tank M: Mashing tank n.d.: not detected

4. Results

4.1 Amount of sulphurous trace gas concentrations in biogas from continuous fermenters

Hydrogen sulphide (H₂S) was the most abundant sulphur species. The amount of H₂S in laboratory fermenters varied from 79 to 2,589 ppm and in the digesters or post-digestion tanks of commercial biogas plants from 42 to 534 ppm. Other sulphur compounds like methanethiol (MeSH) and dimethyl sulphide (DMS) were detected in significant concentrations in biogas from lab fermenters. MeSH was found at concentrations up to 396 ppm and DMS up to 71 ppm. Furthermore traces of carbonyl sulphide (COS) were detected (Table 4).

There is a relevant influence of the substrate's type on the concentration of hydrogen sulphide and carbonyl sulphide. Pure maize silage (L1) causes much lower mean concentrations (H₂S: 150 ppm; COS: <1 ppm) than a mixture with cattle manure (L3) or even with pig manure (L4). The biogas of the latter substrate's mixture contains 1,760 ppm H₂S and 2.0 ppm COS in average. The reasons are supposed in the different sulphur (S) content of the materials (maize silage: 0.158% S; cattle manure: 0.417% S; pig manure: 0.551% S).

In the samples from commercial biogas plants (P1-P3), the content of the volatile sulphur compounds (VSC) was lower than in laboratory samples (L1-L7). Most of the agricultural biogas plants use an internal biological desulphurisation by blowing a little amount of air into the fermenter. However, little amounts of carbon disulphide (CS₂) and carbonyl sulphide (COS) were also detected in biogas plants. The identified compounds and the concentration range tally with the results of Andersson et al. [13] and Rasi et al. [19]. Hydrogen sulphide varied between 32 and 169 ppm in samples from biogas plants with comparable substrates [19] (Table 5).

The concentration of volatile sulphur compounds depends on substrate properties and fermentation processes. The highest amounts of hydrogen sulphide, methanethiol and dimethyl sulphide were found in biogas from a semi-continuously two stage solid

state fermentation with bioleaching (L5-L7). The substrate used was rye silage. In laboratory digesters with pig or cattle manure, the H₂S content varied between 694 and 1,903 ppm.

MeSH and DMS are formed from the degradation of proteins via the release of sulphur-containing amino acids (present e.g. in manure and rye grain) and from the anaerobic methylation of sulphide [19-20]. DMS is reduced to form methane and MeSH which later forms CH₄, CO₂, and H₂S [19].

4.2 Progress of sulphurous trace gas concentrations in biogas from batch fermenters

The batch fermentation tests were operated for 31 days and constant mesophile (mesophilic) and thermophile (thermophilic) conditions were continuously kept (B1 and B2). In both cases, H₂S was the highest concentrated component with peak values of 889 ppm and 1,109 ppm respectively. Moreover, MeSH was detected in a two-digit ppm range and COS as well as CS₂ in a one digit ppm range. All compounds generated maximum concentrations at the beginning of the fermenting process. After reaching the peaks, there was a rapid decrease in concentrations, before plateau concentrations were established at the beginning of the first and second week of the process respectively (Figure 3 and Figure 4).

The concentrations of all sulphide compounds of the thermophile test exceeded the values of the mesophile test. Often the substances were longer present in the thermophile samples. According to the Arrhenius equation, the rate of chemical reaction increases with rising temperature [21-22]. Moreover, growth rates of anaerobic bacteria increase up to a certain point [22]. Higher temperatures cause a quicker degradation of the substrate. Furthermore, thermophile processing leads to faster and more effective hydrolysis of solid and fat containing substrate components. Thus, thermophile fermentation results in higher degradation rates [22-23]. The more efficient degradation of sulphurous compounds on higher process temperatures thus could relate to higher concentrations of sulphurous compounds in biogas. An additional effect is the decrease in solubility of gases, in this present case hydrogen sulphide and other VSCs, at

higher process temperatures. Consequently, under thermophile conditions (approx. 55°C) there is a higher concentration of H₂S in the gas phase, while at mesophile temperatures (approx. 38°C) there is a clearly larger ratio of compound in dissociated, dissolved form (HS⁻, S²⁻), or as non-dissociated hydrogen sulphide in the liquid phase [23].

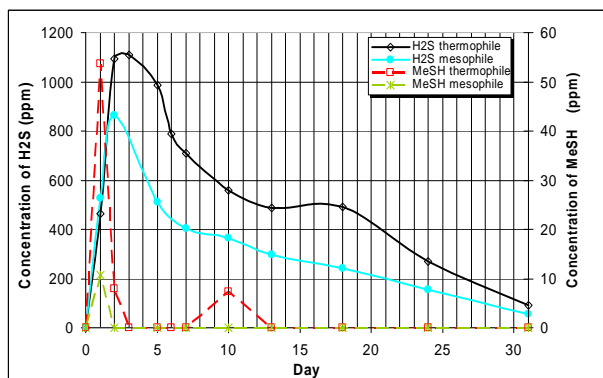


Figure 3. Course of hydrogen sulphide (H₂S) and methanethiol (methyl mercaptan, MeSH) during fermentation of rye-silage in a thermophile and a mesophile lab fermenter (Tests B1 and B2).

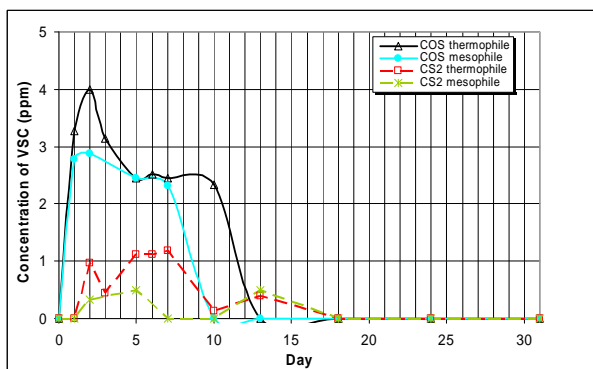


Figure 4. Course of carbonyl sulphide (COS) and carbon disulphide (CS₂) during fermentation of rye-silage in a thermophile and a mesophile lab fermenter (Tests B1 and B2).

5. Conclusion and outlook

The concentration of volatile sulphur compounds (VSC) depends on substrate properties and fermentation processes. Hydrogen sulphide (H₂S) is the most abundant sulphur species. Its content ranges from 42 to 2,576 ppm. Even in biogas produced in commercial plants, which is purified by biological desulphurization, the H₂S concentrations exceed 1,000 ppm. Methanethiol (methyl mercaptan, MeSH) and dimethyl sulphide (DMS) are found in significant concentrations of up to 400 ppm resp. up to 70 ppm. Depending on the fermenter type small amounts of carbonyl sulphide (≤ 8 ppm COS), carbon disulphide (≤ 4 ppm CS₂) and ethanethiol (≤ 8 ppm EtSH) may be also in biogas. The highest concentrations at all were measured in thermophile fermenters. There is an evident influence of the substrate type on the concentration of H₂S and COS, which may be caused by the content of sulphur in the used materials.

In contrast to the continuous fermentation, the batch process is characterized by heavy temporal variations in the gas composition. In general very high peaks of sulphurous trace gases occur during the first 10 days.

Further research will be focused on the determination and quantification of the impact of these trace gases on the durability and efficiency of PEM fuel cell systems.

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