

A Power-2-X Biogas Desulfurization Process for Use in Gas Absorption

Sebastian Borgquist ^a, Sebastian Nis Bay Villadsen ^a, Jens Abildskov ^b, Philip Loldrup Fosbøl ^a

^a DTU-CERE, DTU Chemical Engineering, Søtofts plads 228A, Kongens Lyngby, Denmark

^b DTU-PROSYS, DTU Chemical Engineering, Søtofts plads 228A, Kongens Lyngby, Denmark

seborg@kt.dtu.dk; snbv@kt.dtu.dk; ja@kt.dtu.dk; plf@kt.dtu.dk

Abstract. A new power-2-X desulfurization method has been developed for use in biogas cleaning. This process used a scrubber wherein the H₂S present in biogas was oxidized to elemental sulfur. The oxidant was then regenerated by running an electrical current through an electrochemical cell.

So far a parameter analysis of the system has been done. The system was found to run at an efficiency between 23 and 43%. The primary determinant of system performance was found to be the total amount of H₂S present in the inlet gas. The largest cause of efficiency loss was the consumption of oxidative species used in the formation of sulphate generated by oxidizing elemental sulfur.

During a long-term stability test of the system it was found that the process was stable during extended operation.

Keywords: P2X, Gas cleaning, Desulfurization, Oxidative scrubbing, Electrochemistry

Introduction

Climate change is becoming an increasing concern and alternatives to traditional energy sources are becoming continuously more important.

While green electricity sources, such as wind, hydro and solar will continue to grow in the future, there will still be a market for hydrocarbons for use in heating and fuel production.

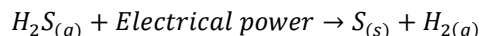
Biogas offers an alternative to traditional fossil sources for hydrocarbon fuels and the biogas sector is therefore expected to grow rapidly over the next decades [1]. Biogas is a hydrocarbon gas produced by anaerobic fermentation of biological material (typically waste). It consists mainly of methane (CH₄) and carbon dioxide (CO₂), but also contains several impurities, most of which are unwanted [2].

Especially interesting among these impurities is hydrogen sulfide (H₂S) as it is especially abundant in the gas where the concentration can be up to several thousand parts per million (ppm). It is important to remove the H₂S from the biogas, since it is highly poisonous to the catalysts, which are used to further react the biogas into biofuel.

Several technologies for desulfurization of biogas currently exists, but they are generally fairly expensive.

Furthermore, the current technologies are not able to quickly adapt to changes in H₂S, which may be seen when the feed biomass is changed [3].

In this project a new Power-to-X (P2X) desulfurization technology is developed, which is both cheaper and more adaptable, than the currently used technologies. This technology utilizes an oxidative agent, which reacts with the H₂S in a scrubber tower to form elemental sulfur [4]. The spent oxidative agent is then regenerated in an electrochemical cell after which it can be reused. In this way, no chemicals are spent and the overall reaction of the system is:



This new biogas cleaning process makes it possible to remove H₂S from biogas without consuming any chemicals and without adding oxygen to the gas. Besides this the process is cheap and can reach removal efficiencies high enough to remove the need for expensive polishing methods before upgrading the biogas.

Furthermore, the process is capable of swiftly adjusting itself to changing concentrations of H₂S, since the power consumption simply needs to be changed to reflect the change in H₂S concentration.

This places the technology ahead of currently used cleaning methods, which are expensive and have difficulties in adapting to changing levels of H₂S concentration [3].

Setup and method

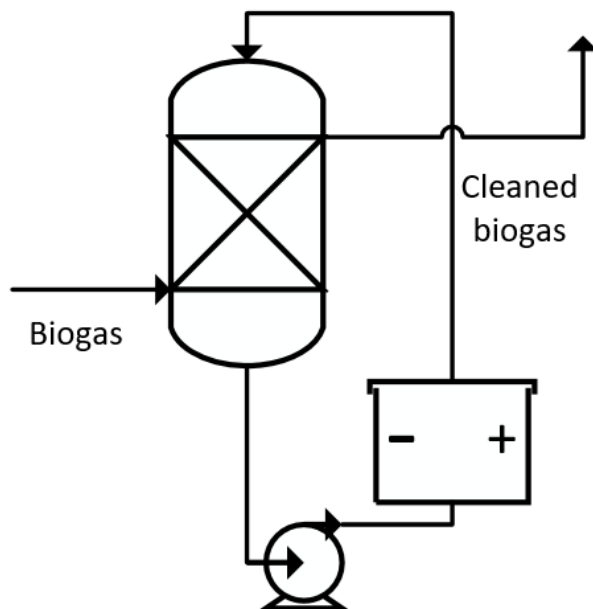


Fig 1: Simple flow diagram of the electroscrubbing process

Experiments were made using a simple electroscrubbing setup. A flow diagram of the setup used can be seen in figure 1. The H_2S rich gas enters the scrubber tower from the bottom where it comes into contact with the oxidant rich solvent. In doing so the H_2S is oxidized and forms elemental sulfur while the oxidant is reduced. The cleaned biogas then exits the scrubber tower from the top.

The spent solvent is pumped from the bottom of the scrubber through an electrochemical cell. In this cell the oxidant is regenerated on the anode while hydrogen gas is formed on the cathode. The solvent is then pumped back into the top of the scrubber tower and the cycle continues without any loss of active species.

The hydrogen gas formed on the cathode of the electrochemical cell is currently vented, but it may be feasible to capture this gas instead.

The inlet biogas and cleaned biogas was measured for H_2S contents in order to determine the efficiency of the process.

The performance of the process was examined by observing two different parameters. One parameter was the removal efficiency defined as:

$$e_R = 1 - \frac{n_{H_2S,out}}{n_{H_2S,in}} \quad (1)$$

This value describes the percentage of H_2S removed in the scrubber tower. A removal efficiency of 1 means that all H_2S is removed, while a removal efficiency of 0 describes a situation where no H_2S is captured in the scrubber. In the electroscrubbing system the removal efficiency is directly impacted by adjusting the electrical current applied to the electrochemical cell. A higher current increases the amount of oxidant in the solvent and therefore increases the solvents capability for capturing H_2S .

Since the removal efficiency is dependent on the electrical current it is useful to introduce another efficiency, which describes the amount of electricity used compared to a theoretical amount. H_2S reacts with the oxidant in a one to one ratio. Since 2 electrons are needed for generating one molecule of oxidant, the theoretical amount of power needed for capturing H_2S can be calculated. The current efficiency of the process can then be calculated as the amount of power actually used compared to the theoretically needed power:

$$e_c = \frac{N_{H_2S} * N_A * 2}{I * C} \quad (2)$$

Where N_{H_2S} is the amount of moles of H_2S removed every second, N_A is Avogadro's number, I is the current running through the electrochemical cell and C is Coulombs number. An efficiency lower than 1 thus signifies that more oxidant is being produced, than what is needed for removing the H_2S present in the biogas. If an efficiency lower than 1 is observed, the oxidant must be consumed by oxidizing other compounds in the solvent. Alternatively some oxidant may be vented in the exhaust gas of the system.

Results

So far an initial parameter analysis of the process has been carried out on a laboratory scale. The influence on the process of the total gas flow, total solvent flow, and the gas H_2S concentration have all been examined. Furthermore, a long-term test has been carried out to ensure that the process is stable over prolonged periods of time.

Influence on liquid flow rate on the process

A series of experiments were done, in order to determine the effect of the solvent flow rate on the scrubber system. In a conventional scrubbing system the amount of solvent flowing through the scrubber is directly correlated with the systems ability to capture gas. In an electroscrubbing system the capacity of the liquid is instead correlated to the amount of current applied to electrochemical cell. This electrical current directly impacts the concentration of active species in the solvent.

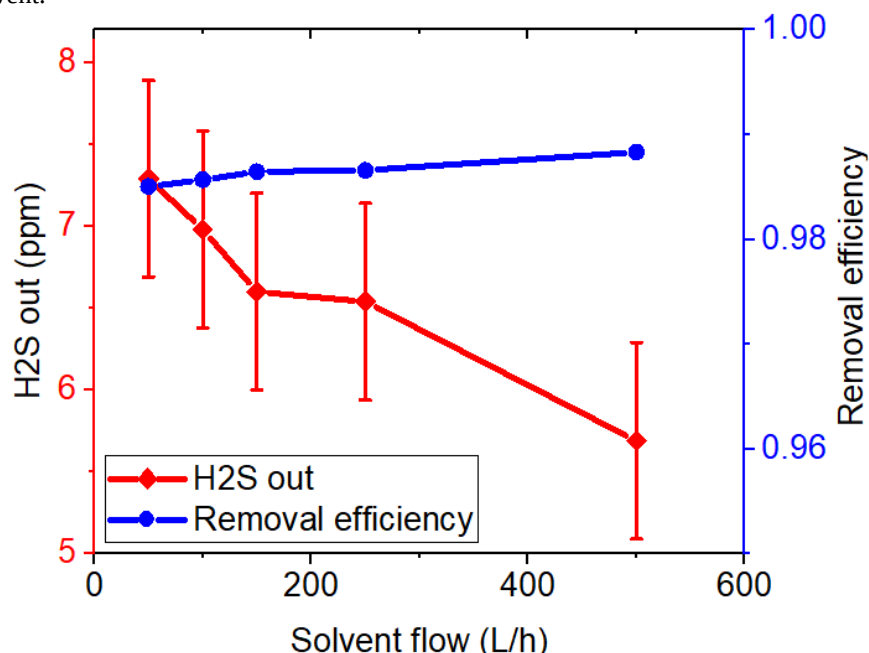


Fig 2: H_2S concentration in the scrubber outlet and removal efficiency through the scrubber as a function of total solvent flow.

A series of experiments were run at different flow rates to determine if the flow rate had an impact on the removal efficiency of the process. This was done for a constant gas inlet of 450 g/h with an H_2S concentration of 500 ppm. The electrical current was also kept stable during the experiments. The removal efficiency of the system is calculated as defined in equation 1 and the results can be seen in figure 2.

It is immediately seen, that the change in solvent flow has only a superficial effect on the amount of H_2S removed by the process. An increase in solvent flow does lead to increased capture, but the change is so small as to be negligible. It was desired to run this experiment at even smaller solvent flows, but problems arose due to inabilities to distribute the solvent evenly through the scrubber.

Influence of gas flow and concentration on the scrubber system

The influence of gas flow and H_2S concentration on the efficiency of the system was also examined as seen in figure 3. The experiments seen in figure 3 were all done at a constant solvent flow rate of 500 L/h. The efficiency was calculated using the definition in equation 2.

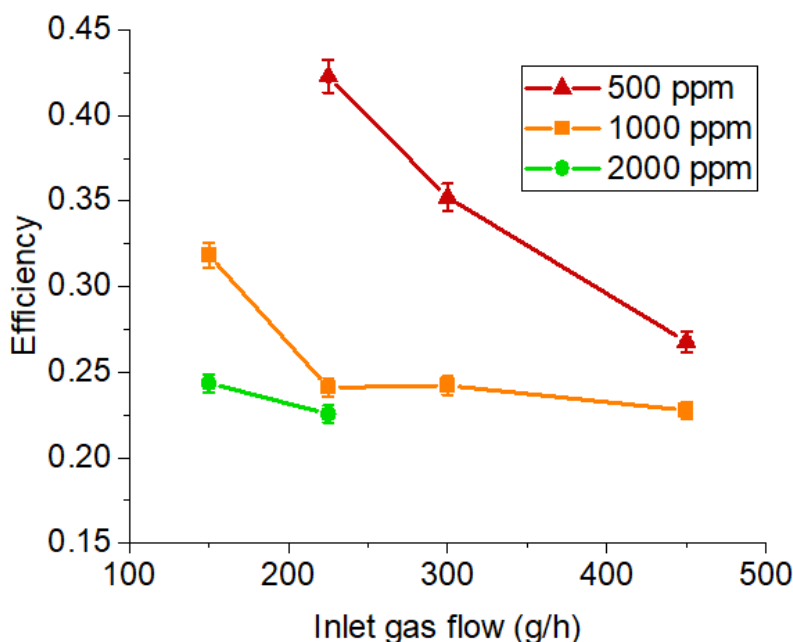


Fig 3: Efficiency of the process as function of inlet gas flow for several different H₂S concentrations.

It is seen that the efficiency of the process decreases both as a function of inlet gas flow as well as the H₂S concentration in the inlet gas. The highest efficiency was found to be approximately 0.43 at a low inlet gas flow and low H₂S concentration. Additionally it is observed that the efficiency curve flattens out at approximately 0.22. This behavior seems to suggest, that the efficiency of the system is determined by the overall amount of H₂S going into the system. This may be caused by an increase in oxidative species facilitating unwanted side reactions.

Long term operation of the system

Additionally a long-term test of the process was performed where the process was run continuously for 30 hours in order to determine the stability of the process over prolonged operation. This test was done at a constant gas flow rate of 300 g/h with an H₂S concentration of 1666 ppm.

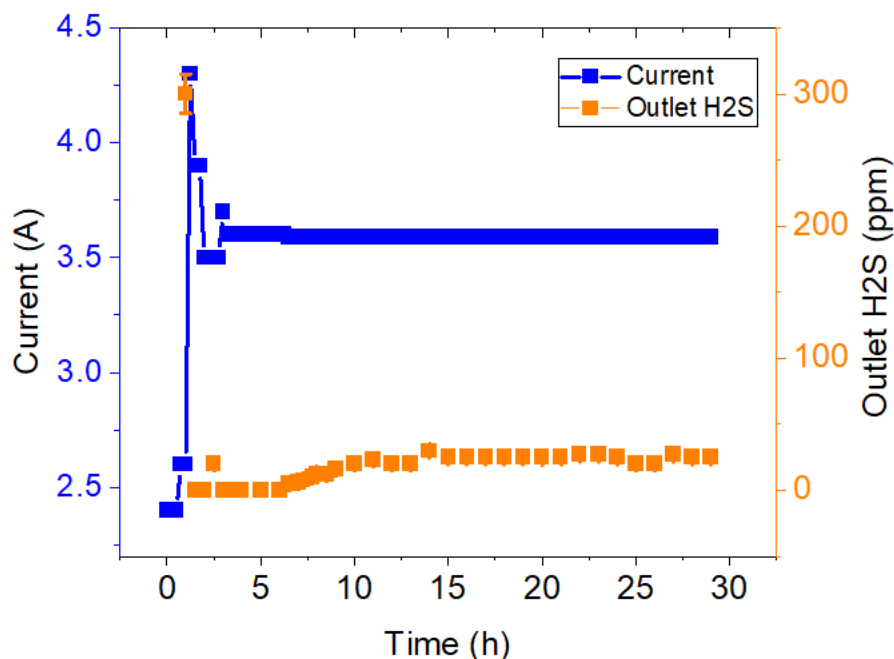


Fig. 4: H₂S concentration in the scrubber outlet during the long-term test.

The results of the test can be seen in figure 4. The process is seen to be extremely stable over longer periods of time, with changes in H₂S outlet concentration changes around 0.1% of the inlet concentration. The current efficiency of the process during the long-term test was approximately 22 %, which corresponds well to the expected value from figure 2.

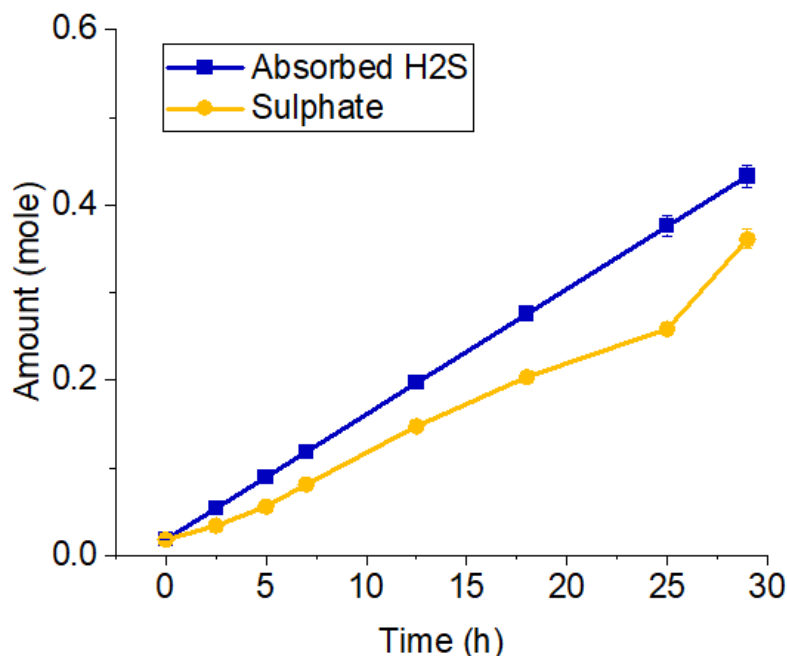


Fig. 5 H₂S concentration in the scrubber outlet during the long-term test.

It was suspected that the loss of current efficiency could be caused by further oxidation of the elemental sulfur into dissolved sulphate. To test this several liquid samples were taken out periodically during the long-term test. These liquid samples were tested for sulphate content by using an ion chromatograph. The results of analysis can be seen in figure 5. As suspected the amount of sulphate dissolved in the liquid in the scrubber is seen to rise linearly during the

experiments. Since the reaction from sulfur to sulphate requires three times as much oxidant as the reaction from H_2S to sulfur, the amount of power use on sulphate formation can be calculated. It was found that 54 % of the power used in the process goes to this formation of sulphate. This means that the efficiency of the process can be drastically increased, if it is possible to remove the elemental sulfur before further reactions can take place.

Future work



Fig. 6: Mobile pilot plant currently being constructed at DTU.

A mobile pilot setup is currently being constructed at DTU. This setup will be transported to biogas facilities in order to test the process on a bigger scale than in the laboratory setup. A picture of the mobile pilot setup can be seen in figure 6. With this setup it will be possible to test the technology on a medium scale before building the full scale facility. Furthermore, it will be possible to test the capability of the system on different H_2S rich gasses. A full scale setup is planned and will be built before the end of 2023.

Conclusions

The feasibility of the new sulfur removal technology was validated. It has been found, that the total amount of H_2S in the system exerts the largest influence on the biogas cleaning process. This is likely caused by an increase in oxidative material, which facilitates side reactions. Furthermore, it was found that the solvent flow through the scrubber had only a negligible influence on the process.

During a long-term test of the process it was found that a large amount of the power used in the electrochemical cell was spent oxidizing elemental sulfur into sulphate. If this reaction can be prevented the efficiency of the process can be raised. The system was found to be stable over long periods of operation

Acknowledgements

This research project has been made possible by funding from the Energy Technology Development and Demonstration Program (EUDP) journal number 64019-0601, Pentair Union, Elplatek and Danish Gas Technology Center (DGC).

References

1. N. Scarlat, J.F. Dallemand, F. Fahl, *Renewable Energy*, 129 (2018), 457-472.
2. S. Rasi, A. Veijanen and J. Rintala, *Energy*, 32 (2007), 1375-1380
3. N. Abatzoglou and S. Boivin, *Biofuels; Bioproducts and Biorefining*, 3(1) 2009, 42-71
4. S.N.B. Villadsen et al, *Separation and Purification Technology*, 2022, 278