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Biogas cleaning for catalytic methanation: Results from long duration experiment in COSYMA

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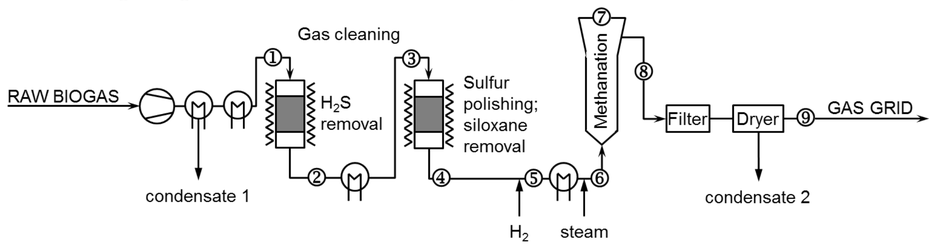
Project introduction

A recently-completed demonstration project at the Werhölzli site in Zürich used raw biogas from a wastewater treatment plant and from a biowaste digester as the CO_2 source for a catalytic methanation process using Power-to-Gas. The plant, named COSYMA, injected synthetic natural gas into the Swiss natural gas grid for 1130 hours of operation.

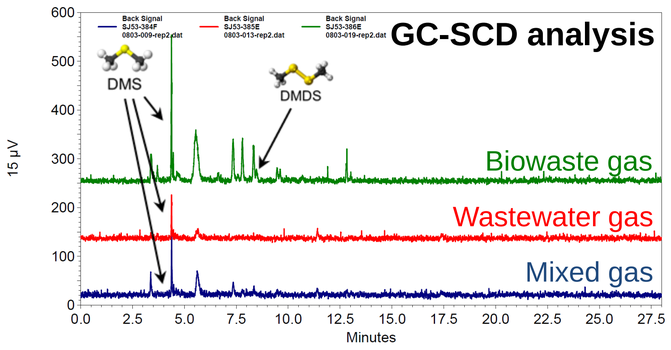


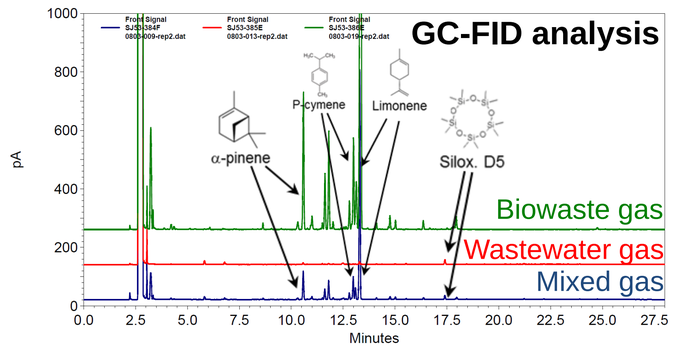
Because the methanation catalyst is sensitive to many biogas contaminants, especially sulfur compounds, specialized gas cleaning is needed. A two-stage gas cleaning process based on commercial sorbents is used. Gas quality is monitored by microGC, GC-SCD/FID, and Dräger tubes.

Gas contaminants

H_2S exists in the mixed gas at a level of 20-50 ppm.
Most of the other trace sulfur compounds originate from the biowaste digester. However, dimethyl sulfide (DMS) exists in both gas sources.

Siloxanes are absent in the biowaste gas, but present in the wastewater gas.
The biowaste gas contains terpenes to a much greater extent than the wastewater gas does.

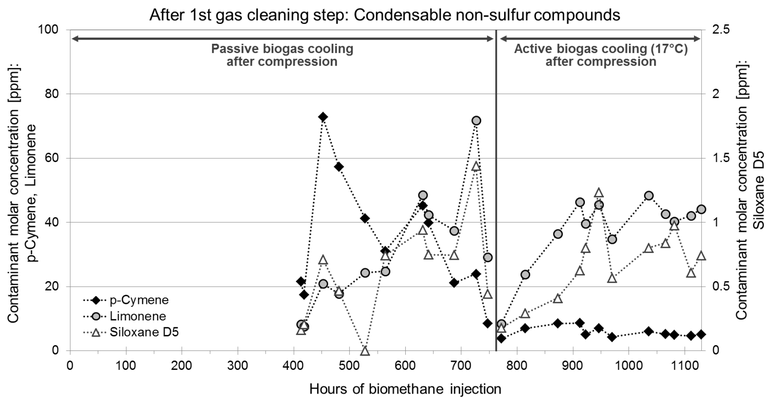


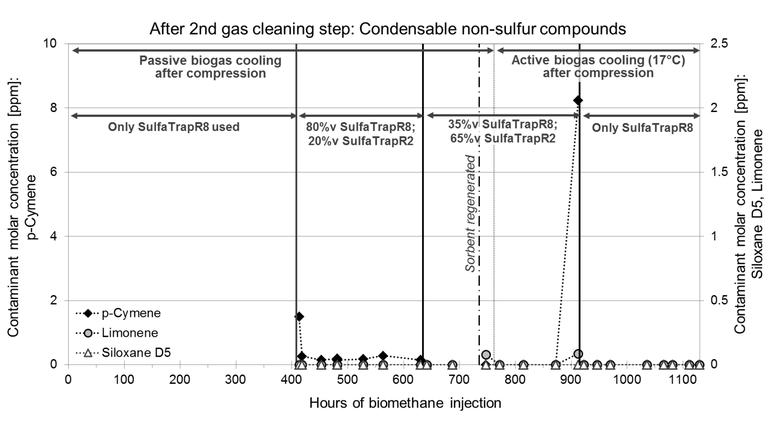


Removal of non-sulfur trace compounds

Of the many non-sulfur trace compounds contained in the biogas, terpenes (e.g. limonene) are the most prevalent, but siloxanes are the most dangerous as they could form SiO_2 deposits in the methanation reactor.

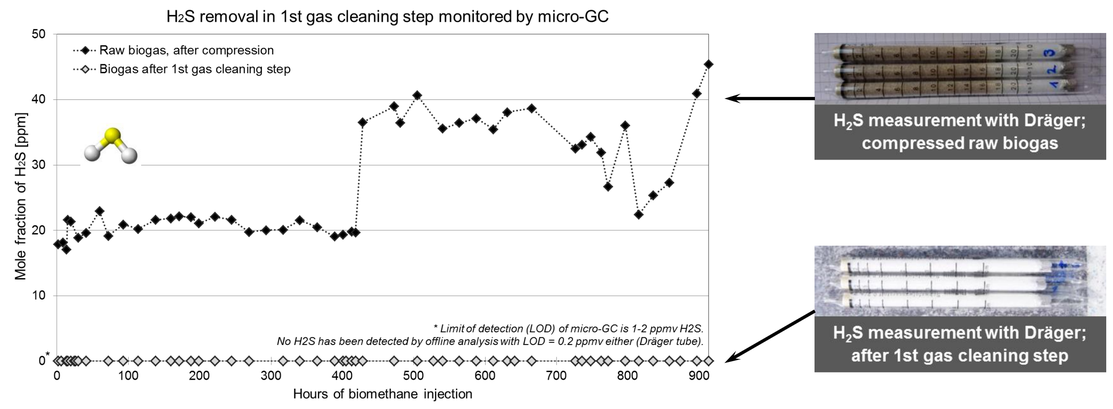
Siloxanes were never detected after the gas cleaning system. Siloxanes, terpenes, and other organics were removed in the 2nd gas cleaning step (mix of two high surface area sorbents), not in the 1st.





H_2S removal

H_2S removal in first step was consistent, even with changes in inlet H_2S concentration and other conditions (temperature, humidity of gas). The commercial sorbent SulfaTrap R7 (a mixed transition metal oxide sorbent) was used. H_2S was never detected after this step (detection limit = 0.2 ppm).



Removal of organic sulfur

Non-H_2S sulfur compounds were mostly not removed in the first gas cleaning step.

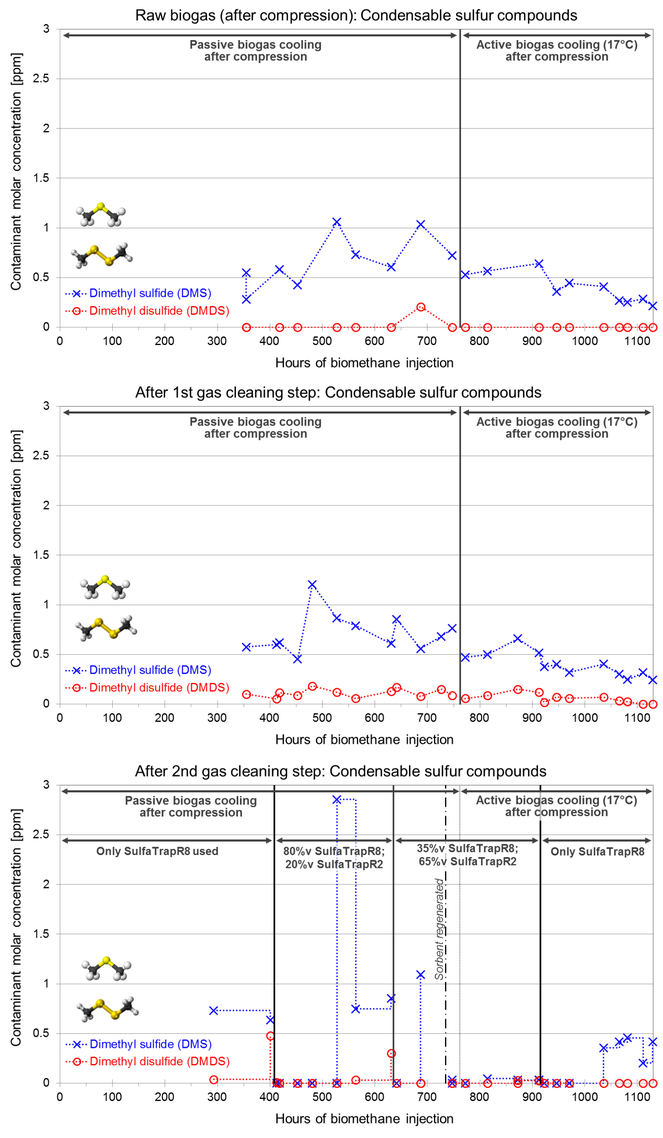
In the 2nd gas cleaning step, several sorbent combinations and conditions were tested to remove trace sulfur. Dimethyl sulfide (DMS) was the most difficult compound to remove.

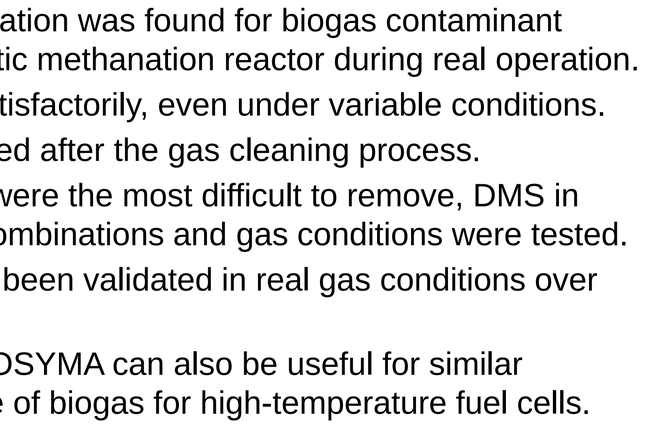
A packed bed of two sorbents (SulfaTrap R8 & R2) was needed to remove all trace organic sulfur compounds.

DMS adsorption was seen to be moisture-sensitive. Drying the biogas partially (at 17°C) was necessary to extend the time to breakthrough of DMS.

Moisture content was thus reduced to 4000 ppm at the system pressure of 6.7 bara.

When DMS was removed from biogas, the methanation catalyst's activity was stable.





Conclusions

- A successful sorbent combination was found for biogas contaminant removal to protect the catalytic methanation reactor during real operation.
- H_2S was always removed satisfactorily, even under variable conditions.
- Siloxanes were never detected after the gas cleaning process.
- Non-H_2S sulfur compounds were the most difficult to remove, DMS in particular. Several sorbent combinations and gas conditions were tested.
- Gas diagnostics toolbox has been validated in real gas conditions over >1000 hours of operation.
- Gas cleaning results from COSYMA can also be useful for similar applications, such as the use of biogas for high-temperature fuel cells.

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