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Cleaning agricultural biogas for high temperature fuel cells at pilot scale

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The author of this report bears the entire responsibility for the content and for the conclusions drawn therefrom.

Summary

This project aims to validate a robust sorption-based gas cleaning system, which removes the contaminants from manure-derived biogas to a degree that is suitable for high-temperature fuel cells, i.e. SOFC. Sulphur and siloxanes are critical compounds for SOFC

We present detailed results of our biogas sampling campaigns performed in 2018 at three Swiss agricultural biogas production sites to study the variation in trace contaminants affecting fuel cells and gas cleaning systems. As expected we could confirm the large variability of contaminants in the raw biogas mainly depending of the feedstock digested and the importance of removing organic sulphur.

Systems for biogas cleaning were assessed by a techno-economic survey of technically feasible options, including the consideration of supplier quotations. In a lab-based test bench using a synthetic biogas mixture, sorbents were evaluated for their capacity for dimethyl sulfide (DMS), as we consider DMS as one of the most difficult organic sulphur compounds to be removed.

A fully automated sulphur chemiluminescence detector (SCD) system was build and commissioned which allows online measurement of total sulphur at concentrations far below 0.5 ppmv. For SOFC application this concentration level is considered as the targed value for a cleaned biogas. This unique online SCD system is considered as critical for testing and evaluating gas cleaning concepts for SOFC application. This analytical system allows a fast testing of different designs and operation conditions tested at pilot scale or in the commissioning phase of demonstration plants.

Based on the sorbent selection in lab tests and on techno-economic considerations this project culminates in a pilot-scale field demonstration of biogas cleaning to a degree that should be suitable for SOFC. The best sorbent experiment performed until end of August 2019, was an experiment with SulfaTrap R7 & CuO-AC for the duration of 200 hrs. During the first 150 hrs of the experiment, no measureable sulphur breakthrough was observed after the second bed. Nevertheless further tests on sorbent materials are needed in order to prepare a scale up of a gas cleaning system. It is not yet fully clear, what the critical factors are for the observed limitation of sorbent capacity for organic sulphur. One hypothesis is that the measured capacity of sorbent material for DMS is dominated by physisorption.

This project has been extremely valuable to further improve the testing capabilities for gas cleaning systems. The application of cleaned biogas from agriculture in a SOFC is most likely one of the most difficult cases. One reason is that the cleaned biogas should not differ much from natural gas in term of gas quality, temperature and pressure. This would allow to use turn-key SOFC systems for biogas application, which have originally be designed for natural gas operation. However, this would also mean, that the biogas should be cleaned at room temperature and low pressure in order to keep the biogas cleaning system simple. From a chemical point of view of the gas cleaning increasing temperature and pressure are both advantageous for a better gas cleaning (technical, economic).

We expect that knowledge of this project will be transfer to other biogas value chains. This can be either for different end uses of the biogas, such as biogas cleaning for upgrading plants based on membrane or scrubbers as well as catalytic methanation. For each value chain a review of the specification of the end use system is needed as well as for the raw gas quality in order to select best option in sorption based gas cleaning. Given the high variance of raw gas qualities and required clean biogas qualities most likely for each value chains a dedicated gas cleaning system has to be designed. Whenever possible these gas cleaning solutions should be built on “standard building block”, which can be easily combined for specific applications.

Our project has confirmed that a fundamental understanding of all relevant processes in gas cleaning is critical for a smart design of gas cleaning systems and good collaboration between industry and academia is a key to success.

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Contents

List of abbreviations

CAPEX	Capital costs
CHP	Combined heat and power
DMS	Dimethyl sulphide
FC	Fuel cell
GC-SCD	Gas chromatograph with sulphur chemiluminescence detector
GC-FID	Gas chromatograph with flame ionisation detector
GC-MS	Gas chromatograph with mass spectrometer
KEV	*Kostendeckende Einspeisevergütung*, feed-in tariff
Micro-GC	Micro- (portable) gas chromatograph
MS	Mass spectrometer
OPEX	Operating costs
SCD	Sulphur chemiluminescence detector
SOFC	Solid oxide fuel cell
TGA	Thermo-gravimetric analyser
TPO	Temperature-programmed oxidation

1 Introduction

This project aims to validate a robust sorption-based gas cleaning system, which removes the contaminants from manure-derived biogas to a degree that is suitable for long-term operation of high-temperature fuel cells such as SOFCs, and verifies this cleaning by appropriate monitoring. In this project, the following objectives are targeted, each corresponding to a separate work package (WP):

1. **Raw gas analysis of different manure biogas and site selection for pilot plant:**
   The goal of this WP is to increase knowledge of biogas contaminant types and amounts from Swiss manure digesters, focusing on sites, which represent different manure origins and co-substrates. Results of this WP are presented and discussed in chapter 2.

2. **Techno-economic analysis of gas cleaning:**
   The goal of this WP is to perform a techno-economic analysis of sorption-based gas cleaning technologies which are appropriate for farm scales in Switzerland (5-150 kW_e). Results of this WP are presented and discussed in chapter 3.

3. **Erection and demonstration of gas cleaning test rig:**
   The goal of this WP is to demonstrate the long-duration field performance of one selected sorption-based gas cleaning system, which successfully cleans the biogas produced at one manure digestion site in Switzerland to meet SOFC requirements. Gas cleaning test rigs are explained in the chapter 4 and results in the chapter 5.

4. **Validation of total-sulphur online diagnostics system:**
   The goal of this WP is to validate a diagnostics system (sampling technique and analytical instruments) for online detection of total sulphur content at sub-ppm level, such that this system could be used in future demonstrations to monitor sulphur breakthroughs upstream of a fuel cell. Diagnostic tools are explained in the chapter 4 and results in the chapter 5.

2 Site selection and biogas sampling

2.1 Background

The types and concentrations of manure biogas contaminants depend on several site-specific parameters, as shown in Figure 1. Making a direct prediction of site-specific contaminants is not yet possible today because of the variety of factors and lack of pre-existing information. Site-specific raw gas measurements are therefore necessary.

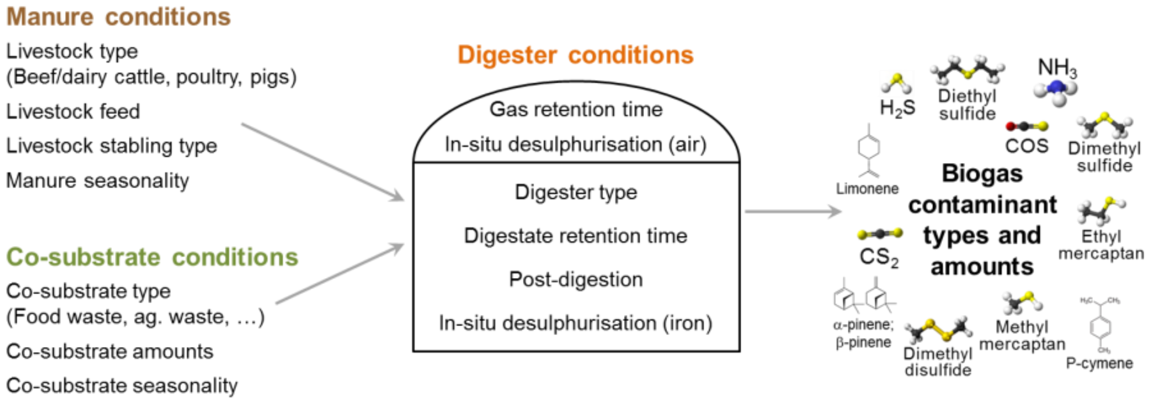

Figure 1: Variables which affect the types and amounts of contaminants in manure biogas.

One important factor in the sulphur content of agricultural biogas is whether an in-digester desulphurisation technique is used. Common techniques are the addition of small quantities of air or oxygen in the gas phases directly into the digester or gas storage, or the addition of aqueous solutions of compounds such as iron chloride into the liquid phase of the digester.

2.2 Biogas site selection

2.2.1 Types of sites

The first goal of the biogas sampling campaigns is to measure biogas contaminants from several representative types of manure-derived biogas. The second goal is to identify an appropriate site for the long-duration gas cleaning experiment within this project on pilot scale.

For the preparation of the sampling campaigns, we focus on three types of existing biogas sites based on the substrate mix:

- **Baseline cow manure:** small installation with primarily cow manure & no/few co-substrates
- **Manure origin effects:** one site with large content of chicken or pig manure
- **Co-substrate effects:** one site with a large content of co-substrates, such as food waste

A set of eight sites were identified for possible sampling campaigns, with at least two options per substrate category. Since then, the site to be sampled in each category was selected: **Hochwald SO** for “baseline cow manure”, **Wagerswil TG** for “manure origin effects” (chicken manure), and the site of SwissFarmerPower in **Inwil LU** for “co-substrate effects”. A short introduction to each site is given here.

2.2.2 Hochwald, SO

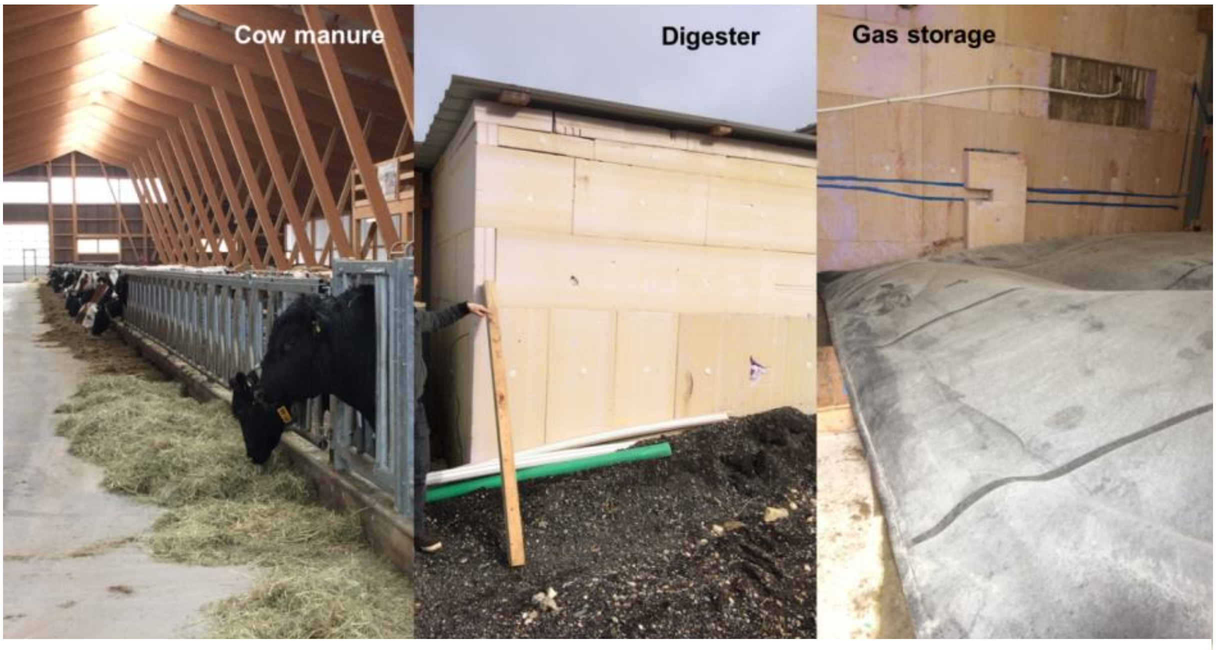

Figure 2: Overview of Hochwald site

The site at Hochwald processes dairy cow manure from around 120 cattle and no co-substrates, which makes this site of very high interest for this project. The digester system was built by the company HARAL. Air addition is used as an in-situ desulphurisation technique. A 50 kW$_e$ CHP system with an internal combustion engine is operated with this biogas. The produced electricity is sold to the grid and using the heat on site.

The first site visit at Hochwald was completed on 23rd March 2018. During this visit, we recognised that no sampling connection existed on site yet. Therefore, PSI arranged for the company HARAL, who had built the digester, to construct a sampling point to allow for biogas sampling (shown in Figure 3). The biogas sampling visit was then completed on 5th June 2018.

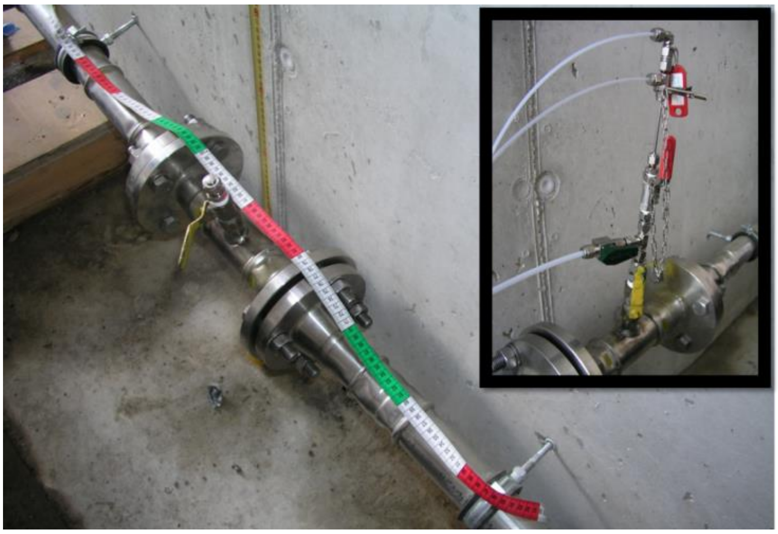

Figure 3: Sampling point built at Hochwald for this campaign

2.2.3 Wagerswil, TG

The site at Wagerswil processes chicken and cattle manure from its own operation and from neighbours', as well as some vegetable and green waste co-substrates (figure 4). Air addition is used as an in-situ desulphurisation technique. A 110 kW_e CHP unit with an internal combustion engine is operated with this biogas, and the electricity produced is sold to the grid (receiving KEV) while the heat is used on site.

The first visit at Wagerswil was completed on 30th January 2018 to assess the availability of sampling points. Sampling of biogas at Wagerswil was completed on 6-7th February 2018.

Figure 4: Overview of Wagerswil site

2.2.4 Inwil, LU

Compared to the first two sites, the site at Inwil is technically more complex, with three different digester vessels as shown in Figure 4. Two of these are wet biomass digesters, which process a mixture of pig and cow manure and a large fraction of co-substrates. The same feedstock mixture is sent to both digesters in parallel. The third is a KOMPOGAS-type dry digester. The combined biogas production from all three digesters is passed through an activated carbon filter and then upgraded to biomethane by separating CO_2 in an amine scrubber.

Figure 5: Overview of Inwil site

Each of the wet digesters uses three in-situ desulphurisation strategies at once: addition of air, addition of oxygen, and addition of $Fe(Cl)_2$ solution. The dry digester uses addition of iron hydroxide.

The sampling campaign at this site was completed on 23-24th July 2018. Biogas sampling was done at each of the two “wet digesters”, which are directly relevant for this agricultural-oriented project. To provide a basis for comparison, the mixed biogas stream from the two wet digesters and from the dry digester was sampled before and after the activated carbon filter protecting the amine scrubber.

2.3 Biogas sampling and analysis methods

2.3.1 Bulk gas composition

The bulk compounds CH_4, CO_2, O_2, and N_2 in the biogas were measured in samples of biogas collected in gas cylinders. The biogas sample was first dried by passing through a cold solvent system. This is the Liquid Quench sampling system described in Section 2.3.3. The dry biogas was then compressed to 7 bar into sample gas cylinders. In order to avoid contamination from ambient air, the cylinders were filled with argon at PSI prior to sampling, and during the sampling campaign were purged twice with biogas before taking the biogas sample on the third filling process. The gas samples were then transported back to PSI, where they were analysed by micro-GC.

2.3.2 On-site trace compound measurement

The trace compounds H_2S and NH_3 were measured on-site using commercially available Dräger indicators. Repeat measurements were performed, at least twice per sampling point, and more often if significant variability was observed.

2.3.3 Off-site trace compound measurement

The agricultural biogas was sampled using a liquid quench (LQ) sampling system, which concentrates condensable trace compounds from the biogas into a liquid solvent [1, 2]. By varying the ratio of biogas flow to solvent flow (“gas/liquid ratio”), the degree to which the trace compounds are concentrated in the solvent is varied. Samples of the solvents were taken and then analysed at PSI using a GC-SCD (for sulphur-containing compounds), GC-FID (for carbon-containing compounds), GC-MS (varied compounds), and GC-ICP-MS (for siloxanes). For each sampling point, a minimum of three samples was taken and analysed.

2.4 Results and discussion

2.4.1 Bulk gas composition

Bulk gas compositions at each of the sites sampled are shown in **Fehler! Verweisquelle konnte nicht gefunden werden.**. Methane content at these sites was between 53-58% by volume. Despite significant variation in manure origin and co-substrate content, there was not a large difference in methane content between these sites. It is worth noting that Hochwald, despite processing only manure and no co-substrates, did not have the lowest methane concentration of the three sites studied.

Table 1. Bulk gas composition at the biogas sites surveyed

% (mole/mole)	**CH_4**	**CO_2**	**N_2**	**O_2**
Hochwald	54.9	39.0	5.0	0.9
Wagerswil	53.0	43.3	3.2	0.4
Inwil, wet digester 1	57.7	40.8	1.2	0.3
Inwil, wet digester 2	56.9	41.3	1.3	0.5

In **Fehler! Verweisquelle konnte nicht gefunden werden.**, we can also see the effect of the in-situ desulphurisation strategy reflected in the nitrogen and oxygen contents of the biogas. In the case of Hochwald and Wagerswil, a continuous injection of air is used for in-situ desulphurisation of the produced biogas. By contrast, the two Inwil digesters use injection of pure oxygen and air simultaneously (as well as addition of $FeCl_2$). Pure oxygen, while markedly more expensive than direct air injection, allows in-situ desulphurisation without increasing the nitrogen content in the resulting biogas. When upgrading of biogas to biomethane is the end goal, as it is in Inwil, N_2 content must be kept low to meet natural gas pipeline specifications. The nitrogen content in the biogas in Inwil is correspondingly lower than at the other sites, and the O_2:N_2 ratio is also higher.

2.4.2 On-site trace compound measurements

The results of the on-site measurements of H_2S and NH_3 with Dräger indicators are shown in Table 2. One of the key messages to take away from this table is the large variability, and hence unpredictability, in H_2S content in agricultural biogas. Across all sites, the H_2S content varied from 2 ppmv to 1’000 ppmv. Even at a single site, large variations could be seen. At Hochwald, six H_2S measurements were taken over the course of one sampling day, and results varied between 400 and 1’000 ppmv. The two wet digesters in Inwil also had different measured H_2S contents (18 ppmv and 2 ppmv), despite processing the same feedstock under the same conditions, possibly indicative of different biology in-digester. Finally, although all sites used some form of in-situ desulphurisation technique, the resulting H_2S content was still very variable.

Table 2: Dräger tube measurements on site. The range indicates the range of all measurements performed during the sampling day.

	Hochwald	Wagerswil	Inwil, wet dig. 1	Inwil, wet dig. 2	Inwil, mixed gas
H_2S (ppmv)	400-1'000	4-10	18	2	300-330
NH_3 (ppmv)	30-53	Undetectable (<0.25)	70	70	*Not measured*

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2.4.3 Off-site trace compound measurements

An important goal of these sampling campaigns was to measure trace sulphur compounds beyond H_2S, as fuel cells are equally sensitive to sulphur atoms regardless of speciation [3]. These were quantified using a GC-SCD (sulphur chemiluminescence detector).

Additionally, several terpenes and one siloxane were quantified using a GC-FID (flame ionisation detector). Although terpenes are not expected to harm high temperature fuel cells, they can affect the gas cleaning steps through competitive adsorption or pore blockage. Siloxanes are harmful to fuel cells even at a level of 70 ppbv [4] but are usually not expected in manure-derived biogas.

Quantified compounds

A set of 21 sulphur compounds which could be expected in biogases were selected to calibrate the GC-SCD results and thus quantify the concentration of the compounds in the gases sampled. A set of 4 carbon containing compounds (alpha-pinene, para-cymene, limonene, and siloxane D5) were also selected for quantification by GC-FID.

The results of this quantification are shown in Figure 6. Shown on the left are the quantified carbon-containing compounds. None of the manure-based sites contained any detectable siloxane, as would be expected of manure-based biogas. The only site to contain measurable siloxane D5, at a barely detectable value of 20 ppbv, was the “mixed gas” sampling point in Inwil. This biogas is a mix of the manure-derived biogas and biogas derived from the dry digester. Meanwhile, the amount of terpenes increased clearly with the amount of co-substrates processed along the manure. Hochwald, which only processes manure, had effectively no quantified terpenes.

Shown on the right of Figure 6 are the sums, in ppmv of total sulphur, of all non-H_2S sulphur compounds quantified. We note that values on this plot represent minimum values. In the gas, sulphur content may be slightly higher, as a fraction of the more volatile compounds may be lost in sampling. It is known that no single sampling technique will be enough to sample all biogas contaminants fully [5]. In particular, high boiling point compounds are often not trapped well by gas-phase sampling because they have a tendency to adsorb on the walls of the sampling vessel; meanwhile, solvent- or sorbent-based sampling methods may not trap low boiling point compounds fully.

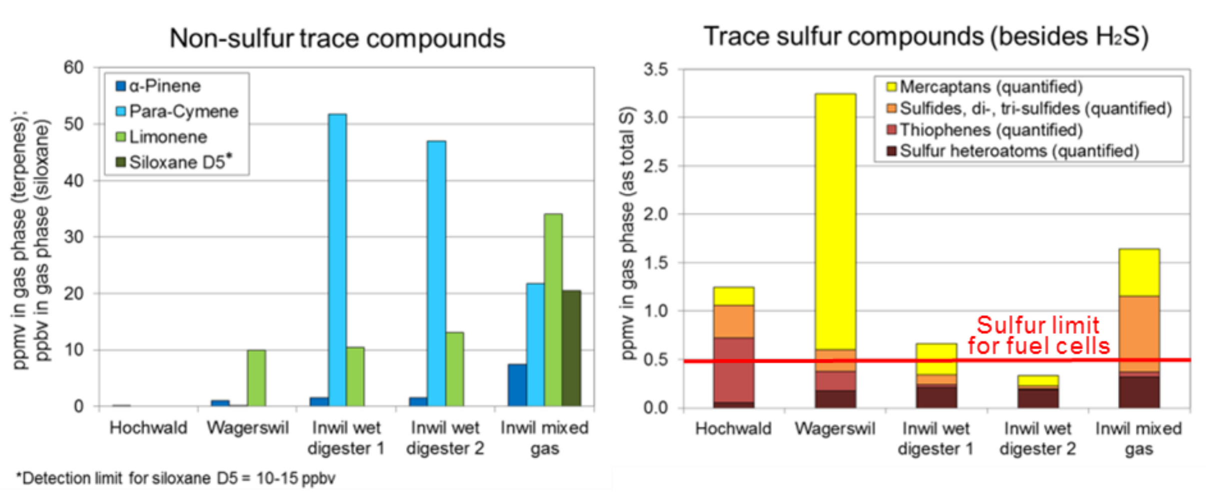

Figure 6: Quantified trace compounds sampled using the Liquid Quench sampling system and analysed using GC-SCD (sulphur compounds) or GC-FID (non-sulphur compounds).

The LQ sampling system captures a wide range of boiling points due to its trapping system at 2 bar and -20°C. However, we do not attempt to quantify trace compounds with boiling points lower than dimethyl sulfide's (38°C) using this system. Sampling efficiency tests of dimethyl sulfide in the LQ system were done in this project. The conclusion was that using gas/liquid ratios <1400 during sampling resulted in trapping >50% of 1 ppmv dimethyl sulfide in the gas phase into the liquid sample, with nearly 80% of dimethyl sulfide trapped with a gas/liquid ratio of 588. From past work with gasifier gas, it is assumed that compounds with a boiling point >80°C are fully captured in the LQ samples.

The 21 quantified sulphur compounds are plotted here based on their chemical designation. The total sulphur is therefore separated into mercaptans (R-SH), sulphides as well as di- and tri-sulphides (R-S-R, R-S-S-R, R-S-S-S-R), thiophenes (containing a C_4H_4S ring), and sulphur heteroatoms. This category includes compounds like dimethyl sulphoxide, which contain other atoms – usually oxygen or nitrogen – beyond sulphur and a hydrocarbon base. Classifying sulphur compounds in this way can be helpful for gas cleaning design. For example, many mercaptans are often removed well by H_2S sorbents, while volatile sulphides are not.

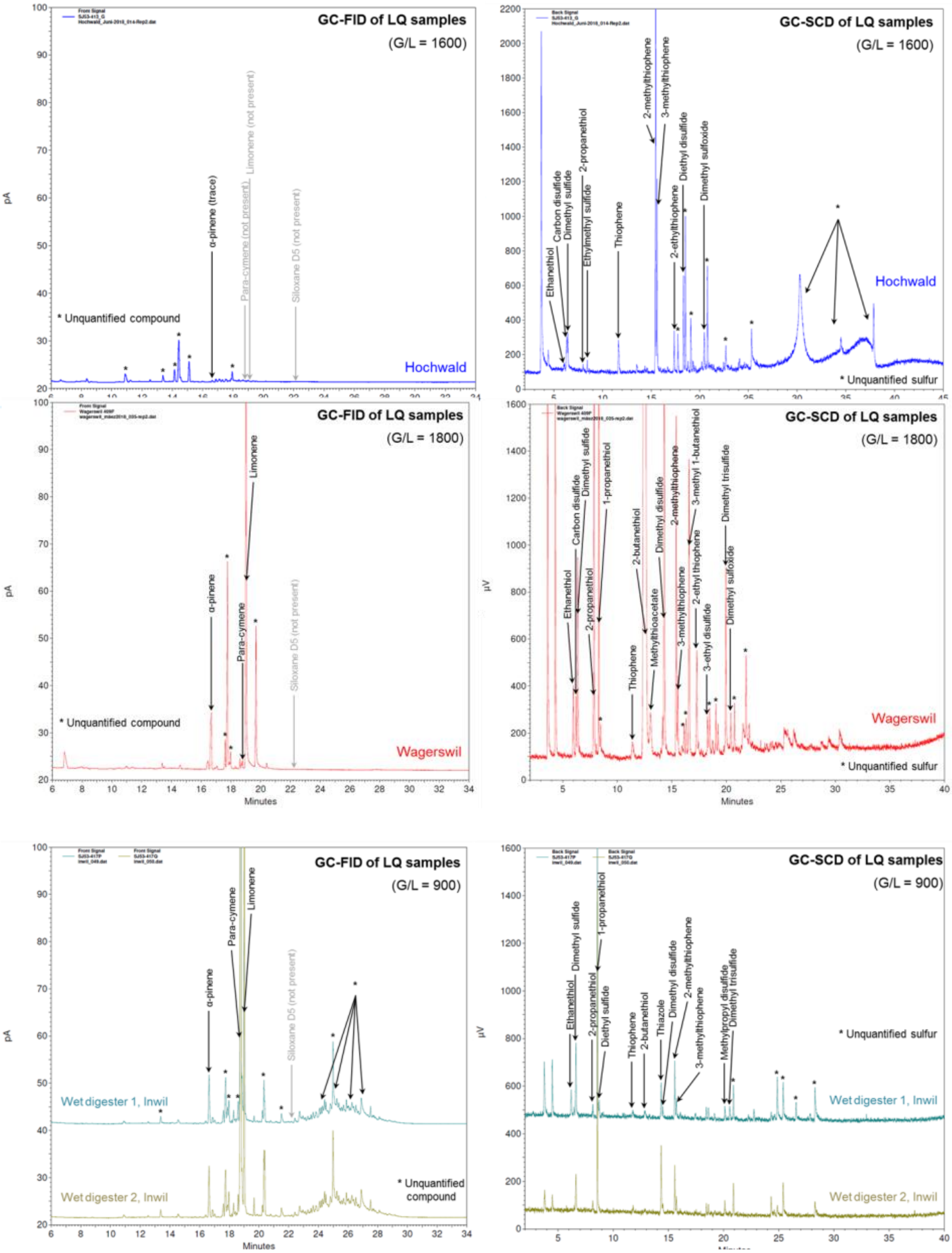

Figure 7: GC-FID and GC-SCD chromatograms of samples from the three agricultural biogas sites. Peak heights should not be directly compared because of changes in the sampling conditions (gas/liquid ratio) and in GC-SCD sensitivity between the sampling campaigns.

From Figure 6, we see that the trends in trace sulphur content do not necessarily follow the trends in H_2S content from Table 2. Although Hochwald had by far the largest H_2S content, Wagerswil had the largest quantifiable trace sulphur content. All sites sampled had total non-H_2S sulphur contents above the fuel cell limit of 0.5 ppmS, except for the second Inwil wet digester. Both Inwil wet digesters had extremely low sulphur content, both in terms of H_2S and of trace compounds. The three-fold in situ desulphurisation strategy used there may be a key reason for this.

Focusing only on quantified compounds, however, only gives a partial understanding of the biogas composition. For a more complete picture, it is worth looking at representative chromatograms.

Chromatograms

In Figure 7, we show representative chromatograms for the manure-derived biogas samples. Results from the GC-FID (carbon-containing compounds, primarily) are shown on the left while GC-SCD (sulphur compounds) are shown on the right. Each peak corresponds to at least one compound, and the quantified compounds from Figure 6 are identified by name.

The clearest trend observed here is the increase in GC-FID signal complexity with increasing fractions of co-substrates. While Hochwald has no co-substrates and a nearly clear GC-FID signal, the Inwil sites with their large fraction of co-substrates show the most complex GC-FID signal. Wagerswil is in the middle on both counts. This can be assumed to be due to the existence of terpenes in food waste and green waste, which are common co-substrates.

Looking at the GC-SCD signals, we can make a few additional comments beyond those from Figure 6. First, we see that in the Wagerswil case (which had the highest quantified trace sulphur), effectively all sulphur peaks were identified and quantified. Only small peaks remain. Therefore, the quantification in Figure 6 can be assumed to represent this sample well.

On the other hand, the Hochwald chromatogram looks more complex. Although only a few small real peaks remain unidentified, there exists a large pattern at the end of the chromatogram, which we were not able to identify during analysis. This pattern appeared in all 9 samples taken at Hochwald, and in none of the others. One possibility is that there exists a mix of large (high boiling point) sulphur-containing compounds, which do not get well separated by the column, but are detected at the end of the program. If that is the case, then the Hochwald quantifications in Figure 6 would be an underestimate. Even considering underestimates due to this effect, the fact remains that the total quantified trace sulphur in this gas is still above the limit for fuel cells.

The GC-SCD chromatograms of the Inwil digester samples also show most peaks as identified, and the relatively simple signal is consistent with the quantifications in Figure 6. As opposed to Hochwald and Wagerswil however, the Inwil site uses a much more aggressive in-digester desulphurisation technique than the other two. There is some uncertainty regarding the effect of air/oxygen addition or iron chloride addition on non-H_2S sulphur compounds, as most studies focus on the effect on H_2S (eg., [6]). One study has found that while iron chloride successfully reduces H_2S and several larger organic sulphur compounds from biogas, the volatile compound dimethyl sulphide is not affected [7].

3 Techno-economic analysis

The techno-economic part of this project first focused on reviewing the available literature on the subject of gas cleaning for biogas-operated fuel cells. This literature included both modelling studies in scientific publications, as well as biogas cleaning quotations from suppliers which were included as the project report known as « Public Deliverable D2.3 » of the DEMOSOFC project in Turin, Italy [8]. DEMOSOFC is an ongoing project aiming to demonstrate a 150 kW_e SOFC system on wastewater biogas. The cost data from these various sources are shown in Table 3 and Figure 8. For the DEMOSOFC quotations, only the ones which were listed as "complete" in deliverable D2.3 ("complete" = all costs including e.g. piping are considered) are included here.

For context, on Figure 8 is also marked the target costs which the US Department of Energy (DOE) Fuel Cell Technologies Office (FCTO) has set as the goals for gas cleaning for fuel cells. These target costs ($500/kWe in the short term, $200/kWe in the long term) are the outcome of a workshop held in 2014 by Argonne National Laboratory, gathering key industry and research players to discuss the state of gas cleaning for fuel cells [9].

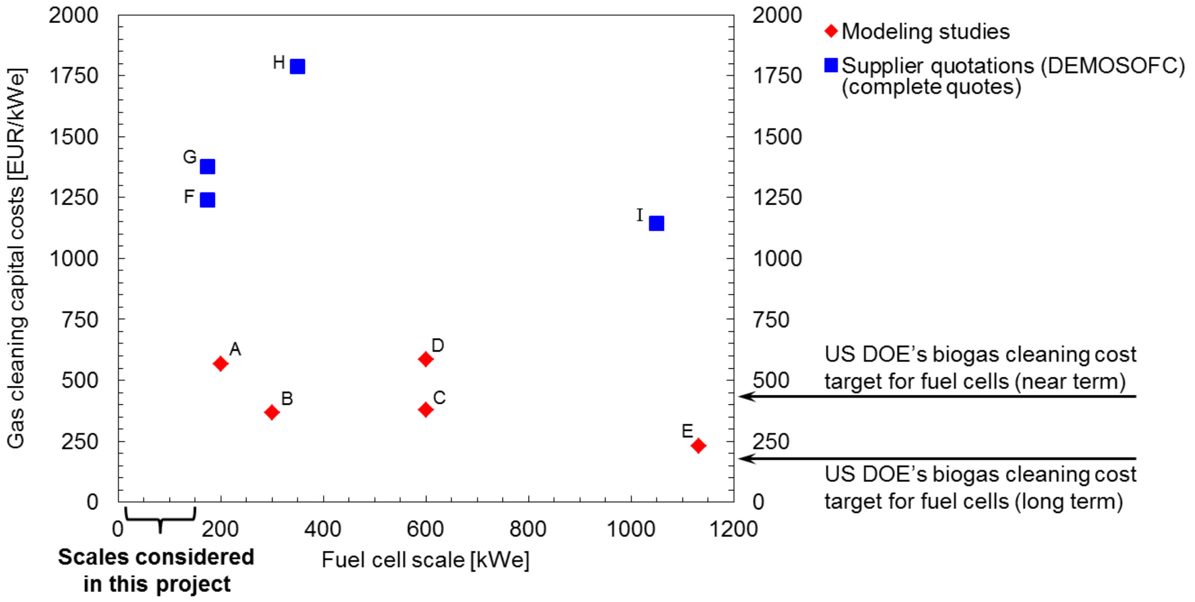

Figure 8: Overview of available literature for cost information of biogas cleaning for fuel cells. Letter labels correspond to the sources listed in Table 3.

Scatter of cost data

First, biogas cleaning systems for fuel cells are not yet standardised; therefore the per-kWe costs in Figure 8 can vary by more than a factor of 3 for any given scale. This is especially notable in the difference between estimates in scientific literature and quotes from suppliers for projects to be built. While the literature values in Figure 8 are relatively close to meeting the DOE cost targets, supplier quotes were significantly more expensive.

A possible reason for this difference could be that systems to be built today still include some aspects of overdesign, such as several vessels in series where fewer may be enough, in order to protect the fuel cell. The degree to which this is truly the case, and the degree to which this could be eliminated in future, is not yet clear. The primary focus so far had been on finding and demonstrating technically feasible and robust solutions; now cost optimisation is also becoming a key focus.

Table 3: Overview of the available literature for cost information of biogas cleaning for fuel cells. CAPEX values are plotted as a function of plant scale in Figure 8. FC = Fuel cell; CAPEX = capital costs; OPEX = operating costs.

	Gas cleaning technique	FC scale kWe	CAPEX €	OPEX €/yr	Context information
Modeling studies					
A [10]	Two-step drying followed by activated carbon	200	113’700	not given	Gas cleaning CAPEX was 0.57 k€/kWe; SOFC was 3 k€/kWe (break-even case) or 7 k€/kWe (base case).
B [11]	Cold sorbents followed by hot hydro-desulphurisation and ZnO	300	109’944	13’287	Cleaning represents ~20% of the cost of electricity, assuming 3.3 k€/kWe FC.
C [12]	Cold sorbents (Fe oxides, activated C)	600	226’000	136’500	Costs of the full process chain (with FC) not given.
D [12]	Biotrickling filter followed by cold sorbents (Fe oxides, activated C)	600	350’000	26’200	Costs of the full process chain (with FC) not given.
E [13]	Hot ZnO two-fluidised-bed reactor	1132	262’395	not given	Cleaning capital costs represent ~20% of the cost of the anaerobic digester.
Supplier quotations (from DEMOSOFC project)					
F [14]	Adsorption in activated C.	175	241’000	not given	From company HyGear.
G [14]	Adsorption in activated C.	175	217’000	49’000	From company BIOKOMP.
H [14]	Biogas drying, cold sorbent, then H_2 addition, hot hydrodesulphurisation	350	625’000	33’200	From company Quadrogen. Hydrogen addition not included in OPEX quote.
I [14]	Biogas drying, cold sorbent, then H_2 addition, hot hydrodesulphurisation	1050	1’200’000	99’600	From company Quadrogen. Hydrogen addition not included in OPEX quote.

Based on the data in Table 3 and Figure 8, several statements can be made.

Hot vs. cold cleaning systems

Second, we can consider the types of gas cleaning processes used in the systems in Figure 8 and Table 3. Of these nine systems, four used exclusively cold sorbents with biogas dehumidification, and three used a combination of cold sorbents and hot hydrodesulphurisation (HDS) processes. The other two systems were specialty designs. No system used HDS without preceding it with a cold sorbent step.

In the US DOE workshop summary [9], suppliers of fuel cells and gas cleaning systems also made statements about the relative merits of cold sorbents or HDS for biogas fuel cells. It was agreed that HDS had significant technical value, especially thanks to the long history of HDS use in oil and gas industries. However, it was also agreed that the integration into a fuel cell system is particularly difficult, especially at small scales. HDS requires hydrogen mixed into the biogas to function correctly. In principle, this is possible by recirculating hydrogen-containing gas from the exhaust of the fuel cell’s anode. In practice, this would require an external hydrogen supply during fuel cell start-up, and the anode gas recirculation would need to be cooled, actively dried, and to have precise flowrate control.

At small scales, each additional vessel or system component adds significant expenses. HDS systems for fuel cells based on anode gas recirculation, in the state they exist today (based on designs in [11] and [14]), would always include more complex process design than cold sorbents, and are therefore not considered to be affordable at the very small scales (< 150 kW$_e$) considered in this project. One clear statement from the US DOE workshop on gas cleaning for fuel cells is that “although there is extensive experience utilizing HDS in refineries, there has been little work done towards the development of HDS for smaller systems.”

Data at small scales

As shown in Figure 8, the scales considered in economic assessments of biogas cleaning for fuel cells in literature are generally larger than even the top of the 5-150 kW_e range of scales considered in this project. Gathering quotations in this scale range is therefore required, focusing on cold sorbents.

A request for quotations was sent to SulfaTrap, as their H_2S sorbent had already been selected based on results in the Direct Methanation of Biogas project. The system specifications sent to them are listed in Table 4. The focus was on capturing the effect of scale and the effect of operating pressure. While certain fuel cell suppliers operate their SOFC system at only a slight overpressure (corresponding to the 0.5-1.5 barg pressure range in Table 4), others operate at higher inlet pressure (e.g., the DEMOSOFC module is at 4 barg).

Table 4: System specifications submitted to SulfaTrap for quotation request

		Mini	**Small**	**Medium**	**Large**
Plant scale information					
Fuel cell power	kW_e	5	25	75	150
Fuel cell efficiency	%, LHV basis	55%	55%	55%	55%
Biogas CH_4 content	%v	55%	55%	55%	55%
Biogas flowrate	Nm^3/hr	1.67	8.33	25.0	50.0
Biogas flowrate	SLPM	28	139	417	833
Approx. cow equivalent	# of cows[1]	14	71	212	424
Gas cleaning conditions					
Biogas H_2S content	ppmv	300	300	300	300
Biogas other S content	ppmv	6	6	6	6
Operating pressure	barg	**Low pressure case:** 0.5-1.5 barg **High pressure case:** 4 barg			

The quotations from SulfaTrap are shown in Figure 9 and Figure 10. A 4-vessel system was proposed, where the first two vessels are used in lead-lag configuration for H2S removal, and the last two are used for various trace sulphur compound removal.

Based on this quotation, increasing the pressure has the effect of increasing per-kWe capital costs by 10-30%. Discussions are ongoing with the supplier about the possible beneficial effect on the sorbent capacities of the reduced moisture in biogas at higher pressures, an effect not yet considered here.

The effect of scale is significant. At 150 kW_e, the low-pressure capital costs are at 933 $/kWe, which is in line with the less expensive values in Figure 10. However, at smaller scales the per-kWe costs increase drastically, to > 3’000 $/kWe at 25 kWe and > 13’000 $/kWe at 5 kWe.

Putting the numbers in absolute terms is illuminating : at a gas cleaning target cost of 500 $/kWe as suggested by the US DOE FCTO and illustrated in Figure 9, a 5 kWe fuel cell has a total budget of $2500 for gas cleaning capital costs. This very low number means that

(1) Every effort must be made to minimize the number of independent sorbent vessels used ;

(2) Capital costs associated with active drying of biogas must be reduced (for example, by cooling biogas at ~15-20°C using tap water rather than at 4°C using a refrigeration cycle) or eliminated completely;

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[1] Based on the assumption that 1 dairy cow produces 100 ft^3 = 2.83 m^3 of biogas per day, from [14].

(3) Any analytical device used to monitor gas quality or sulphur breakthrough must be very inexpensive.

At all scales, the removal of trace non-H_2S sulphur compounds represents half of the vessels, and – as will be shown in the sorbent testing chapter – may require more significant gas conditioning (drying, etc.) than simple H2S removal would. Removal of these trace, non-H_2S sulphur compounds therefore represents a significant fraction of the gas cleaning capital costs.This is despite the fact that the estimated biogas composition in Table 4 assumed only 2% of the sulphur was not contained as H_2S. If the tolerance to sulphur of fuel cells and reformers could be increased to a few ppmv, rather than the 0.5 ppmv today, significant cost reductions in gas cleaning would be possible.

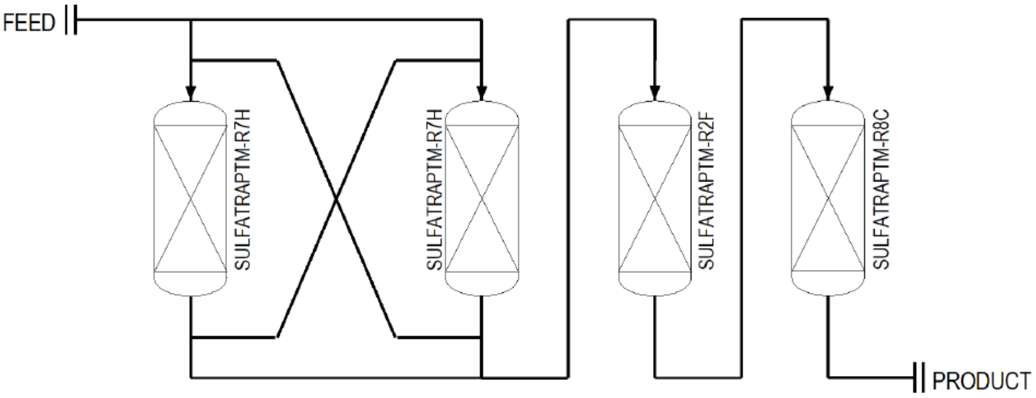


Figure 9: Process flow diagram of the desulphurisation system proposed by SulfaTrap for small-scale agricultural biogas. The first two vessels are intended for H_2S removal, the third for dimethyl sulfide, the fourth for other sulphur.

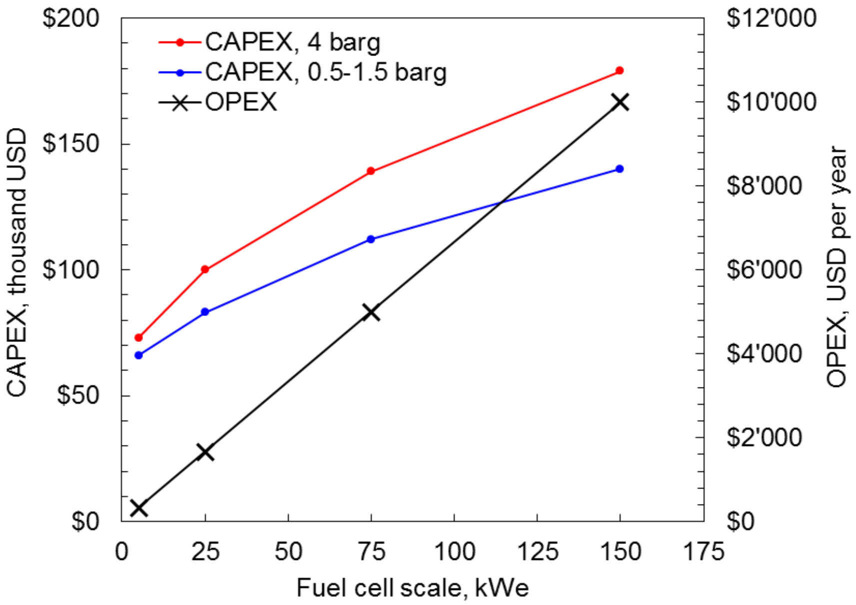


Figure 10: Quotation received for the biogas cleaning system, at 4 different scales and 2 different operating pressures

4 Gas cleaning test rigs and diagnostic tools

Activites related to Work Package 3 are the design, upgrade, and testing of the gas cleaning test rigs and includes following phases:

- Adaptation of the COSYMA gas cleaning test rig to fulfil the requirements of this project
- Sorbent tests using synthetic gas mixtures in the lab
- Gas cleaning option selected based on biogas sampling, lab tests, and techno-economic analysis
- Long-duration field test of the chosen gas cleaning system.

At the time of proposal writing in Fall 2017, we kept open the choice of the test rig to be use for sorbent tests with synthetic gas mixtures (COSYMA or a separate test rig). In May 2018 a safety analysis led to the conclusion that the lab tests must be performed inside a ventilated lab room which is authorised for experiments with reactive and poisonous gases. In this final report we present the lab-based tests performed as well as results of the COSYMA field tests.

Based on a review of existing scientific literature and on discussions with several sorbent suppliers, six commercial sorbents were selected for DMS testing. A brief description of each sorbent is given here and in Figure 11. Because prices of these sorbents are discussed in the results, commercial names are not disclosed.

(a) **NaOH-AC**: This sorbent is based on activated carbon impregnated with sodium hydroxide, and is recommended for H_2S removal in reducing gases (oxygen-free).

(b) **Cer-AC**: This sorbent is a composite of ceramic and activated carbon, which was recommended by the supplier for removal of low boiling point compounds such as DMS (boiling point = 38°C).

(c) **Cu-Fe-AC**: This sorbent is based on activated carbon functionalised with copper and iron, and is recommended for volatile disulfides and mercaptans.

(d) **Cu-Z**: This sorbent is a zeolite functionalised with copper, recommended for removal of dimethyl sulfide. Supplier states that moisture must be kept to a few 1000’s ppm.

(e) **CuO-AC**: This sorbent is based on activated carbon functionalised with copper oxide, intended for removal of H_2S and mercaptans.

(f) **KI-AC**: This sorbent is based on activated carbon functionalised with potassium triiodide, specifically recommended for removal of dimethyl sulfide and dimethyl disulfide.

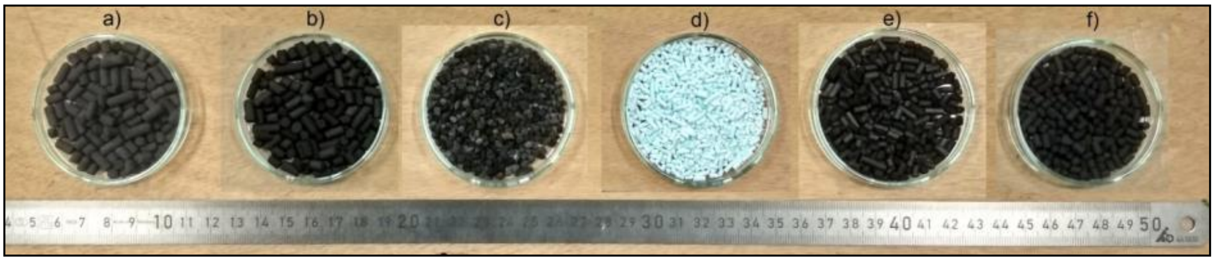


Figure 11: Tested sorbents a) NaOH-AC, b) Cer-AC, c) Cu-Fe-AC, d) Cu-Z, e) CuO-AC, f) KI-AC (Photo courtesy of Chirayu Thakur)

4.1 Lab-based tests

In the framework of the SCCER-BIOSWEET Work Package 2 and the objectives of ESI plattform, a gas cleaning test rig was built in 2018 at PSI. A first series of sorbent tests were performed using synthetic biogas mixtures in this test rig as part of the SFOE Manure-to-Electricity gas cleaning project.

The newly build gas cleaning test rig, shown in Figure 12 and Figure 13, allows gas cleaning experiments from room temperature to 450°C. Cold sorbents are generally operated in the range of temperatures from 20-40°C, i.e. ambient temperature, while the 400-450°C temperature range is relevant for hydrodesulphurisation and high-temperature sorbents such as zinc oxide.

The set-up allows the creation of synthetic gas mixtures which simulate the complexity of biomass-derived gases, which could come from a waste water treatment plant (WWTP), agriculture biomass digester or green waste digester. In particular, sulphur compounds, moisture, and organic compounds such as terpenes can be added in controlled amounts to the main gas flow. For the needed gas flows a gas mixing section, including the addition of moisture, existed at PSI as part of the Micro Fluidised Bed ("MiWi") set-up. The gas cleaning test set-up was built as an extension of this existing infrastructure, which can now be used alternately as a methanation test bench (MiWi) or as a gas cleaning test bench, as needed. In the gas cleaning test bench, monitoring of the gas composition is done by mass spectrometer and micro-GC, with additional monitoring by FTIR in the case of high moisture content.

The gas cleaning reactor beds were designed to allow the testing of commercial sorbents, which generally come as pellets in the range of a few mm in size. To allow a minimum ratio of bed diameter to particle size of 10, the beds were built with inner diameters of 3 cm and 4.5 cm to accommodated different pellet sizes of commercial sorbents. All metal parts from the point of sulphur addition until the analysis sampling points at the reactor outlet were treated with Silconert® to minimise the adsorption of sulphur compounds on the set-up itself.

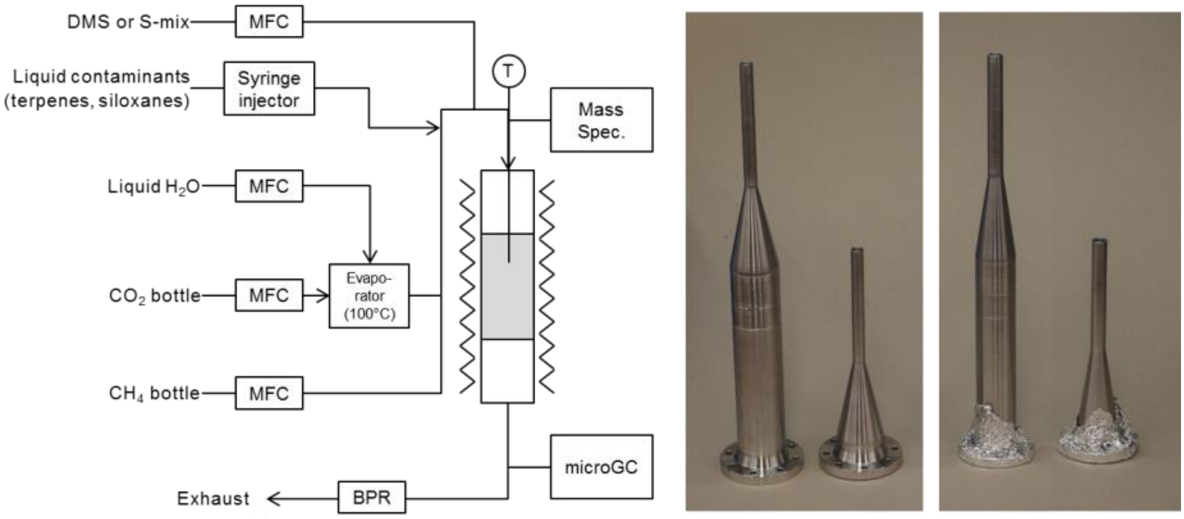


Figure 12: (left) Schematic of the gas cleaning test set-up used for the sorbent tests. MFC = mass flow controller; BPR = back pressure regulator; DMS = dimethyl sulphide. (right) Photos of the two reactor beds, of inner diameter 4.5 cm and 3 cm respectively, which can be used in the gas cleaning test set-up.

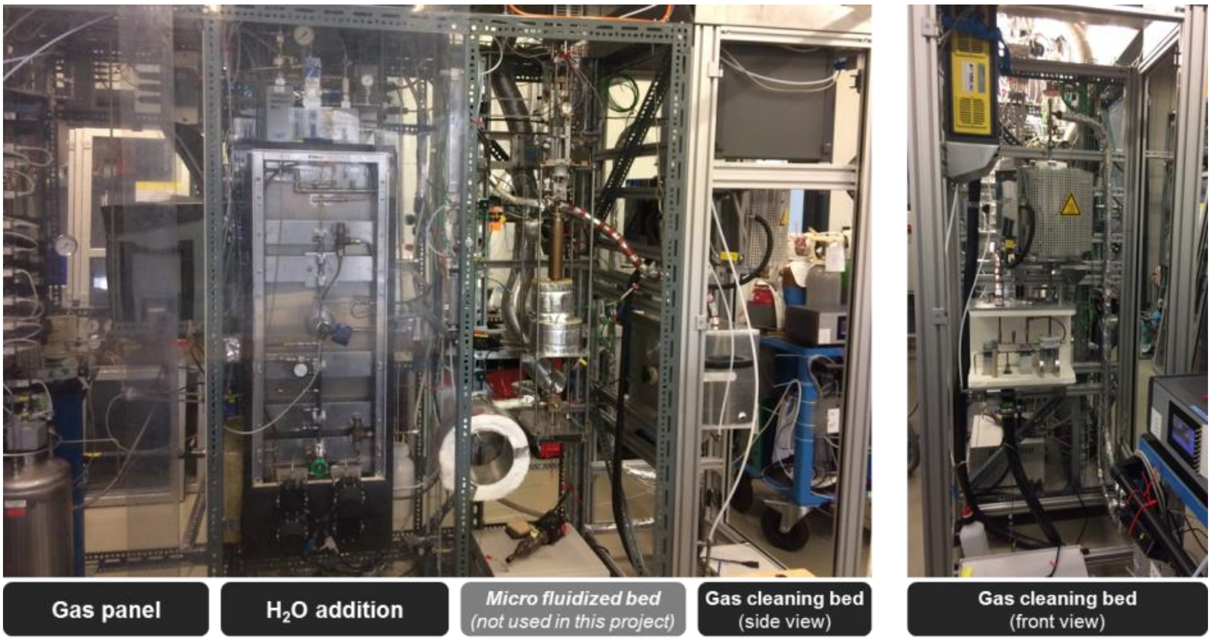


Figure 13: Gas cleaning test set-up used for the sorbent tests

Lab-based tests in this project focused on the evaluation of materials for the removal of dimethyl sulfide (DMS) from biogas. In the Direct Methanation of Biogas project, DMS was the most difficult sulphur compound to remove [15], which is also consistent with previous literature. Although a solution was found in the Direct Methanation of Biogas project, a specific study of DMS removal to optimise the process had not yet been undertaken. Other trace sulphur compounds (mercaptans, thiophenes, larger sulphides) are generally better retained than DMS – either because they are more reactive (mercaptans) or because they have higher boiling points and therefore physisorb more strongly in ambient-temperature sorbents (thiophenes, larger sulphides). Therefore we focus on DMS tests as an indicator of the worst-case sulphur compound which must be retained by the gas cleaning.

4.2 Test facility: COSYMA

COSYMA was prepared for the field demonstration of gas cleaning and is now connected to the biogas supply at Inwil, as shown in Figure 14 below. The biogas is taken from the mixed gas source at Inwil, passed through the gas cleaning system in COSYMA, from where slipstreams are sent to the

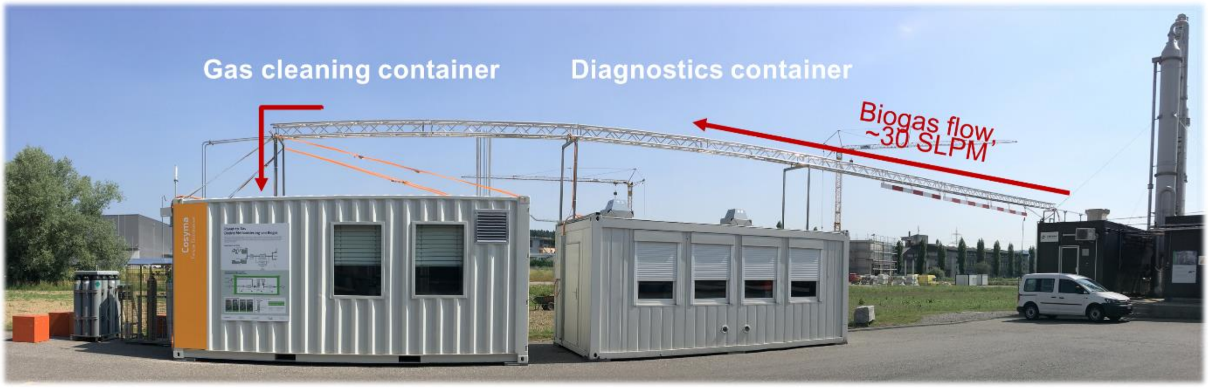


Figure 14: COSYMA and the diagnostics container on site in Inwil for the gas cleaning tests.

diagnostics container to monitor impurities, and the gas is finally sent back to the Inwil plant. The withdrawal point and feed-back point are separated by a large activated carbon filter at the main plant (gas re-injected after the filter), so that possible back-mixing is avoided. The COSYMA and diagnostics container configuration has been inspected and received the approval to operate from the TISG (*Technisches Inspektorat des Schweizerischen Gasfaches*).

The updated P&ID of COSYMA for the gas cleaning demonstration within the SFOE Manure-to-electricity gas cleaning project is shown in Figure 15, noted in red. For gas cleaning tests, COSYMA contains 2 sorbent vessels, which can be heated to a specified temperature, which are preceded by a biogas compressor up to 3 bara and an optional cooling unit for gas dehumidification. In case sorbent tests must be accelerated to observe breakthrough and thus measure sorbent capacity, COSYMA also contains the ability to spike the biogas with a specified amount of mixed sulphur species (in the current mix: H_2S, dimethyl sulfide [DMS], carbon disulfide [CS_2]). This P&ID has been through a HAZOP analysis, completed in June 2018.

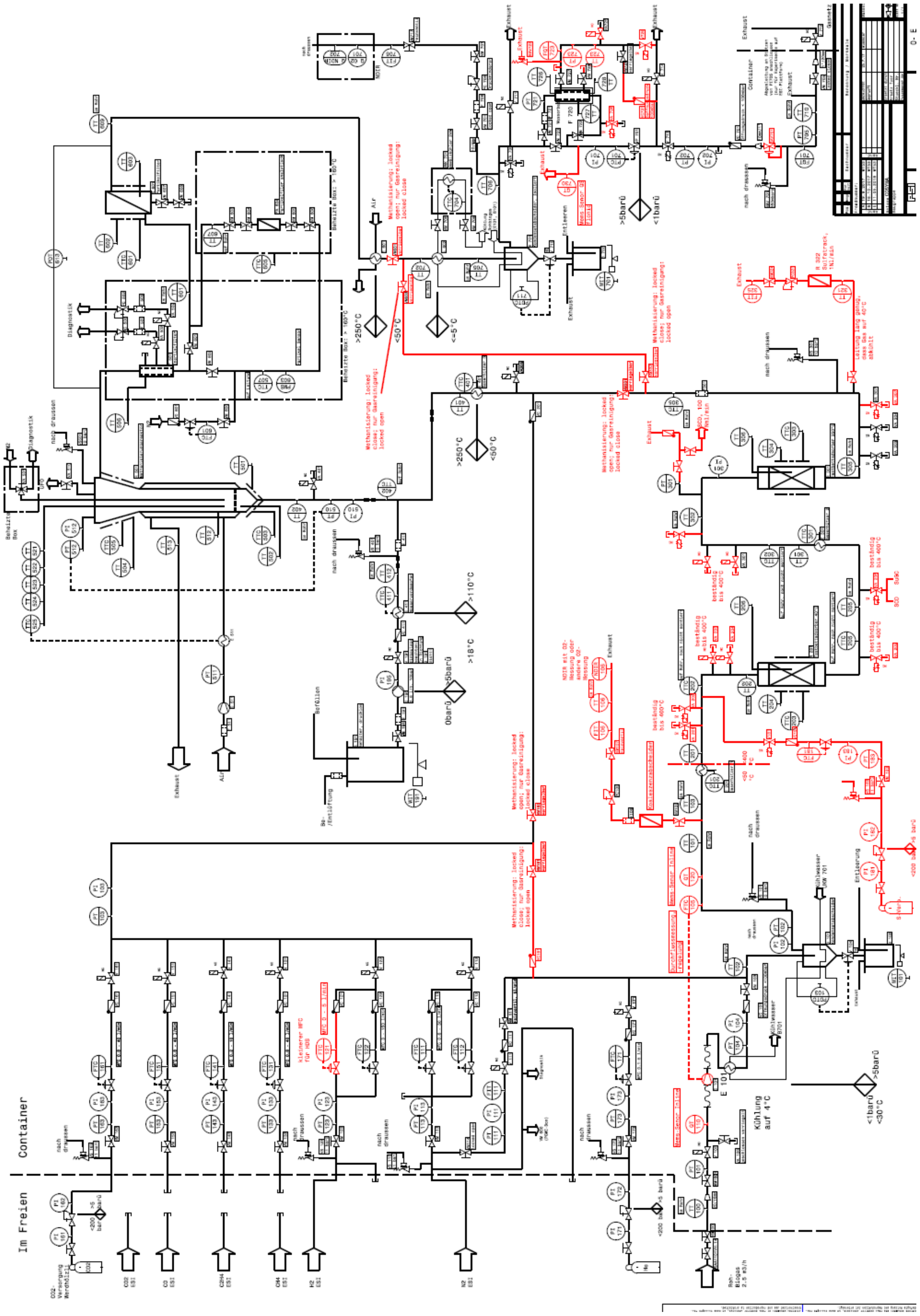


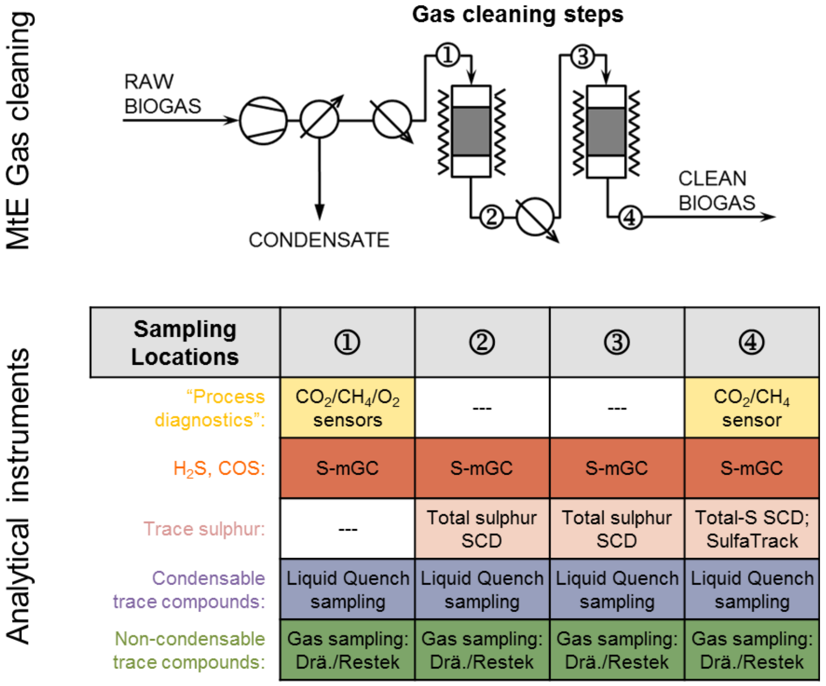
Figure 15: P&ID of COSYMA, with updates completed as part of this project noted in red.

4.3 Diagnostics requirements

4.3.1 In the COSYMA research facility

The diagnostics systems used during the long-duration test of the COSYMA research facility are shown in Figure 16. This set of tools contain both « research diagnostics » which are used to understand the behaviour of the gases in the sorbents, and a set of « process diagnostics » which are tested with the view to be used in a commerical plant. The project phases for the work to be completed in diagnostics within this project are :

- Testing the total-sulphur diagnostics system in the lab with synthetic gas mixtures containing known amounts of sulphur compounds, such as H_2S, COS and DMS
- Verifying the operation of the diagnostics system in the field on real biogas independently of the gas cleaning test rig;
- Using the diagnostics system at PSI to monitor sorbent testing with synthetic gas mixtures;
- Demonstrating the diagnostics system in the long-duration field test of gas cleaning, including demonstration of one low-cost total-sulphur indicator to validate its use for future industrial projects.



Sampling Locations	①	②	③	④
"Process diagnostics":	$CO_2/CH_4/O_2$ sensors	---	---	CO_2/CH_4 sensor
H_2S, COS:	S-mGC	S-mGC	S-mGC	S-mGC
Trace sulphur:	---	Total sulphur SCD	Total sulphur SCD	Total-S SCD; SulfaTrack
Condensable trace compounds:	Liquid Quench sampling	Liquid Quench sampling	Liquid Quench sampling	Liquid Quench sampling
Non-condensable trace compounds:	Gas sampling: Drä./Restek	Gas sampling: Drä./Restek	Gas sampling: Drä./Restek	Gas sampling: Drä./Restek

Figure 16: Diagnostic concept for the gas cleaning test rig used in the field (for research purposes. The requirements for an industrial plant are discussed in section 5.1.2.)

The process diagnostics S-mGC and Dräger indicators had already been validated during the completed Direct Methanation of Biogas project. As there the S-mGC instrument had shown some sensitivity to temperature variation, which had led to imprecise results in in the past, a refrigerated case was purchased and implemented. Then, the liquid quench (LQ) sampling system was upgraded from a manually operated system as used in the Direct Methanation of Biogas project to an automated system to significantly reduce the operator hours needed for sampling during long-duration operation. The Total-Sulphur SCD and Sulfatrack were the main focus area for new developments in this project.

5 Results

5.1 Lab-based tests

Breakthrough tests were undertaken following the experimental plan in Table 5, placing special focus on the effect of matrix complexity on DMS adsorption, an effect which was not well explored in existing literature. A first scan of all 6 sorbents was done in a gas mixture comprising 55%v CH_4, 45%v CO_2, 100 ppmv dimethyl sulfide, and moisture corresponding to saturation at 4°C (5420 ppmv H_2O at the 1.5 bara system pressure used). This moisture level corresponds to the lowest humidity which could be expected in biogas if an active cooling system were used between the digester and the sorbents.

Table 5: Experimental plan. All experiment were run at room temperature, at a pressure of 1.5 bara, using sorbent pellets as received from the supplier.

Run #	**Sorbent ID**	**Gas composition**				**Reactor properties**	
		Bulk (%v, dry)	**DMS (ppmv)**	**H_2O (ppmv)**	**Limonene (ppmv)**	**Bed ID x L (cm)**	**GHSV (h^{-1})**
1-1	Cu-Z	55% CH_4, 45% CO_2	100	5'420	0	3 x 7	1'557
1-2	CuO-AC	55% CH_4, 45% CO_2	100	5'420	0	3 x 7	1'557
1-3	Cu-Fe-AC	55% CH_4, 45% CO_2	100	5'420	0	3 x 7	1'557
1-4	Cer-AC	55% CH_4, 45% CO_2	100	5'420	0	3 x 7	1'557
1-5	KI-AC	55% CH_4, 45% CO_2	100	5'420	0	3 x 7	1'557
1-6	NaOH-AC	55% CH_4, 45% CO_2	100	5'420	0	3 x 7	1'557
2-1	Cu-Z	55% CH_4, 45% CO_2	100	15'593	0	3 x 7	1'557
2-2	CuO-AC	55% CH_4, 45% CO_2	100	15'593	0	3 x 7	1'557
2-3	Cu-Fe-AC	55% CH_4, 45% CO_2	100	15'593	0	3 x 7	1'557
2-4	Cer-AC	55% CH_4, 45% CO_2	100	15'593	0	3 x 7	1'557
3-1	Cu-Z	55% CH_4, 45% CO_2	100	5'420	200	3 x 7	1'557
3-2	CuO-AC	55% CH_4, 45% CO_2	100	5'420	200	3 x 7	1'557
3-3	Cu-Fe-AC	55% CH_4, 45% CO_2	100	5'420	200	3 x 7	1'557
3-4	Cer-AC	55% CH_4, 45% CO_2	100	5'420	200	3 x 7	1'557

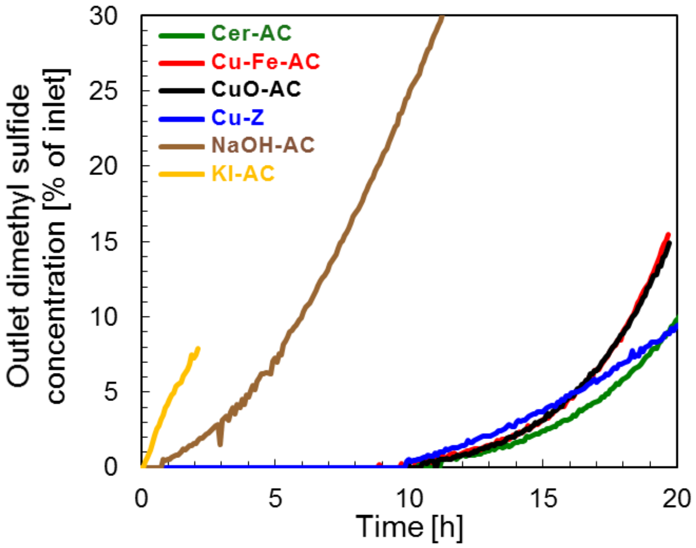


Figure 17: Dimethyl sulfide breakthrough curves of commercial sorbents in a synthetic biogas mixture (Baseline conditions, corresponding to Runs 1-# in Table 5: 55%v CH_4, 45%v CO_2, saturated with H_2O at 4°C)

Results are shown in Figure 17 for the first series of scans under baseline conditions (series 1 in Table 5). Four sorbents had nearly identical DMS breakthrough times under these conditions : Cer-AC, Cu-Fe-AC, Cu-Z, and CuO-AC. NaOH-AC and KI-AC experienced a very rapid breakthrough. Therefore, the four best performing sorbents were selected for further tests.

The breakthrough experiments were run once again in a 2nd series of tests, as listed in Table 5. Here, the gas contained 55%v CH_4, 45%v CO_2, 100 ppmv dimethyl sulfide, but this time with moisture corresponding to saturation at 20°C (15’600 ppmv H_2O at the 1.5 bara system pressure used). This is typical of biogas which is saturated at ambient conditions, which is what can be expected in a system where no active cooling is included.

Finally, a 3rd series of tests explored the effect of limonene in biogas on the sorbents’ capacity for DMS. Terpenes like limonene are common in biogas, especially when food or green waste is used as a substrate, and readily adsorb in high surface area sorbents where they may compete with DMS.

Results of all 3 series of tests are shown in Figure 18. In this figure, DMS breakthrough capacities are given for all 4 commercial sorbents which performed best in the baseline tests. These capacities are given on the basis of mass, on the basis of volume, and on the basis of sorbent cost. The mass basis indicates how much sorbent must be bought for a specific amount of sulphur removed ; the volume basis relates to the size of the sorbent vessel which must be built and thus has an impact on the capital costs of the gas cleaning system; and the cost basis has a direct impact on the operation costs of the gas cleaning system.

All 4 sorbents had lower DMS breakthrough capacities in the presence of increased moisture. The effect is most strongly marked in Cu-Z, which lost nearly all its capacity in the wet gas. By contrast, CuO-AC’s performance was reduced the least by the increased moisture. The presence of limonene in the gas had a relatively low impact on the breakthrough capacity of the sorbents. Based on these series of tests, the sorbents CuO-AC and Cer-AC were chosen as the best options for field testing, as they were the two best resistant sorbent to changes in matrix complexity. CuO-AC was the most resistant, especially to increased moisture effects, and was therefore technically the best performing. However, Cer-AC always had the best capacity on a cost basis, and it still maintained a reasonable technical performance without too much capacity loss in complex gas mixtures. On the basis of cost minimization, it was chosen to begin the field tests using Cer-AC for trace sulphur polishing, and to keep CuO-AC as a second choice in case Cer-AC showed a poor performance in real biogas.

Finally, a Masters thesis was completed in December 2018 on the basis of these breakthrough experiments, and a scientific publication is in preparation.

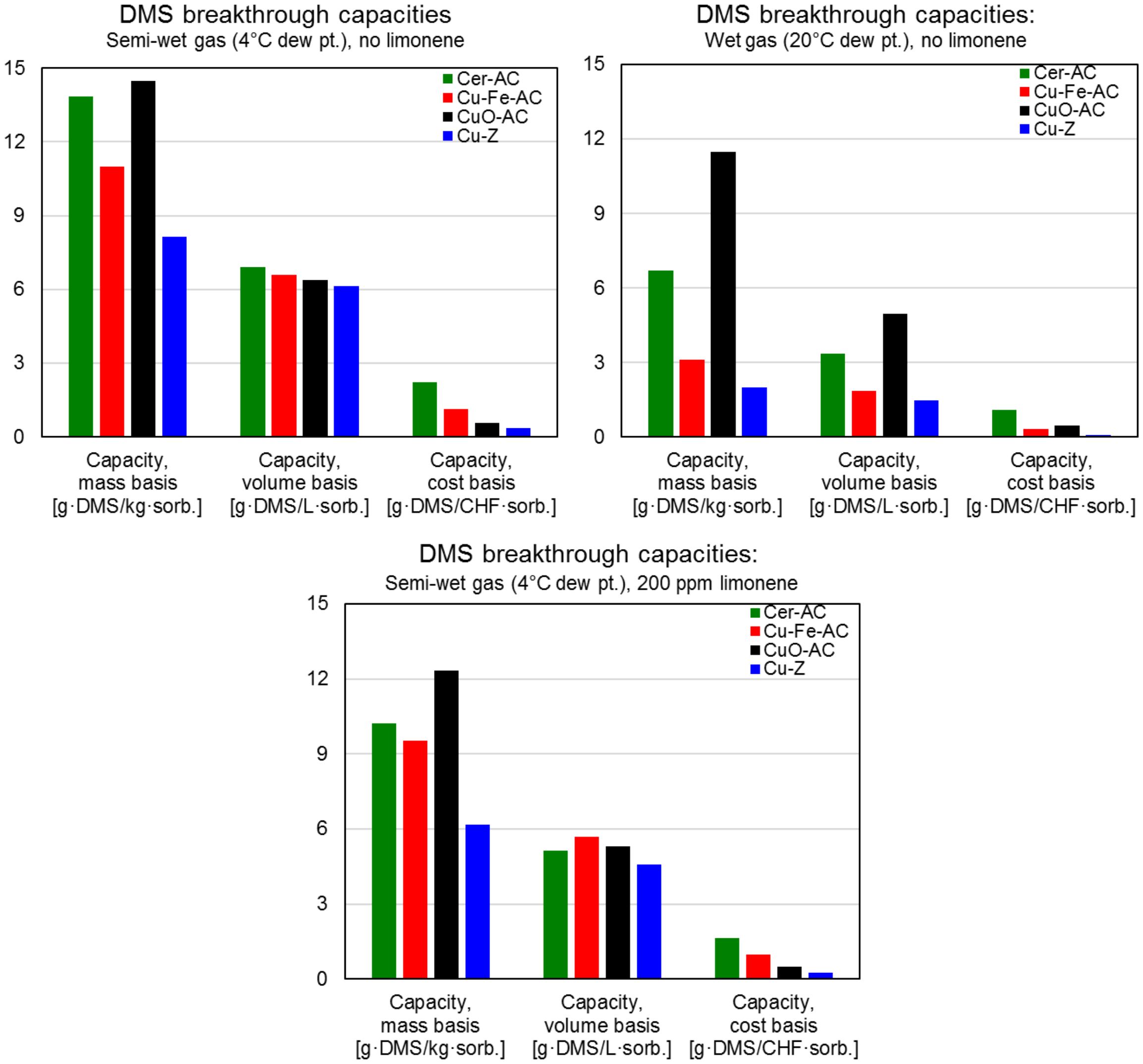


Figure 18: Breakthrough capacities of different commercial sorbents for DMS under different levels of gas matrix complexity.

While the field tests were in preparation and in early phases of testing, further analysis was done on the sorbent samples from the lab-based tests, which yielded further insight into the effect of limonene on the sulphur capacity. After the completion of each lab-based breakthrough test, three used sorbent samples were extracted: one at the bed inlet, one in the middle of the bed, and one at the bed outlet. The total sulphur loaded on these extracted samples during the DMS breakthrough testing were measured by a CHNS analyzer. In addition, the full capacity of the sorbent for DMS was calculated, by subtracting the DMS concentration measured in the gas at the bed outlet from the inlet amount.

If the DMS were equally loaded in the bed, the sulphur found on the used sorbent samples by total-sulphur CHNS analysis should be everwhere equal to the full integrated capacity measured from the gas phase breakthrough curve. Figure 19 shows the results for the DMS breakthrough tests in presence of limonene. For all activated carbon sorbents, we see that the sulphur loading is nearly 0 at the bed inlet, and very high at the bed outlet. In addition, the total loading of the used sorbent, including H2O and limonene in addition to DMS, is always high at the bed inlet and low at the bed outlet for activated carbons.

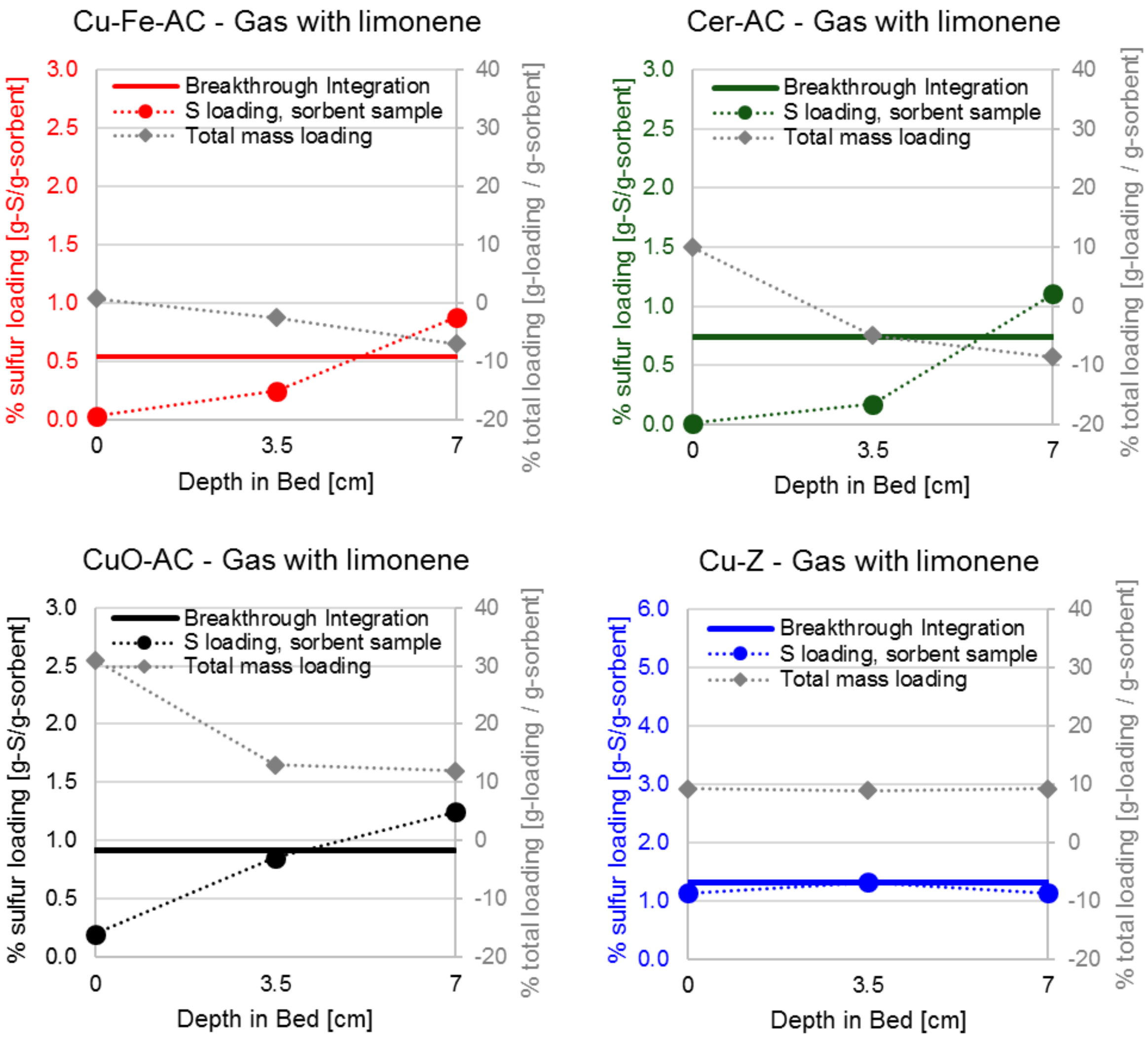


Figure 19: Sulphur loading profiles throughout the sorbent beds, after completion of the experiments with limonene in the gas. This shows that for all activated carbons tested, limonene reduced sulphur loading at the bed's inlet, indicating a strong competition effect.

These results indicate that limonene in the gas has a strong competing effect with DMS adsorption in activated carbons. Although limonene had not strongly affected the DMS breakthrough capacities in Figure 19, we see here that limonene is strongly loaded in the first parts of the bed and has strongly reduced the capacity for DMS locally.

The implications for field tests are clear: in cases where the terpene concentration in biogas is much higher than the trace sulphur concentration, activated carbon based sorbents may experience very early breakthrough of sulphur, due to competitive adsorption with terpenes. This is despite the fact that terpenes are not a problem for high-temperature fuel cells, and do not need to be removed in gas cleaning. The zeolite-based Cu-Z sorbent did not suffer this capacity loss effect in Figure 19; it is therefore much more selective to DMS in the presence of terpenes relative to activated carbons. However, it is very strongly affected by moisture.

We therefore make the following recommendations for trace sulphur removal during the field test of sorbents, with all technical and economic information in mind:

- **Cer-AC is to be tested first**, as it has the best per-CHF DMS capacity in all lab-based tests. It should first be tested with no biogas drying, in order to see if biogas can be cleaned without the additional expense of a drying unit, based on the good performance of this sorbent even in gas saturated at 20°C in the lab.
- If an early breakthrough is observed, the biogas should be cooled and dried with 15°C cooling fluid, to simulate an inexpensive cooling system with regular tap water.
- If an early breakthrough is again observed, **CuO-AC should be tested as second**, as it was more technically robust in lab-based tests. It is more expensive but should perform better than Cer-AC under variable contaminant concentrations.
- In case early breakthroughs are still occurring and can be seen to be caused by terpenes, we recommend using an additional bed or layer of inexpensive activated carbon (e.g. Cer-AC) before the DMS removal to first remove terpenes.
- The final, **technically most robust solution**, which will also be the most expensive, would be to dry biogas to a dew point of 4°C using a dedicated refrigeration unit, then use **Cu-Z** (which is resistant to terpenes) for trace sulphur removal.

5.2 Field test of the most promising sorbents

Two gas cleaning vessels are available in COSYMA. Based on the assessment in the previous section that hydrodesulphurisation is not appropriate for small scales, cold sorbents were selected for the demonstration. The first vessel is filled with SulfaTrap R7 for H_2S removal, based on extensive testing of different H_2S sorbents completed as part of the Direct Methanation of Biogas project [15].

The second vessel is filled with a sorbent for trace sulphur removal. Based on the series of lab-based tests, we follow a set of different sorbent choices and process configurations to validate a robust solution. These different process conditions are listed, in the order in which they have been tested, in the table below. Key outcomes are also listed.

Table 6. Field test. Experimental plan at various temperatures.

	Biogas cooling setpoint	H_2S sorbent	Polishing sorbent	Outcome/Comments
A	---none---	SulfaTrap R7	Cer-AC	Sulphur breakthrough of polishing bed in 19 hours
B	15°C	SulfaTrap R7	Cer-AC	Sulphur breakthrough of polishing bed in 19 hours
C	15°C	SulfaTrap R7	CuO-AC	Sulphur breakthrough of polishing bed in 55 hours
D	4°C	SulfaTrap R7	Cu-Z	Setpoint could not be reached, Cu-Z was not dryed prior to testing; cyclical breakthroughs.
E	15°C	SulfaTrap R7	CuO-AC, after removing terpenes	Sulphur breakthrough of polishing bed after ~120 hrs (3x longer bed)

As seen in the the table above, the simple solutions with only two sorbents and minimal gas cooling (configurations A, B, and C above) were not successful in retaining trace organic sulphur compounds in this biogas. Based on the lab-based sorbent scanning test results, we can hypothesize that the cause of early breakthrough was not moisture, but instead the mix of terpenes and other volatile organic compounds (VOCs) in this biogas source. This hypothesis is in the testing phase, to be confirmed based on analysis of extracted sorbent samples from runs B and C.

This biogas source was chosen as a test site specifically for its complexity in terms of impurities, so that a solution developed here could be considered validated for most or all agricultural biogas sources. We have seen that a biogas containing both significant amounts of organic sulphur and large concentrations of VOCs cannot be desulphurized to the level required by fuel cells without resorting to either (1) a drying/cooling step to enable the use of a terpene-resistant material (Cu-Z), or (2) addition of an intermediate sorbent step to remove VOCs.

5.2.1 Test E, the best performed sorption

By end of August 2019, we have performed an experiment with SulfaTrap R7 & CuO-AC for the duration of 200 hrs. During the first 150 hrs of the experiment, no measureable sulphur breakthrough was observed after the second bed, which confirms our hypothesis in the Figure 20. Even though the terpenes were adsorbed in the first bed, we observed a sulphur breakthrough after the second bed. The lower capacity of sorbent compared to the lab experiments (10 times less) is in this case not caused by terpenes. We assume that the low organic sulphur concentration is mainly responsible.

The previous experiments in the laboratory have shown that the investigated sorbents retain organic Sulphur by adsorption, but in part also by chemisorption-like mechanisms. The latter allows relatively high capacities even at low input concentration, while with pure physiosorption the capacity depends on the concentration. In Inwil, the many impurities (terpene, moisture, etc.) and low concentrations of organic Sulphur have probably caused the chemisorption mechanism to malfunction and therefore the capacity is much lower compared to the results of the laboratory experiments.

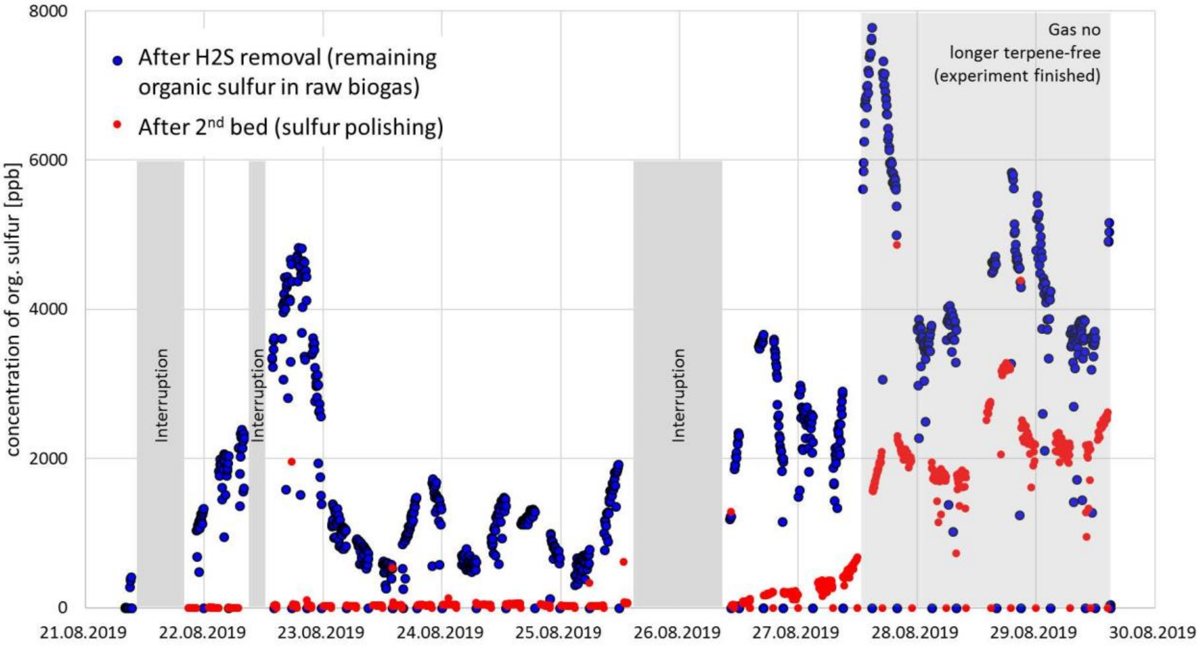


Figure 20. 200 hours test with Sulfa Trap R7 and CuO-AC. No sulphur up to 124 hrs, from 124 to 148 hrs up to around 0.5 ppm was detected.

5.3 Online measurement of sub-ppm total sulfur

5.3.1 Solution for research purposes: the SCD

The stand-alone Sulphur Chemiluminescence Detector (SCD) is currently being used for total sulphur breakthrough measurement at sub-ppm levels in the long-duration field test, and therefore represents our most sensitive online instrument.

Before the field campaign, lab tests were done to verify the feasibility of using this technique with biogas. Tests on synthetic gas mixtures showed that the SCD response to sulphur compounds was strongly dependent on the composition of the matrix gas sampled. As shown in Figure 21, sulphur signals were significantly attenuated in methane-heavy gas mixtures relative to sulphur signals in a nitrogen matrix. Additionally, the SCD response decreased when the matrix gas was humid. As biogas is generally humid and contains 50-70% CH_4, neither effect is acceptable. Conversely, tests with gas containing 150-250 ppmv of para-cymene showed no effect of terpenes in the biogas mixture on the response of the SCD, which is good news for the expected variability of biogas trace compounds.

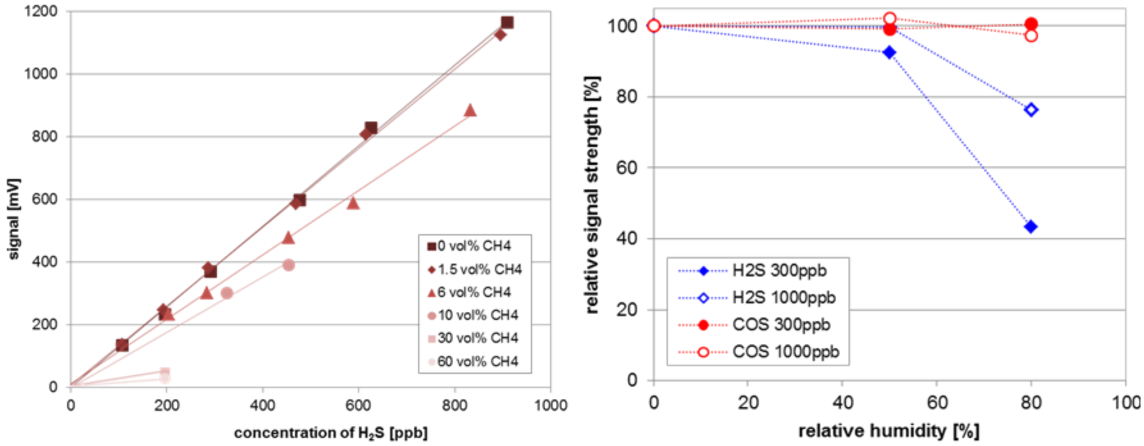


Figure 21: (left): Effect of methane in the gas matrix on the response of the stand-alone SCD for total sulfur measurement; (right): Effect of humidity in the gas matrix on the response of the stand-alone SCD for total sulfur measurement.
Results adapted from Julian Indlekofer.

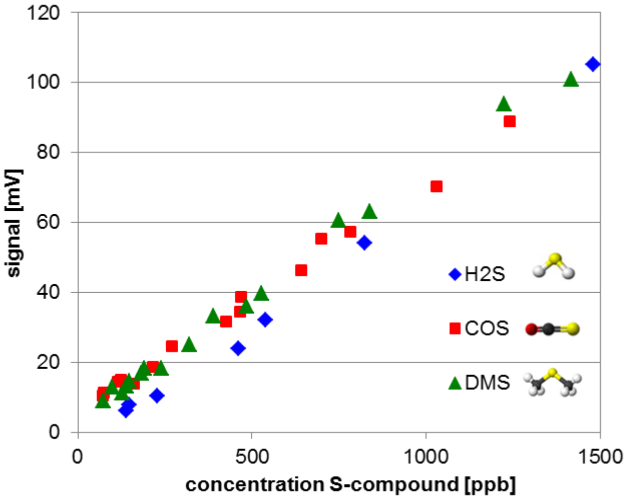


Figure 22: Equimolarity of stand-alone SCD response to different sulphur compounds in a dry matrix of 55% CH4 / 45% CO2. *Results adapted from Julian Indlekofer.*

The interference effects of methane and moisture were addressed. Automated pre-dilution of the gas with nitrogen during the SCD's sampling process allowed a good response to be achieved. Figure 21shows the equimolar response of the SCD on a dry synthetic gas mixture of 55% CH4 / 45% CO2 after implementation of the pre-dilution strategy. To rectify the moisture sensitivity issue, a calcium chloride drying agent (inert relative to sulphur compounds) was added to the gas sample line. Final tests were completed on real biogas from biowaste digestion at the site of Werdhölzli in Zürich, where < 200 ppbv of sulphur was detected without problem during sorbent breakthrough experiments. The detection limit was then further improved to ~40 ppbv by adjustments in the operation parameters. The total sulphur limit for fuel cells is 500 ppbv, so this detection limit is more than acceptable for online

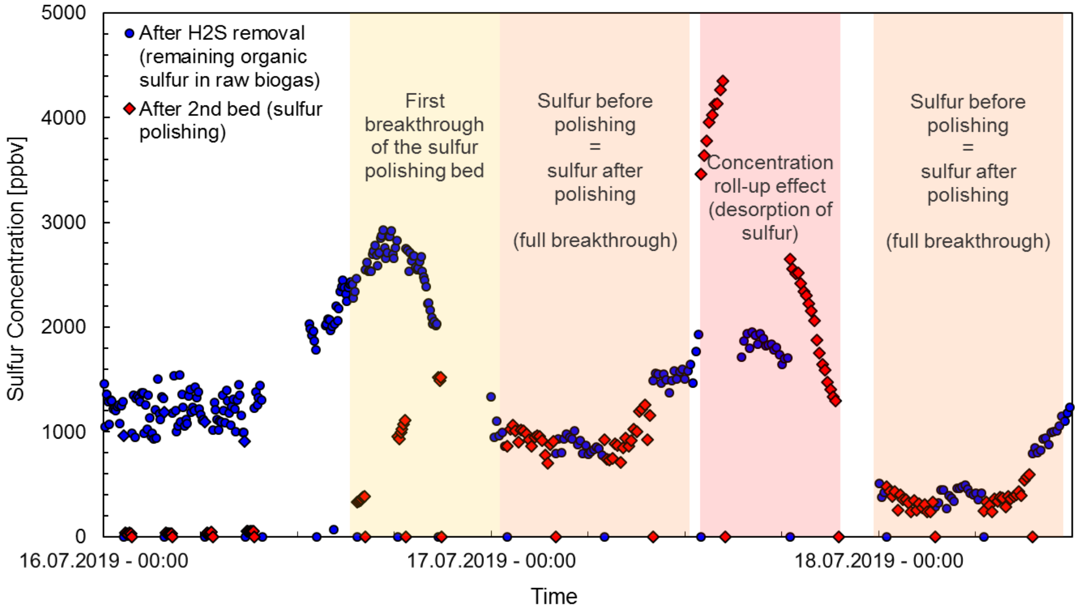


Figure 23. Demonstration of the use of the SCD in detecting a breakthrough of the gas cleaning system in the field

breakthrough monitoring. The SCD has now been in use in Inwil for the field test in COSYMA, where it has successfully detected breakthroughs of trace amounts of sulphur. It has also been used to monitor the total organic sulphur remaining after the H2S sorbent, which has varied in the range of 1 – 2.5 ppmv. The online and fast response of the instrument has allowed continuous monitoring of biogas conditions and of any breakthrough effects, as shown in Figure 23.

The work done for validating the SCD system for the application with biogas was published in a Masters thesis and a peer-reviewed journal publication.

5.3.2 Solution for commercial purposes: SulfaTrack

The SCD is being used as reference measurement to test the SulfaTrack sensor for its response to breakthrough. As shown in Figure 24, this device relies on a cartridge of material which changes from blue or grey to darker colours (black or others, depending on the gas conditions) in the presence of sulphur. This colour change is then detected by an electronic sensor supplied by the company.

First tests were performed to find correct operation conditions for biogas. Further tests are needed and a deepend discussion with the supplier. If the system is validated, this device would be a good option for a sulphur breathrough indicator in a commercial plant.

Figure 24. Demonstration of the color change of the total sulphur indicator SulfaTrack caused by sulphur in biogas in COSYMA.

5.3.3 In a future commercial plant

In a commercial plant, especially a small-scale plant, the costs of diagnostics would have to be kept as low as possible. However, key components may need to be monitored. For this reason, we use the COSYMA long-duration field campaign as a testing base for a low cost sensor :

- SulfaTrack colorimetric sensor for detection of a sulphur breakthrough

A dialog with small-scale fuel cell manufacturers has started in order to determine which sensors, if any, would be needed in a commercial small-scale plant. There is no final concensus yet, but *at maximum* this would include :

- A methane or heating value sensor for the gas quality entering the reformer
- An oxygen sensor for safety
- A total sulphur detector, such as the low-cost one tested in this project, to protect the fuel cell from deactivation or have an indication of when to replace the sorbents.

The fuel cell community is in the process of defining these requirements, and we can contribute technical suggestions based on the solutions tested in this project.

6 Conclusions and outlook

6.1 Sampling campaigns and site selection

Based on our three-site sampling campaign, we found a clear correlation between co-substrate (food & green waste) use and complexity of non-sulphur impurities, especially concerning terpenes. Manure-only biogas was nearly completely free of trace non-sulphur compounds. Siloxanes were undetectable (limit of detection = 10-15 ppbv) with GC-FID at all manure sites sampled. No clear effect of manure origin (chicken vs. cow vs. pig) was observed on the trace sulphur impurities. H_2S content varied between 2 and 1'000 ppmv for the sites studied. All sites except one had trace (non-H_2S) sulphur contents above the fuel cell limit of 0.5 ppmv. Acknowledging that our sampling campaigns are single-point measurements and that trace compound concentrations will change in time, the test bench for the long-duration field test will be equipped with online systems for continuous measurement of trace compounds.

6.1.1 Implications for long-duration field test

One of the goals of these sampling campaigns was to identify a suitable site for the completion of the long-duration field test planned for 2019. We prefered to test at the “worst case” gas, in order to validate the robustness of the gas cleaning system.

Of the three sites sampled, there is not a clear “worst case” biogas. The Hochwald gas contained the most H_2S by far, the Wagerswil gas contained the most trace sulphur impurities, and the Inwil gas from the wet digesters contained the most non-sulphur impurities.

With its 100% manure feedstock, the Hochwald gas represents an idealised extreme of Swiss agricultural biogas, as most sites in the short term will likely process some co-substrates. Its H_2S content is high, but removing H_2S from biogas is a technologically mature process. Rather, it is removal of trace sulphur, especially in the presence of many other (non-sulphur) contaminants, which is a particular challenge.

The Wagerswil and Inwil sites are therefore better options from the point of view of biogas complexity. Of these two options, Inwil offers significant advantages for the technical integration of our test system, thanks to the existence of more monitoring systems (pressure sensors, flow measurements, etc.) at the plant itself than at Wagerswil. The HAZOP analysis of our test system COSYMA completed in June 2018 recognised that a better control of biogas on the digester side will make the combined operation more robust, in addition to offering better flowrate control to make a more accurate sorbent capacity measurement. Inwil was therefore chosen as the site of the long-duration gas cleaning field test.

6.2 Sorbent choice: Techno-economics and lab tests

Following a review of available literature, it was recognized that systems quoted by suppliers today to clean biogas for fuel cells are at least three times as high as the target costs identified by key industry and research stakeholders (target: $500/kWe in the short term, $200/kWe in the long term). Scales in the range of 5-150 kWe, which are relevant for this project, were not considered in existing literature. However, clear statements were made that hot gas cleanup based on hydrodesulphurisation had not been developed for small scales.

Putting the numbers in absolute terms: at a gas cleaning target cost of 500 $/kWe, a 5 kWe fuel cell has a total budget of $2500 for gas cleaning capital costs. This very low number means that

(1) Every effort must be made to minimize the number of independent sorbent vessels used ;

(2) Capital costs associated with active drying of biogas must be reduced (for example, by cooling biogas at ~15-20°C using tap water rather than at 4°C using a refrigeration cycle) or eliminated completely;

(3) Any analytical device used to monitor gas quality or sulphur breakthrough must be very inexpensive.

At all scales, the removal of trace non-H_2S sulphur compounds represents half of the vessels, and may require more significant gas conditioning (drying, etc.) than simple H_2S removal would. Removal of these trace, non-H_2S sulphur compounds therefore represents a significant fraction of the gas cleaning capital costs. This is despite the fact that only a very small percentage of total sulphur in biogas is present other than H_2S. If the tolerance to sulphur of the fuel cell and reformer system could be increased to a few ppmv, rather than the 0.5 ppmv today, significant cost reductions in gas cleaning would be possible. Nevertheles, we assume, that a SOFC system for natual gas and cleaned biogas should be identical (gas supply, exhaust, heat) in order to lower the manufacturing costs of SOFC systems. Due to this, developing a cost-optimized gas cleaning system for a biogas-SOFC system is a crucial task.

Two sorbent vessels are available in the field test set-up, COSYMA. The first vessel is filled with **SulfaTrap R7 for H_2S removal**, based on extensive testing of different H_2S sorbents completed as part of the Direct Methanation of Biogas project [15].

The second vessel is filled with a sorbent for trace, non-H_2S sulphur removal. Lab-based tests in this project focused on the evaluation of materials for the removal of dimethyl sulfide (DMS) as a representative compound, especially focusing on achieving process conditions which were economically realistic (minimal gas drying, minimal number of vessels).

The implications of the lab-based tests are clear: in cases where the terpene concentration in biogas is much higher than the trace sulphur concentration, activated carbon based sorbents may experience very early breakthrough of sulphur, due to competitive adsorption with terpenes. This is despite the fact that terpenes are not a problem for high-temperature fuel cells, and do not need to be removed in gas cleaning. The zeolite-based Cu-Z sorbent did not suffer this capacity loss effect; it is therefore much more selective to DMS in the presence of terpenes relative to activated carbons. However, it is very strongly affected by moisture.

The following recommendations were therefore made for field testing of sorbents for trace sulphur removal, with all technical and economic information in mind:

- The sorbent with the best per-CHF DMS capacity in all lab-based tests (Cer-AC) should be the first choice. It should first be tested with no biogas drying, in order to see if biogas can be cleaned without the additional expense of a drying unit, based on the good performance of this sorbent even in wet gas in the lab.
- If an early breakthrough is observed, the biogas should be cooled and dried with 15°C cooling fluid, to simulate an inexpensive cooling system with regular tap water.
- If an early breakthrough is again observed, the sorbent CuO-AC should be tested, as it was more technically robust in lab-based tests. It is more expensive but should perform better than Cer-AC under variable contaminant concentrations.
- In case early breakthroughs are still occurring and can be seen to be caused by terpenes, an additional bed or layer of inexpensive activated carbon can be used before the DMS removal to first remove terpenes.
- The final, most robust solution, which will also be the most expensive, would be to dry biogas to a dew point of 4°C using a dedicated refrigeration unit, then use Cu-Z (which is resistant to terpenes) for trace sulphur removal.

Further recommendations after performing test E:

- Selected experiments in the laboratory on the test rig "MIWI gas cleaning" in order to validate or falsify different hypotheses, i.e. concerning physio- vs. chemiesorption
- Test and reproduce results from field measurements in the laboratory
- Inclusion of the research partners from the EU project Waste2Watt (ENEA, Polito), to carry out complementary lab experiments on their experimental equipment.
- Post-test analyzes of various sorbents to understand how organic sulphur is sorbet on the various materials and derived needed material properties of more promising sorbent.

6.3 COSYMA and diagnostics for field operation

The multi-functional-pilot-plant COSYMA is now successfully in operation in Inwil. The biogas is taken from the mixed gas source at Inwil, passed through the gas cleaning system in COSYMA, from where slipstreams are sent to the diagnostics container to monitor impurities, and the gas is finally sent back to the Inwil plant.

COSYMA includes a diagnostics toolbox to properly monitor the breakthrough of sulphur compounds. Particular focus was placed on developing a stand-alone sulphur chemiluminescence detector (SCD) for detection of < 0.5 ppmv of total sulphur in a real biogas matrix. This validated instrument is now used as a reference to test an inexpensive, semi-quantitative total sulphur detector which could be used in a commercial plant.

A first series of tests have been completed in COSYMA, with the conclusion that simple solutions with only two sorbents and minimal gas cooling were not successful in retaining trace organic sulphur compounds in this biogas. Based on the lab-based sorbent tests, we can hypothesize that the cause of early breakthrough was not moisture, but instead the mix of terpenes and other volatile organic compounds (VOCs) in this biogas source.

This biogas source in Inwil was chosen as a test site specifically for its complexity in terms of impurities, so that a solution developed here could be considered validated for most or all agricultural biogas sources. We have seen that a biogas containing both significant amounts of organic sulphur and large concentrations of VOCs cannot be desulphurized to the level required by fuel cells with the sorption materials tested. There are different strategies which need further investigation in order to solve that problem. One approach is a drying/cooling step to enable the use of a terpene-resistant material such as Cu-Z. An alternative approach is the addition of an intermediate sorbent step to remove VOCs. The decision which way to go depends on many aspects, i.e. expected raw gas quality, targeted quality of cleaned biogas, techno-economic performance of sorption materials and others. Such a decision has to be taken based on the expertise of all suppliers involved for a turn-key biogas-SOFC system.

This project has been extremely valuable to further improve the testing capabilities for gas cleaning systems. The application of cleaned biogas from agriculture in a SOFC is most likely one of the most difficult cases. One reason is that the cleaned biogas should not differ much from natural gas in term of gas quality, temperature and pressure. This would allow to use turn-key SOFC systems for biogas application, which have originally be designed for natural gas operation. However, this would also mean, that the biogas should be cleaned at room temperature and low pressure in order to keep the biogas cleaning system simple. From a chemical point of view of the gas cleaning increasing temperature and pressure are both advantageous for a better gas cleaning (technical, economic).

We expect that knowledge of this project will be transfer to other biogas value chains. This can be either for different end uses of the biogas, such as biogas cleaning for upgrading plants based on membrane or scrubbers as well as catalytic methanation. For each value chain a review of the specification of the end use system is needed as well as for the raw gas quality in order to select best option in sorption based gas cleaning. Given the high variance of raw gas qualities and required clean biogas qualities most likely for each value chains a dedicated gas cleaning system has to be designed. Whenever possible these gas cleaning solutions should be built on “standard building block”, which can be easily combined for specific applications.

Our project has confirmed that a fundamental understanding of all relevant processes in gas cleaning is critical for a smart design of gas cleaning systems and good collaboration between industry and academia is a key to success.

7 Communications

Results generated in the framework of this project have been formally communicated in the following ways:

Peer reviewed paper: A. S. Calbry-Muzyka, J. Indlekofer, J. Schneebeli, S. M. A. Biollaz, "Online Measurement of Sub-ppmv Total Sulfur in Biogas by Chemiluminescence," Energy & Fuels, vol. 33, no. 10, pp. 9859-9869, 2019.

Masters thesis: Julian Indlekofer, 27 Feb. 2018, Validierung und Optimierung eines Schwefel-Chemilumineszenz-Detektors zur Onlinemessung des Gesamtschwefelgehaltes in Biogasen, HTWG Konstanz (Fakultät Maschinenbau, Studiengang Umwelt- & Verfahrenstechnik).

Masters thesis: Chirayu Thakur, 15 Dec. 2018, Removal of Dimethyl Sulfide from Biogas for Catalytic Applications, Hanze University of Applied Sciences (Groningen, Netherlands) and EUREC European Master in Renewable Energy.

Masters thesis: David Rast, 23 August 2019, Mechanisms of Dimethyl Sulfide Adsorption from Biogas on Activated Carbons and Zeolites, ETH Zürich.

Poster presentations: A.S. Calbry-Muzyka, J. Schneebeli, A. Frei, S.M.A. Biollaz, “Trace Sulphur and Organic Compounds in Biogas from Different Biomass Sources”, presented 3-4th May 2018 at the 5th International Conference on Renewable Gas Technology (**REGATEC 2018**) conference in Toulouse as well as 16th May 2018 at the 26th European Biomass Conference & Exhibition (**EUBCE 2018**) in Copenhagen.

Oral presentation: S.M.A. Biollaz, “Desulphurisation of Biogas from Varied Sources for Sensitive Energy Converters”, presented 17th May 2018 at the 26th European Biomass Conference & Exhibition (**EUBCE 2018**) in Copenhagen.

Oral presentation: S.M.A. Biollaz, “Trace sulphur and organic compounds in biogas from different biomass sources”, presented 18th June 2019 at the **GAS Analysis 2019** Conference & Exhibition in The Hague (NL).

Several parallel activities with a direct relationship to this project have also been undertaken.

Our research group at PSI became a project partner of the project proposal “Waste2Watts”, submitted and accepted to the Horizon2020 “Efficient and cost-optimised biogas-based co-generation by high-temperature fuel cells” proposal call. One of the key goals of this project is the demonstration of a fuel cell at a small agricultural biogas installation in Switzerland. PSI is responsible for biogas sampling and analysis as well as for gas cleaning experiments. The learnings from the ongoing BFE project will be able to be used directly in this new European project.

We also had a BRISK2-funded project to perform biogas measurements at the DEMOSOFC site in Turin, Italy. The focus of this campaign is particularly on siloxanes, but other trace biogas compounds are of interest as well. A joint publication of the involved partner is in preparation.

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