A Novel Electroscrubbing Process for Gas Cleaning
Sebastian Nis Bay Villadsen

PhD Thesis
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The front page art is made by Danish artist Anders Morgenthaler as a personal favour to the author.
Preface

This thesis is submitted as partial fulfilment of the requirements for obtaining the degree of Ph.D. at the Technical University of Denmark (DTU). The project was funded by ForskEL through the project MeGa-StoRE 2, phase 2, journal number 12393. The project was carried out from the 15th of September 2016 to the 14th of September 2019, partially at the gas laboratory at Elplatek A/S in Horsens and at the Technical University of Denmark, Department of Mechanical Engineering, Section of Materials and Surface Engineering (MTU).

The project was supervised by Professor Per Møller, Department of Mechanical Engineering, Associate Professor Philip Loldrup Øbro Fosbøl, Department of Chemical and Biochemical Engineering, Director Lars Pleth Nielsen, Danish Technological Institute and Professor Hans Nørgaard Hansen, Department of Mechanical Engineering.
Abstract (English)

This doctoral thesis presents three years of research and development within a new electroscrubbing process for biogas desulfurization. The process is designed to remove hydrogen sulfide (H₂S) from biogas by using an active compound that is generated through electrochemistry. Independent on the downstream application of biogas, H₂S has to be removed and all biogas plants have desulfurization processes implemented. However, the H₂S removal technologies of today suffer from either high operating expenses (OPEX) or residual oxygen (O₂) in the purified biogas. Electroscrubbers have several advantages, including no residual O₂ in the purified gas, high efficiency and no consumption of chemicals. The main disadvantage is that currently, there are no commercial electroscrubbing systems available.

This research has been carried out within the MeGa-StoRE project. Part of the project objectives has therefore been to construct a pilot plant for field testing of the electroscrubbing technology. The MeGa-StoRE project investigated second-generation upgrading of biogas through catalytic conversion of carbon dioxide (CO₂) to methane (CH₄). This process takes place over a catalyst, which is very sensitive to H₂S.

Electroscrubbing biogas for second-generation upgrading is a multidisciplinary scientific field. Research within this field require fundamental knowledge of electrochemistry, surface technology, gas scrubbing, process chemistry, biogas and catalytic processes. In this thesis, an empirical approach has been widely used for the research and development of the new electroscrubbing process.

Two laboratory and two campaign electroscrubbers have been designed, constructed and operated in this thesis. The laboratory electroscrubbers were used to investigate the fundamentals of the process and the dimensions required for the pilot plants. The campaign electroscrubbers were used to investigate the process on real biogas and optimize the process parameters.

The main conclusion of this thesis is that the new electroscrubbing process has proved to successfully remove H₂S from biogas down to non-detectable concentrations. The process does not produce any waste as the two side products, H₂ and sulfur, can be used within the biogas plant. The H₂ can be used for the second-generation upgrading process, and the sulfur as a fertilizer.

Scaling up the process to a pilot plant size proved possible. The campaign electroscrubbers did have a lower current efficiency than the laboratory electroscrubbers, although this was partly compensated with an optimization of the electrical properties. Overall, the maximum power efficiency of the laboratory electroscrubbers was found to be 16 ± 1.6% while the campaign
electroscrubbers achieved $13.4 \pm 0.9\%$. A power efficiency of approximately 30% would make this electroscrubbing process the cheapest desulfurization technology based on OPEX for biogas plants. Both the laboratory and the campaign electroscrubbers proved capable of removing H$_2$S down to non-detectable concentrations.
Resumé (Dansk)

Denne afhandling præsenterer tre års forskning og udvikling af en ny elektroskrubbeprocess for svovlrensning af biogas. Processen er designet til at fjerne svovlbrinte (H₂S) fra biogas ved at bruge et aktivt stof, der er produceret via elektrokemi. Uafhængigt af hvad biogassen skal bruges til, så skal H₂S fjernes og alle biogasanlæg har derfor en svovlrensningsproces installeret. Technologierne, der bliver benyttet i dag lider dog under enten høje omkostninger (OPEX) eller at der er ilt (O₂) til stede i den rensede biogas. Elektroskrubber har en række fordele, inklusiv at der ingen O₂ er i den rensede gas, høj effektivitet og intet forbrug af kemikalier. Hovedulempen er, at der i dag ikke eksisterer kommercielle elektroskrubberanlæg.

Forskningen har fundet sted inden for MeGa-StoRE projektet. En del af projektet har derfor været at udvikle et pilotanlæg til at teste elektroskrubberteknologien af på ægte biogas. MeGa-StoRE projektet undersøgte andengenerationsopgradering af biogas via katalytisk konvertering af karbondioxid (CO₂) til metan (CH₄). Denne proces finder sted over en katalysator der er meget sensitiv over for H₂S.

Elektroskrubning af biogas til andengenerationsopgradering er et multidisciplinært forskningsfelt. Forskning inden for dettefelt kræver kendskab til elektrokemi, overfladeteknologi, gasskrubning, proceskemi, biogas og katalytiske processer. I dette studie er en empirisk tilgang blevet vidt benyttet til forskning og udvikling af denne nye elektroskrubningsproces.

To laboratorie- og to kampagneelektroskrubber er blevet designet, konstrueret og benyttet i denne afhandling. Laboratorieelektroskrubberne blev brugt til at undersøge fundamentale dele af processen og de fysiske dimensioner, der var nødvendige for at skalere processen op. Kampagneelektroskrubberne blev benyttet til at undersøge processen på ægte biogas og optimere processen.

Hovedkonklusionen i denne afhandling er, at den nye elektroskrubningsproces er i stand til at fjerne H₂S fra biogas ned til ikke-detekterbare koncentrationer. Processen producere ikke affaldsprodukter, idet de to biprodukter, brint (H₂) og svovl, kan bruges på biogasanlægget. H₂ kan bruges i andengenerationsopgraderingsanlægget mens svovlet kan bruges som gødningsmiddel. Det viste sig at det var muligt af skalere processen op. Kampagneelektroskrubberne havde en lavere strømeffektivitet end laboratorieelektroskrubberne, hvilket dog delvist blev kompenseret ved optimerede elektriske egenskaber. Overordnet set opnåede laboratorieelektroskrubberne en energieffektivitet på 16 ± 1.6% mens kampagneelektroskrubberne opnåede 13.4 ± 0.9%. En energieffektivitet på omtrent 30% vil gøre elektroskrubningsprocessen til den billigste svovlrensningsteknologi blandt de eksisterende baseret på OPEX.
I would like to thank the Danish funding programme ForskEL for supporting the MeGa-StoRE 2, phase 2 project, journal number 12393, which funded this Ph.d.-project.

I would like to express my gratitude to all my supervisors. To Professor Per Møller for his energy and ideas that kept encouraging me to try new things. For our lively discussions and common goal of developing a desulfurization technology that can be of both scientific and commercial interest. To Associate Professor Philip Lødrup Øbro Fosbol for taking me in. Thank you for helping me navigate the scientific part of being a ph.d.-student and give me the opportunity to develop the process further. To Lars Pleth Nielsen for scientific discussion and help with the writing. Finally, to Professor Hans Nørgaard Hansen for taking over the responsibility as main supervisor.

Thank you to all the people at Elplatek Horsens for your support. Thanks to Sonja and Benny From Okholm for allowing me to perform all my experiments and helping me with electrochemical know-how. Special thanks to the three Jans: Jan Boye Rasmussen for managing and supporting the gas cleaning project. Jan Pedersen for improving the design and constructing the important components of the electroscrubber. Finally, to Jan Pihl Rasmussen, my closet college, thank you for keeping my feet on the ground when I needed it and making sure that the MeGa-StoRE project actually made methane from biogas. I have learned a lot working with you.

A special thanks to Poul Christian Toftgaard from GreenHydrogen.dk, not only for programming the PLCs for the electroscrubbers, but for being available every time I needed help with the components. To Christian Warm, with whom the first electroscrubbers were designed and constructed. Finally to Nicolai Frost-Jensen Johansen for a lot of scientific discussions and help with the figures.

Thank you Randi Neerup for your help with analysing the gas at Midtfyn and the thermodynamic model.

I would like to thank the people at Nysted and Midtfyn biogas plants for their support during the experiments.

Thank you to the interns I have had, Christian Bang and Niels Peter Nielsen, for your help.

Thank you to all the colleagues at DTU MEK, especially Malene Kaab for her assistance with the scanning electron microscope. Also thanks to Peter Westermann, Marianne Burggraaf, Rohit Gaikwad, Saber, Jacob, and Emilie.

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A special thanks to Knud Strange, even though you regretted your own PhD, you supported my decision and helped me throughout the project.

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<th>Description</th>
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<tr>
<td>ATEX</td>
<td>ATmosphères EXplosives, an EU directive regarding explosive atmospheres</td>
</tr>
<tr>
<td>AV</td>
<td>Automatic Valve</td>
</tr>
<tr>
<td>BE-Clean</td>
<td>Biogas Electro Clean</td>
</tr>
<tr>
<td>BF</td>
<td>Bag Filter</td>
</tr>
<tr>
<td>BV</td>
<td>Bypass Valve</td>
</tr>
<tr>
<td>CAPEX</td>
<td>CAPital EXpenditures</td>
</tr>
<tr>
<td>CCU</td>
<td>Carbon Capture and Utilization</td>
</tr>
<tr>
<td>CERE</td>
<td>Center for Energy Resources Engineering</td>
</tr>
<tr>
<td>CHP</td>
<td>Combined Heat and Power</td>
</tr>
<tr>
<td>CT</td>
<td>Collection Tank</td>
</tr>
<tr>
<td>CS</td>
<td>Capacity Sensor</td>
</tr>
<tr>
<td>CV</td>
<td>Closing Valve</td>
</tr>
<tr>
<td>D4</td>
<td>Octamethylcyclotetresiloxane</td>
</tr>
<tr>
<td>D5</td>
<td>Decamethylcyclopentasiloxane</td>
</tr>
<tr>
<td>DSA</td>
<td>Dimensionally Stable Anode</td>
</tr>
<tr>
<td>DTU</td>
<td>Technical University of Denmark</td>
</tr>
<tr>
<td>DTU MEK</td>
<td>Mechanical Engineering Department at the Technical University of Denmark</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive x-ray Spectroscopy</td>
</tr>
<tr>
<td>eH</td>
<td>Electrical potential</td>
</tr>
<tr>
<td>EH</td>
<td>Electrode Holder</td>
</tr>
<tr>
<td>ELCC</td>
<td>Electrolyte level control connection</td>
</tr>
<tr>
<td>EUDP</td>
<td>Energy Technology Development and Demonstration Program, Danish funding programme</td>
</tr>
<tr>
<td>GAP</td>
<td>Gas analysis point</td>
</tr>
<tr>
<td>GC/TCD</td>
<td>Gas chromatograph equipped with thermal conductivity detection</td>
</tr>
<tr>
<td>K-value</td>
<td>Reaction rate constant</td>
</tr>
</tbody>
</table>
LECA | Lightweight Expanded Clay Aggregate, used for packing material in the laboratory electroscrubbers
LRSR | Liquid Redox Sulfur Recovery
MeGa-StoRE | Methane Gas for Storage of Renewable Energy
MMO | Mixed Metal Oxide
MRU | MRU SWG 100 stationary biogas analyzer
ND | Not Detected
NDIR | Non Dispersive InfraRed
OPEX | OPerating E xpenses
Os | Oxidizing species
PLC | Programmable Logic Controller
ppb | Parts per billion
ppm | Parts per million
PS | Pressure Sensor
P&ID | Piping and Instrumentation Diagram
RS | Redox Sensor
SEM | Scanning Electron Microscopy
TD/GC/MS | Thermal Desorption combined with a Gas Chromatograph and a Mass Spectrometer
VOC | Volatile Organic Compounds

Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G_T$</td>
<td>The change of Gibb’s free energy for a reaction at a certain temperature (T)</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>Removal efficiency, amount of pollutant removed. [%]</td>
</tr>
<tr>
<td>$\delta x_1$</td>
<td>Uncertainty of the parameter $x_1$.</td>
</tr>
<tr>
<td>$\delta x_n$</td>
<td>Uncertainty of the parameter $x_n$.</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Porosity of the packing material</td>
</tr>
<tr>
<td>$\eta_g$</td>
<td>Viscosity of biogas [Pa s]</td>
</tr>
<tr>
<td>$\eta_i$</td>
<td>Current efficiency</td>
</tr>
<tr>
<td>$\eta_p$</td>
<td>Power efficiency</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>Density of biogas [kg/m$^3$]</td>
</tr>
<tr>
<td>Symbols</td>
<td>Definition</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$a$</td>
<td>Surface area of packing material ([\text{m}^2/\text{m}^3])</td>
</tr>
<tr>
<td>$A$</td>
<td>Cross sectional area of the scrubber</td>
</tr>
<tr>
<td>$C_g$</td>
<td>Gas film factor</td>
</tr>
<tr>
<td>$D_{cg}$</td>
<td>Diffusion coefficient of the gas phase</td>
</tr>
<tr>
<td>$d_h$</td>
<td>Hydraulic diameter of the packing material</td>
</tr>
<tr>
<td>$E$</td>
<td>Enhancement factor</td>
</tr>
<tr>
<td>$E^0$</td>
<td>Standard potential</td>
</tr>
<tr>
<td>$E_{eq}$</td>
<td>Equilibrium potential</td>
</tr>
<tr>
<td>$ER$</td>
<td>Electrical resistance ([\Omega])</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>$G_V$</td>
<td>Gas volume flow ([\text{Nm}^3/\text{s}])</td>
</tr>
<tr>
<td>$G_M$</td>
<td>Molar gas flow ([\text{mol/s}])</td>
</tr>
<tr>
<td>$h$</td>
<td>Height of the scrubber ([\text{m}])</td>
</tr>
<tr>
<td>$HTU$</td>
<td>Height of a Transfer Unit ([\text{m}])</td>
</tr>
<tr>
<td>$i$</td>
<td>Current ([\text{A}])</td>
</tr>
<tr>
<td>$i_{\text{theory}}$</td>
<td>Theoretical current required for the removal of the pollutant ([\text{A}])</td>
</tr>
<tr>
<td>$J$</td>
<td>Current density ([\text{A/dm}^2])</td>
</tr>
<tr>
<td>$K_g$</td>
<td>Overall gas phase mass transfer coefficient</td>
</tr>
<tr>
<td>$k_g$</td>
<td>Mole fraction mass transfer in the gas phase</td>
</tr>
<tr>
<td>$k_l$</td>
<td>Mole fraction mass transfer in the liquid phase</td>
</tr>
<tr>
<td>$k_{cg}$</td>
<td>Mole fraction mass transfer coefficient</td>
</tr>
<tr>
<td>$m$</td>
<td>Equilibrium constant</td>
</tr>
<tr>
<td>$M_g$</td>
<td>Molar mass of biogas ([\text{g/mol}])</td>
</tr>
<tr>
<td>$M_{\text{pollutant}}$</td>
<td>Molar mass of the pollutant ([\text{g/mol}])</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrochemical cells</td>
</tr>
<tr>
<td>$n_{\text{pollutant}}$</td>
<td>Amount of pollutant ([\text{mole}])</td>
</tr>
<tr>
<td>$\text{Nm}^3/\text{h}$</td>
<td>Normal cubic meter per hour, i.e. a cubic meter of gas at room temperature and atmospheric pressure</td>
</tr>
<tr>
<td>$NTU$</td>
<td>Number of Transfer Units</td>
</tr>
<tr>
<td>$[\text{Ox}]$</td>
<td>Activity of the oxidizing species</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure ([\text{Pa}])</td>
</tr>
<tr>
<td>$P$</td>
<td>Power ([\text{W}])</td>
</tr>
<tr>
<td>$P^0$</td>
<td>Power required per kilogram of pollutant removed ([\text{kWh/kg}])</td>
</tr>
<tr>
<td>$P^0_{\text{industry}}$</td>
<td>Minimum power required per kilogram of sulfur removed based on numbers from industry ([\text{kWh/kg}])</td>
</tr>
<tr>
<td>$r$</td>
<td>Radius of scrubber</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
</tr>
<tr>
<td>$R_E$</td>
<td>Electrical resistance ([\Omega])</td>
</tr>
<tr>
<td>$R_S$</td>
<td>Electrical resistance of the electrochemical system ([\Omega])</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynold’s number</td>
</tr>
<tr>
<td>$[\text{Red}]$</td>
<td>Activity of reducing species</td>
</tr>
<tr>
<td>$S$</td>
<td>The amount of pollutant removed per time ([\text{g/h}])</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$Sc$</td>
<td>Schmidt’s number</td>
</tr>
<tr>
<td>$t$</td>
<td>Time [s]</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature [K]</td>
</tr>
<tr>
<td>$U$</td>
<td>Potential [V]</td>
</tr>
<tr>
<td>$U_C$</td>
<td>Cell potential [V]</td>
</tr>
<tr>
<td>$U_T$</td>
<td>Terminal cell potential [V]</td>
</tr>
<tr>
<td>$v$</td>
<td>Superficial liquid velocity [m/s]</td>
</tr>
<tr>
<td>$x$</td>
<td>Mole fraction of the pollutant in the solution</td>
</tr>
<tr>
<td>$x_{Bm}$</td>
<td>Logarithm of the average fraction of the component B in the liquid film</td>
</tr>
<tr>
<td>$y_i^*$</td>
<td>Mole fraction of the pollutant in the gas that is in equilibrium with the liquid at the bottom of the scrubber</td>
</tr>
<tr>
<td>$y_u^*$</td>
<td>Mole fraction of the pollutant in the gas that is in equilibrium with the liquid at the top of the scrubber</td>
</tr>
<tr>
<td>$y_i$</td>
<td>Mole fraction of the pollutant in the gas at the bottom of the scrubber</td>
</tr>
<tr>
<td>$y_{in}$</td>
<td>Gas concentration of the pollutant entering the system</td>
</tr>
<tr>
<td>$y_{out}$</td>
<td>Gas concentration of the pollutant exiting the system</td>
</tr>
<tr>
<td>$y_{pollutant}$</td>
<td>Gas concentration of the pollutant</td>
</tr>
<tr>
<td>$y_u$</td>
<td>Mole fraction of the pollutant in the gas at the top of the scrubber</td>
</tr>
<tr>
<td>$z$</td>
<td>Overall reaction valency</td>
</tr>
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</table>
Chapter 1

Introduction

Biogas is a remarkable renewable energy source. Most renewable energy sources, such as wind turbines and solar power plants, are not carbon-based and suffer from fluctuating production. Biogas production is steady, and it is a carbon-based energy resource that produces carbon dioxide (CO$_2$) upon combustion. The biogas quality is lower than natural gas, although biogas may be upgraded to completely resemble fossil natural gas. In 2017, more than 17,000 biogas plants were in use in Europe compared to only 6,200 plants in 2009 [1]. However, biogas is more than just a renewable energy source. Biogas plants link waste management with agriculture and energy production through the utilization of various feedstock in the biogas production.

1.1 Biogas Production

Biogas is produced through anaerobic digestion of organic material. The digestion of the organic material takes place in an oxygen-free environment either under mesophilic (35-42 °C) or thermophilic (45-60 °C) temperature conditions [2]. Under these conditions, different bacteria are used to ferment the feedstock and produce biogas. Biogas usually consists of 45%-70% methane (CH$_4$), 30%-45% CO$_2$, with several different pollutants [3, 4]. Hydrogen sulfide (H$_2$S) is the main pollutant with concentrations from 100 to 10,000 parts per million (ppm) [5]. Other pollutants may include methyl mercaptane (CH$_3$SH), ammonia (NH$_3$) and siloxanes [4].

The composition of the biogas depends on the applied feedstock. Many biogas plants are manure-based. Here, the manure from farms are mixed with other feedstock and digested in the biogas reactor tanks. The degassed manure is returned to the farmers where it is used as a fertilizer. Generally, the degassed manure is considered a better fertilizer than raw manure. Several biogas plants, including the Midtfyn Biogas plant in Figure 1.1, use food waste as supplement to the manure-based feedstock. This is especially common for biogas plants located close to cities.
Wastewater treatment plants may also produce biogas from the organic sludge. Biogas produced from wastewater treatment plants have been found to have the highest concentration of siloxane pollutants, octamethylcyclotetresiloxane (D4) and decamethylcyclopentasiloxane (D5) [6].

1.1.1 Biogas as Carbon Capture Technology

Biogas may be considered a carbon capture technology. A large amount of the feedstock used in biogas plants would degas directly to the atmosphere under normal conditions. Manure is an example of this, as the CH$_4$ and CO$_2$ released by the manure in a biogas plant would otherwise have been released when the manure would have been used as a fertilizer. Thus, carbon is captured in biogas plants that would otherwise have polluted the atmosphere. Due to this, the utilization of CH$_4$ from biogas may even be considered to have a negative carbon footprint, as CH$_4$ is a more harmful greenhouse gas than CO$_2$ [7].
1.2 Biogas Utilization

In Figure 1.2, an overview of biogas utilization is presented. Today, biogas is primarily used in combined heat and power (CHP) engines (a). There are a few exceptions to this utilization today. Biogas plants can also refine the biogas to produce pure methane, for injection into the natural gas grid. This is only possible when the biogas plants are connected to the natural gas grid (b) in Figure 1.2. This refining of biogas is referred to as first-generation upgrading [8] (Appendix I), and will be discussed below.

Future applications could use biogas as a carbon feedstock for energy storage. This is showed in the bottom half of Figure 1.2. Here, energy in the form of hydrogen (H\textsubscript{2}) is added to the biogas to synthesise liquid hydrocarbon (c) or additional CH\textsubscript{4} (d). In these future applications of biogas, the CO\textsubscript{2} is used as a carbon source and not vented into the atmosphere. These technologies are referred to as second-generation biogas upgrading [8] (Appendix I), and will be discussed below.

The different applications of biogas are discussed in detail in the manuscript *The Potential of Biogas; The Solution to Energy Storage*, Appendix I.

1.2.1 First-Generation Upgrading

Upgrading the biogas to pure methane by removal of CO\textsubscript{2} is called first-generation upgrading [8], Appendix I. More than 540 biogas plants in 2017 had already implemented first-generation upgrading, and more are expected to come [1]. In order to refine the biogas to natural gas quality, the CO\textsubscript{2} and pollutants have to be removed. The CH\textsubscript{4} produced from the separation is referred to as biomethane and can be injected into the natural gas grid [9]. The off-gas, containing mostly CO\textsubscript{2}, is vented into the atmosphere. This process is referred to as first-generation upgrading of biogas. Currently, there are four different technologies that all have a similar share of the upgrading market; chemical scrubbing, water scrubbing, membrane separation and pressure swing adsorption [10]. The biogas plant in Figure 1.1 uses water scrubbing for first-generation upgrading of biogas. The large tower in the biogas facility belongs to the water scrubbing system.

1.2.2 Second-Generation Upgrading

Second-generation upgrading of biogas refers to upgrading technologies where the CO\textsubscript{2} content of the biogas is used instead of vented into the atmosphere. The difference between first- and second-generation upgrading is that the CO\textsubscript{2} is used as a carbon source in second-generation upgrading. If biogas plants are considered carbon capture plants, second-generation upgrading is directly comparable with carbon capture and utilization (CCU) technologies known from the literature [11]. Using biogas as carbon source instead of exhaust gas from power plants has the advantage of a higher carbon content. While most flue gasses contain only \textasciitilde10% CO\textsubscript{2}, biogas contains only carbon-based gasses and \textasciitilde30% CO\textsubscript{2}.

In Figure 1.2, two different second-generation technologies are presented, i.e. methanation and synthesis of organic compounds, e.g. methanol synthesis. Both processes require a catalyst for the reduction of CO\textsubscript{2}. For the methanation process, the CO\textsubscript{2} can be directly reduced to CH\textsubscript{4} over a nickel catalyst. The methanol production requires a reforming of the biogas over a
nickel catalyst followed by a synthesis over a copper catalyst. However, \( \text{H}_2\text{S} \) is poison for the nickel-based catalysts [12]. Deep removal of \( \text{H}_2\text{S} \) is therefore required for utilization of biogas to e.g. methanation, methanol synthesis or solid oxide fuel cells [13]. Due to the high reactivity of \( \text{H}_2\text{S} \), the allowed total sulfur concentrations should be 10-100 ppb in the purified biogas [14]. This is much lower levels of \( \text{H}_2\text{S} \) than is currently available with the biogas desulfurization systems of today. This may be the largest hurdle for the implementation of second-generation biogas upgrading.

Figure 1.2: Biogas utilization, disconnected and connected, today and tomorrow. The technologies of today, a) and b), vent \( \text{CO}_2 \) into the atmosphere while the technologies of tomorrow, c) and d), does not. a) Combustion in combined heat and power engines are the most common use of biogas today. b) First-generation upgrading of biogas is also in use today. Here, biogas is separated into \( \text{CO}_2 \) and \( \text{CH}_4 \). c) Second-generation upgrading of biogas to liquid carbon compounds, e.g. methanol. d) Methanation is another second-generation biogas upgrading technology. Here, the \( \text{CO}_2 \) content of the biogas is converted to \( \text{CH}_4 \) by addition of \( \text{H}_2 \). Reprinted with permission from [8], Appendix I.
1.3 H₂S Removal

Removal of H₂S is the key to biogas utilization. Most advanced biogas applications require the H₂S content to be low, with the second-generation upgrading having the highest requirements to the biogas purification [11, 14].

Today, biogas desulfurization is an issue for the industry. During the second campaign, the Midtfyn biogas plant had to flare the biogas twice and both times, it was due to malfunctions of the desulfurization system. The biogas technologies of today suffer, among other things, from lack of flexibility. This is unfortunate, as the biogas composition changes over time depending on the feedstock.

The most popular desulfurization technology for large biogas plants is biological scrubbing. This technology is popular due to low operating expenses (OPEX) under regular operating conditions. However, the process is sensitive and requires supervision and maintenance. Furthermore, the process adds O₂ to the purified biogas which is highly unwanted.

New biogas desulfurization technologies that do not add O₂ to the purified biogas are sought for both first- and second-generation biogas upgrading.

1.4 The MeGa-StoRE Project

The first Methane Gas Storage of Renewable Energy (MeGa-StoRE) project started in 2013. The project was a collaboration between project leader Aarhus University, GreenHydrogen.dk, Elplatek A/S, Lemvig Biogas A.m.b.A and the Mechanical Engineering Department at the Technical University of Denmark (DTU MEK). Following the first successful campaign at Lemvig biogas plant, the project was continued. The new project, MeGa-StoRE 2, phase 1 and 2, was led by DTU MEK and kept the project partners GreenHydrogen.dk and Elplatek A/S, while Nature Energy A/S replaced Lemvig as the hosting biogas plant. MeGa-StoRE 2, phase 1 designed and tested components for the demonstration campaign, and MeGa-StoRE 2, phase 2 constructed the demonstration plant and performed tests at the Nature Energy biogas plant at Midtfyn. This PhD project was part of the MeGa-StoRE 2, phase 2, project¹, supported by ForskEl, journal number 12393.

1.4.1 Project Description

The MeGa-StoRE project was based on the Sabatier reaction²:

\[
CO_2 + 4H_2 = CH_4 + 2H_2O \quad \Delta G_{300°C} = -61.2 \text{ kJ/mol}.
\] (1.1)

The process takes place over a nickel catalyst, preferably at a temperature of 300 °C and an elevated pressure.

The MeGa-StoRE project aimed to store electrical energy as natural gas. By using biomass in the form of biogas as carbon source, the MeGa-StoRE project combines three large energy

¹Throughout the thesis, the MeGa-StoRE project refers to the MeGa-Store 2 phase 2, project.
²Thermodynamic data from the HSC Chemistry programme is used throughout the thesis unless otherwise stated.
infrastructures in Denmark, i.e. the power grid, the natural gas grid and the biomass cycle, see Figure 1.3. Denmark has large natural gas storage facilities underground, which makes it possible to store electrical energy as natural gas.

Figure 1.3: The MeGa-StoRE concept. Electrical energy is stored as it is used to generate H$_2$. The H$_2$ is used to convert CO$_2$ from biogas to CH$_4$, which can be stored in the natural gas grid. Thus, electrical energy is stored in the natural gas grid by using biomass as carbon source.

1.4.2 Project Organization

The MeGa-StoRE project was funded by ForskEL$^3$ and was a joint project of four partners; Elplatek, Greenhydrogen.dk, Nature Energy and the Technical University of Denmark. Elplatek A/S, Horsens, is specialized in electrochemical processes for industrial applications and has extensive knowledge of surface technology. Greenhydrogen.dk ApS, Kolding, is specialized in research and development of electrolysers for production of renewable hydrogen. Nature Energy Biogas A/S, Odense, is an innovative Danish biogas provider that has several biogas plants in Denmark. DTU MEK, Kgs. Lyngby, is a research group with competences within surface technology and electrochemical surface treatment. In the project, Nature Energy hosted the final campaign on one of their biogas plants, Greenhydrogen.dk supplied a container for hydrogen production and DTU MEK and Elplatek supplied a container with the biogas purification unit and the methanation unit.

1.4.3 Project Objectives

The goal of the MeGa-StoRE project was to upgrade biogas to natural gas using renewable electricity. The technology should be demonstrated in a pilot plant, going from raw biogas to

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$^3$Journal number 12393.
natural gas. The upgrading technology was based on methanation of the CO\textsubscript{2}-content of the biogas over a catalyst, using the Sabatier process. As described in Section 1.2.2, the catalyst for this reaction is highly sensitive to H\textsubscript{2}S and part of the demonstration would therefore be to purify the biogas in a suitable way. The overall project goals were:

- 10 Nm\textsuperscript{3}/h proof-of-concept plant
- Removing H\textsubscript{2}S without generating waste
- The process to taking place in a single step

1.4.4 Project Design Philosophy

The demonstration project aimed for full scalability. A module-based design philosophy was developed, based on 90-95% standard components, that should be able to operate completely automatically. Two module sizes were chosen, a micro level consisting of 60 cm × 60 cm × 200 cm racks and a macro level consisting of 20/40 feet containers. The pilot plant designed, constructed and tested during the MeGa-StoRE project was projected to be the micro level module. The high level of standard components was designed to keep the cost price down and to ensure scalability.

1.4.5 Project Delay

The MeGa-StoRE 2, phase 2 project was projected to last 2 years. The initial project had planned for a 1-year campaign at the Midtfyn biogas plant from June 2017 to June 2018, however, the project was delayed. Ultimately, the project moved to the Midtfyn biogas plant in the fall of 2018 and the project ended in May 2019.

1.4.6 Relationship between this Project and the MeGa-StoRE Project

One of the project goals of the MeGa-StoRE project was to develop a biogas desulfurization technology, which led to this PhD project. As part of the MeGa-StoRE project, a pilot plant should be developed and constructed for the demonstration campaign. This PhD project started in September 2016 and the demonstration campaign was scheduled to start in June 2017. This left only 8.5 months for development, design and construction of the cleaning pilot. As the deadline for the demonstration campaign approached, it became clear that the combined project would not be ready for the campaign. However, the gas purification pilot plant was ready and started on a separate campaign at the Nysted biogas plant. Following that campaign, the MeGa-StoRE project went on the scheduled combined campaign at the Midtfyn biogas plant.

1.5 Outline of the Dissertation

This thesis is made as a collection of papers submitted throughout the project and is therefore not a monograph. The thesis consists of 10 individual chapters, where Chapter 1 and 2 introduce biogas and biogas desulfurization technologies of today.
Chapter 3 introduces the concept of electroscrubbers and a brief overview of the literature within the subject. This chapter summarizes the literature review performed in the manuscript *A review of Electroscrubbers*, Appendix II. The design of the electroscrubbing process studied in this thesis is described in Chapter 4.

The Chapters 5, 6 and 7 present the experimental work performed during this project which is also described in manuscripts. Chapter 5 describes the laboratory experiments and is covered in the manuscript *New Electroscrubbing Process for Desulfurization*, Appendix III. Chapter 6 covers the first campaign and the results are described in the manuscript *Pilot Plant Testing of Novel Electroscrubbing Process for Biogas Desulfurization*, Appendix IV. The second campaign is covered in Chapter 7 and the results are presented in the manuscript *Holistic Biogas Desulfurization within the MeGa-StoRE Project*, Appendix V.

The main results from all experiments are discussed in Chapter 8, with the conclusion and future work presented in Chapters 9 and 10, respectively.

### 1.5.1 Published and Submitted Manuscripts (Included in this Thesis)


### 1.5.2 Conferences Contributions


II 27th European Biomass conference and exhibition (EUBCE), 27th-30th May 2019 in Lisbon, Portugal. *Storing Renewable Energy by Biogas Upgrading*. Villadsen, Sebastian Nis Bay; Fosbøl, Philip Loldrup; Rasmussen, Jan Pihl; Rønne, Anders; Svendsen, Jonas Clement Gonge; Møller, Per. Poster presentation.

Chapter 2

Biogas Desulfurization Technologies

H₂S is both toxic and corrosive, with the lethal concentration reported in the order of 1000 ppm [15]. Therefore, H₂S requires removal no matter the downstream application [16]. Currently, there are three main technologies for desulfurization of biogas: biological scrubbing, chemical precipitation and activated carbon. These technologies will be presented in this chapter.

First-generation upgrading is not considered a H₂S removal technology. Most first-generation upgrading facilities require the biogas to contain 150 ppm or less H₂S. However, some first-generation upgrading facilities treat the raw biogas without any desulfurization process first. The off-gas separated during operation on raw biogas thus contains a fairly large amount of H₂S and requires desulfurization for environmental reasons. Thus, first-generation upgrading is not considered a H₂S removal technology because desulfurization happens either up- or downstream the upgrading process.

2.1 Biological Scrubbing

Biological scrubbing uses a lithoautotrophic sulfur-oxidizing bacteria to remove the H₂S [17]. The process requires two reactors, an adsorption column, where H₂S is scrubbed from the biogas, and a bioreactor, where H₂S is oxidized. The process does not generate any waste and removes H₂S down to 25-100 ppm [18]. The process can be simplified to the following steps [19]:

Firstly, adsorption to remove the H₂S from the biogas

\[ \text{H}_2\text{S(g)} + \text{OH}^- = \text{HS}^- + \text{H}_2\text{O} \quad \Delta G_{40^\circ C} = -34.4 \text{ kJ/mol}, \quad (2.1) \]

Secondarily, oxidation in the bioreactor

\[ 2 \text{HS}^- + \text{O}_2 = 2 \text{S(s)} + 2 \text{OH}^- \quad \Delta G_{40^\circ C} = -341 \text{ kJ/mol}. \quad (2.2) \]
The bacteria require nutrients and air to operate, and both are added to the bioreactor. The addition of air to the scrubbing liquid results in $O_2$ being present in the desulfurized biogas. This is an issue for both first- and second-generation biogas upgrading facilities where $O_2$ is highly unwanted [20,21]. For first-generation upgrading, $O_2$ is not allowed in the biomethane and for the second-generation upgrading, the $O_2$ will react with $H_2$ in the reactor, consuming valuable $H_2$, and increase the reactor temperature.

The biological desulfurization process prefers a constant gas flow with constant values as the bacteria may be harmed by both too much and too little $H_2S$.

The main advantages of the biological scrubbing technology for desulfurization are the low OPEX (1 € pr. kg $H_2S$) and that no waste is generated [18]. Currently, it is the cheapest available option for removal of $H_2S$ for biogas plants compared on OPEX. However, the capital expenditure (CAPEX) is rather high and thus biological scrubbers are mainly used on larger biogas plants. Furthermore, the operation of the biological desulfurization plant requires supervision.

### 2.2 Chemical Precipitation

Desulfurization by chemical precipitation is a $H_2S$ removal technology, where the sulfur is not removed in gas form. Instead, the addition of iron salts to the digester inhibits $H_2S$ formation [22]. The most common chemical precipitation technology is to mix an iron chloride (FeCl$_2$) solution into the feedstock for the biogas reactor. Once inside the digester, the iron from the FeCl$_2$ will react with sulfide to form iron sulfide as:

$$Fe^{2+} + S^{2-} = FeS$$

$\Delta G_{40^\circ C} = -99.2$ kJ/mol. (2.3)

The iron sulfide bind the sulfide and thus $H_2S$ is not formed. Instead, the iron sulfide will leave the biogas reactor with the degassed manure [23]. In this way, the $H_2S$ content in the biogas can be kept at a low level, and practical implementations often operate with 100-150 ppm $H_2S$ in the biogas. Removing $H_2S$ to lower levels is not recommended, as it requires a lot more iron chloride and may result in unwanted foaming and pH depression [24].

The major advantage of this technology is the ease of installation, as the only requirement is a tank with a dosing pump to the biomass mixer. The disadvantages include high OPEX and lack of flexibility. While the amount of FeCl$_2$ added to the biomass can be changed immediately, it often takes 24 hours before the effect on the $H_2S$ content in the biogas is observed. The OPEX is estimated to be 4.3 € pr. kg $H_2S$, which is more than 4 times the OPEX of biological desulfurization [18,23]. The high operating cost limits the application of the process. However, the ease of installation and operation makes it suitable for smaller biogas plants and desulfurization during planned maintenance of other $H_2S$ removal technologies, e.g. biological desulfurization.

### 2.3 Activated Carbon

There are many applications for activated carbon within removal of polluting gasses, and purifying biogas is one of those. Activated carbon for $H_2S$ removal is often impregnated with an
active chemical such as KOH or KI to achieve higher removal rate. Generally, there are three
different interactions between H\textsubscript{2}S and the activated carbon that is used for desulfurization.
These interactions may be represented by [25]:

Physical adsorption:\textsuperscript{1}

\[ H_2S(g) = HS^-(ads) + H^+(ads), \quad (2.4) \]

oxidation:

\[ H_2S + 2 O_2 = H_2SO_4 \quad \Delta G_{20^\circ C} = -659 \text{ kJ/mol}, \quad (2.5) \]

and chemisorption:

\[ H_2S + 2 KOH = K_2S + 2 H_2O \quad \Delta G_{20^\circ C} = -45.3 \text{ kJ/mol}. \quad (2.6) \]

The oxidation of H\textsubscript{2}S, Eq. 2.5, requires that O\textsubscript{2} is present in the biogas. As described in
Section 2.1, the addition of O\textsubscript{2} is highly unwanted for both first- and second-generation biogas
upgrading. Removal of H\textsubscript{2}S by activated carbon without O\textsubscript{2} is usually 5-10 times less efficient
[23].

The main advantage of desulfurization by activated carbon is the ease of operation and
installation, as the activated carbon filter is a small component. The main disadvantage is the
price, which is reported to be in the order of 13-22 € per kg H\textsubscript{2}S [4,23]. While activated carbon
can be regenerated by air to a certain extent, the OPEX is usually too high for bulk removal
of H\textsubscript{2}S. However, H\textsubscript{2}S may be removed down to very low levels with activated carbon, and it
is therefore often used as a polishing filter following bulk H\textsubscript{2}S removal. Currently, activated
carbon is considered the only available option for purifying biogas to advanced utilization, e.g.
application in solid oxide fuel cells [26].

2.4 Alternative Desulfurization Technologies

H\textsubscript{2}S is not only present in biogas. Removal of H\textsubscript{2}S from gas is central to the field of odor
control, and H\textsubscript{2}S is often used as the reference compound to evaluate new gas purification
technologies [16]. H\textsubscript{2}S removal in other gas industries differs from biogas desulfurization mainly
in size. Biogas streams are usually much smaller than industrial gasses that contain H\textsubscript{2}S, such
as natural gas from a drilling platform or coke oven gas from a steel plant. Two desulfurization
technologies of interest have been included here.

2.4.1 Liquid Redox Sulfur Recovery (LRSR)

Liquid redox sulfur recovery systems use a redox couple to remove H\textsubscript{2}S. H\textsubscript{2}S is removed by
oxidation and the active compound used for oxidation is regenerated by O\textsubscript{2}. Several different
redox couples have been used, including arsenate and vanadium compounds, however, the most
successful processes operate with iron [27].

\textsuperscript{1}(ads) refers to the compound being adsorbed on the surface.
An example of a LRSR process is the LO-CAT process. It uses iron chelates suspended in water to remove H$_2$S [28]. The H$_2$S is adsorbed into the solution where it is oxidized by iron [27]:

\[ 2 \text{Fe}^{3+} + \text{HS}^- = 2 \text{Fe}^{2+} + \text{S}(s) + \text{H}^+ \quad \Delta G_{20^\circ C} = -160 \text{ kJ/mol}. \] (2.7)

The iron is then regenerated by aeration

\[ 4 \text{Fe}^{2+} + \text{O}_2 + 2 \text{H}_2\text{O} = 4 \text{Fe}^{3+} + 4 \text{OH}^- \quad \Delta G_{20^\circ C} = -137 \text{ kJ/mol}. \] (2.8)

The process is operated under neutral conditions as the chelate solution deactivates at higher pH values and the absorption of H$_2$S declines with lower pH values [28]. The LO-CAT process is reported to operate with very high removal rates (> 99.9%) [29]. The LO-CAT process is designed to treat > 1000 kg sulfur per day, with a smaller version of the process, MINI-CAT designed to treat 200 – 1000 kg sulfur per day [30]. Some of the largest biogas plants in the world are situated in Denmark, with biogas productions of 2400-2500 Nm$^3$/h [31,32]. Assuming concentrations of 2000 ppm H$_2$S, these biogas plants will have a daily sulfur production of 150-160 kg, just outside the specifications of the MINI-CAT process.

### 2.4.2 The Claus Process

The Claus process is the most widely used process for removal of H$_2$S from natural gas and other industrial gases [33]. The process recovers elemental sulfur and steam from H$_2$S containing gases using a catalyst and oxygen [27]. Due to the process being widely used and on a large scale, the elemental sulfur production is high and 90% of the consumed sulfur in the US in 2018 was recovered sulfur [34]. The process takes place in two steps, as first one third of the H$_2$S is burned to form sulfur dioxide (SO$_2$) and steam:

\[ \text{H}_2\text{S} + 1.5 \text{O}_2 = \text{SO}_2 + \text{H}_2\text{O} \quad \Delta G_{1100^\circ C} = -411 \text{ kJ/mol}. \] (2.9)

The SO$_2$ is then mixed with H$_2$S to form elemental sulfur and steam:

\[ 2 \text{H}_2\text{S} + \text{SO}_2 = 3 \text{S} + 2 \text{H}_2\text{O} \quad \Delta G_{200^\circ C} = -60.9 \text{ kJ/mol}. \] (2.10)

The Claus process is often operated on the off-gas produced by an amine scrubbing process that removes the sour gases, mainly CO$_2$ and H$_2$S, from natural gas. The amine process is very similar to first-generation biogas upgrading, however, the Claus process is not suitable for biogas off-gasses due to the size.

### 2.5 Summary of Biogas Desulfurization Technologies

Of the biogas desulfurization technologies on the market, only activated carbon is capable of reaching the H$_2$S concentrations required for second-generation upgrading. Currently, the best suitable option would be to have biological desulfurization for bulk H$_2$S removal followed by activated carbon for polishing. The LO-CAT process could prove a suitable option due to the high removal efficiencies. However, even the small-scale version, the MINI-CAT, is oversized for biogas plants.
Electroscrubbers represent an alternative to the established desulfurization technologies. In this chapter, the overall concept of electroscrubbers will be presented. The scientific field of electroscrubbers have been reviewed in a literature review in the manuscript *A review of Electroscrubbers*, Appendix IV.

The term *electroscrubbers* was first introduced in 2012 by Govindan et al. [35]. The technology, however, goes back to the 1920s when Franz Fischer developed a new method for purification of water gas [36]. The overall idea is based on electrochemical generation of an active compound for removal of gas pollutants.

### 3.1 Process Concept

In Figure 3.1, the process concept is presented. The active compound is generated in an electrochemical cell and then used in a scrubber. It is a combination of two technologies, i.e. electrochemical regeneration of an active compound and removal of the pollutant in a scrubber. Thus, the concept resembles that of LRSR processes, see Section 2.4.1. For electroscrubbers, electrochemical oxidation is used for regeneration while for LRSR air is used for oxidation. The electrochemical regeneration and pollutant scrubbing will be discussed below.
Figure 3.1: The concept of an electroscrubber. An active compound is generated by electrochemistry and used to remove a pollutant in a scrubber. The active compound is then regenerated and used again in a closed cycle.
3.2 Electrochemical Regeneration

Electrochemical regeneration of the active species has several advantages over using air or chemicals. Fast reaction kinetics allows for electrochemical regeneration to use less space than the alternatives. Using electricity also results in easier infrastructure and more adjustable regeneration. The main disadvantage is the expected high OPEX due to the utilization of electrical energy which is more costly than e.g. air.

To decrease the OPEX of an electroscrubber is to decrease the consumption of electrical power. This means that the electrochemical regeneration should be optimized. The current efficiency and cell voltage are the two main parameters to optimize. The current efficiency will be discussed in detail in Section 3.6.2. The cell voltage depends on the equilibrium potential ($E_{eq}$) for the redox reaction, which can be calculated using the Nernst equation [37]:

$$E_{eq} = E^0 + \frac{RT}{zF} \ln \left( \frac{[\text{Ox}]}{[\text{Red}]} \right),$$

(3.1)

where $E^0$ is the standard potential for the redox reaction, $R$ is the gas constant, $T$ is the temperature, $z$ is the overall reaction valency, $F$ is Faraday’s constant and $[\text{Ox}]/[\text{Red}]$ is the ratio between the activity of the oxidizing and reducing species.

From the Nernst equation, it is observed that an increase in $[\text{Red}]$ would decrease $E_{eq}$ and thus lower the energy consumption. For an oxidizing scrubber, H$_2$ development at the cathode is the most common reaction:

$$2 \text{H}^+ + 2 e^- = \text{H}_2,$$

(3.2)

with the oxidizing species (Os) oxidized at the anode:

$$\text{Os}^+ = \text{Os}^{3+} + 2 e^-.$$

(3.3)

Increasing the $[\text{Red}]$ for this reaction would be to increase the amount of $\text{Os}^+$ and $\text{H}^+$. Thus, lowering the pH-value has a beneficial effect on $E_{eq}$ and therefore the overall power consumption of the electroscrubber.

3.3 Scrubbing

The active compound interacts with the pollutant in a scrubbing tower. Here, the gas pollutant is absorbed into a liquid. This is the most widely used method for pollutant control [27]. In order to facilitate the interaction between the pollutant and the absorbing liquid, scrubbing towers are filled with packing elements which has a large surface area. Furthermore, scrubbing towers are often operated counter current, i.e. the gas enters in the bottom and exists in the top and vice versa for the liquid. Counter current operation ensures that the fresh absorbent with the largest driving force for absorption is in contact with the lowest concentration of the pollutant.

Dimensioning the scrubbing tower depends on the reaction kinetics of the removal process, the purification level and the amount of gas. Generally, the diameter of the scrubbing tower dictates the amount of gas that can be cleaned while the height of the tower dictates the purification level.
3.4 Electroscrubbers in the Literature

Currently, 54 publications within the field of electroscrubbers have been published all of which are presented in Table 3.1. H$_2$S and NO$_x$/SO$_2$ are the most frequently targeted pollutants having 27 and 20 publications, respectively. Oxidation is the most common removal technology although a few papers investigate reduction of the pollutant as well. The active elements investigated are mostly transition metals with a suitable redox couple that have been suspended in an electrolyte. The different volatile organic compounds (VOC) investigated are acetaldehyde (CH$_3$CHO), trichloroethylene (C$_2$HCl$_3$), tetrafluoromethane (CF$_4$), carbon tetrachloride (CCl$_4$) and trimethylamine (N(CH$_3$)$_3$).

Overall, the electroscrubbers have been reported to be highly effective. Pollutants, such as H$_2$S, have been removed down to non-detectable limits in a single stage [38–42]. The absence of industrial applications of the electroscrubbers have been widely explained by the high OPEX due to the electrical consumption [43].

Table 3.1: Overview of the publications, papers and patents, within the field of electroscrubbers. The main part of the literature is focused on the oxidation of H$_2$S or NO$_x$/SO$_2$. Transition metals are observed to be applied frequently as the active element. The manuscripts from this thesis have been included as well. From unpublished work [44], Appendix II.

<table>
<thead>
<tr>
<th>Active Element</th>
<th>H$_2$S</th>
<th>CH$_3$SH</th>
<th>NO$_x$/SO$_2$</th>
<th>VOC + NH$_3$ Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td>[45]</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>[49–51]</td>
<td></td>
<td></td>
<td>[46–48]</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>[49–51]</td>
<td></td>
<td></td>
<td>[52]</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>[53–55]</td>
<td></td>
<td></td>
<td>[52]</td>
<td>[56]</td>
</tr>
<tr>
<td>V</td>
<td>[53–55]</td>
<td></td>
<td></td>
<td>[52]</td>
<td>[56]</td>
</tr>
<tr>
<td>Cr</td>
<td>[53–55]</td>
<td></td>
<td></td>
<td>[52]</td>
<td>[56]</td>
</tr>
<tr>
<td>Fe</td>
<td>[36,38,39,57–60]</td>
<td>[61,62]</td>
<td>[61,62,64–66]</td>
<td>[65,67,68]</td>
<td>[69,70]</td>
</tr>
<tr>
<td>Co</td>
<td>[56,61–64]</td>
<td></td>
<td></td>
<td>[69]</td>
<td>[71]</td>
</tr>
<tr>
<td>Ni</td>
<td>[56,61–64]</td>
<td></td>
<td></td>
<td>[71]</td>
<td>[72]</td>
</tr>
<tr>
<td>Cu</td>
<td>[53,73]</td>
<td>[53]</td>
<td>[74–79]</td>
<td>[73]</td>
<td></td>
</tr>
<tr>
<td>Br</td>
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<td>[53]</td>
<td>[74–79]</td>
<td>[73]</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>[80,81]</td>
<td></td>
<td></td>
<td>[72]</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
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<td>[40]</td>
<td>[35,82–86]</td>
<td>[53]</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>[41,42,53,87]</td>
<td></td>
<td></td>
<td>[89,90]</td>
<td>[56]</td>
</tr>
<tr>
<td>Ce</td>
<td>[88]</td>
<td></td>
<td></td>
<td>[89,90]</td>
<td>[56]</td>
</tr>
</tbody>
</table>
3.5 Overall Requirements

From the literature review, the following list of overall requirements for electroscrubbers has been compiled [44] (Appendix II):

- High enough oxidation potential to remove the targeted pollutant
- High reactivity with the targeted pollutant
- Solubility of both reduced and oxidative form
- Stability under operating conditions
- No unwanted side reactions
- Well-known electrochemistry
- Low chemical cost
- Environmental friendly

These requirements must be taken into account when choosing an electroscrubbing process.

3.6 Evaluation Parameters

In the literature review, several calculated parameters for comparison are presented [44] (Appendix II). These calculated parameters are introduced in order to facilitate comparison across process parameters and different electroscrubbers. Throughout the literature, the overall efficiencies of the electroscrubbers are rarely calculated or commented.

3.6.1 Theoretical Current

The current that is theoretically required for removal of the pollutant \(i_{\text{theory}}\) can be calculated based on Faraday’s law:

\[
i_{\text{theory}} = \frac{n_{\text{pollutant}}}{t} zF = y_{\text{pollutant}} \frac{pG}{RT} zF,
\]

where \(n_{\text{pollutant}}\) is the amount of pollutant, \(t\) is time, \(y_{\text{pollutant}}\) is the gas concentration of the pollutant and \(p\) is the pressure of the polluted gas. It is assumed that the pollutant gas is an ideal gas.

To evaluate the electroscrubber, it is often preferable to compare the current applied with the theoretical current as \(i/i_{\text{theory}}\). This calculated parameter can be used to compare performance across different process parameters.
3.6.2 Current Efficiency

The performance of the electroscrubber is most simply evaluated by comparing the amount of pollutant removed with the amount of current used. The amount of pollutant removed \((S)\) is most conveniently calculated as mass per time:

\[
S = \left( y_{\text{in pollutant}} - y_{\text{out pollutant}} \right) \frac{pG}{RT} M_{\text{pollutant}},
\]

where \(M_{\text{pollutant}}\) is the molar mass of the pollutant. The mass of the pollutant per time is then directly compared with the applied current in the system:

\[
\frac{S}{i} = \frac{\left( y_{\text{in pollutant}} - y_{\text{out pollutant}} \right) \frac{pG}{RT} M_{\text{pollutant}}}{i}.
\]

The calculated parameter \(S/i\) gives the amount of pollutant removed in mass per coulomb. This parameter is convenient for comparison of different electroscrubbing systems. Furthermore, it can be compared with the theoretical amount of pollutant removed per coulomb \((S/i)_{\text{theory}}\), which can be calculated as:

\[
\left( \frac{S}{i} \right)_{\text{theory}} = \frac{M_{\text{pollutant}}}{zF}.
\]

The current efficiency \((\eta_i)\), can then be calculated as:

\[
\eta_i = \frac{S/i}{(S/i)_{\text{theory}}} = \frac{\left( y_{\text{in pollutant}} - y_{\text{out pollutant}} \right) \frac{pG}{RT} M_{\text{pollutant}}}{i} \frac{M_{\text{pollutant}}}{zF} = \frac{\left( y_{\text{in pollutant}} - y_{\text{out pollutant}} \right) pG zF}{iRT}.
\]

This current efficiency is different from the Faraday efficiency. The Faraday efficiency refers to the efficiency of the applied current inside an electrochemical cell. It is directly determined by measuring a product from the electrochemical reaction. The current efficiency of an electroscrubber is measured indirectly. The amount of pollutant removed is measured instead of the active compound produced. \(\eta_i\) therefore also depends on the reaction between the active compound and the pollutant. In other words, \(\eta_i\) will always be lower or equal to the Faraday efficiency.

The current efficiency of an electrochemical cell can be optimized on several different parameters. Suitable electrodes may be implemented to favour the desired reaction over an unwanted side reaction. Furthermore, a membrane can be implemented to ensure that the active compound is not oxidized at the anode and then reduced at the cathode, or vice versa. Even with a suitable diaphragm implemented as membrane, the unwanted transport of \(\text{OH}^-\) between the electrodes is assumed to account for a loss of 0.1-1.0\% of the current efficiency for \(\text{Cl}_2\) production [91]. Without a suitable membrane, the loss of current efficiency may be assumed to be higher.
3.6.3 Removal Efficiency

The overall current efficiency do not take into account the concentration of the pollutant in the purified gas. Optimization of the electroscrubber based only on the overall current efficiency do not necessarily result in sufficient removal of the pollutant. Thus, the removal efficiency also has to be considered when optimizing the electroscrubber. The removal efficiency $\Delta S$ may be calculated as:

$$\Delta S = \frac{y_{in}^{pollutant} - y_{out}^{pollutant}}{y_{in}^{pollutant}}.$$  \hspace{1cm} (3.9)

Optimization of the removal efficiency depends on the design of the scrubber. In order to a high removal efficiency, the scrubber height must be optimized, as discussed in Section 8.7.1. Liquid distribution and packing material inside the scrubber is also important to ensure that the removal efficiency is optimized.

3.6.4 Power Efficiency

Ultimately, the overall performance of the electroscrubber is evaluated by the power consumption per pollutant. For an electroscrubber, the OPEX is dominated by the power consumption ($P$) in the electrochemical cell given by:

$$P = iU_T,$$  \hspace{1cm} (3.10)

where $U_T$ is the terminal cell potential, which can be described as [91]:

$$U_T = E_{eq} + \eta_a + (-\eta_c) + \sum iR_E,$$  \hspace{1cm} (3.11)

where $\eta_a/c$ are the overpotentials at the anode and cathode, respectively and $\sum iR_E$ is the sum of ohmic voltage drop throughout the system. In order to increase the power efficiency, $U_T$ and $i$ must be optimized. The $E_{eq}$ and the current efficiency have been discussed in Sections 3.2 and 3.6.2, respectively.

The overpotentials, $\eta_a$ and $\eta_c$ depend on the electrodes for the process. Surface coatings of a an active catalyst on the electrodes are widely used. A suitable electrode surface decreases the overpotential for the desired reaction.

The ohmic voltage drop throughout the system, $\sum iR_E$, depends both on the ohmic resistance in the equipment and on the resistance of the electrolyte. For electroscrubbers, H$_2$-formation on the cathode is common, which results in an increase in ohmic resistance due to gas bobbles. For high current densities, the bobble resistance is a large part of the ohmic resistance of the system. Suitable electrolyte flow can be implemented to ensure the bobbles are removed from the electrode surface.

The overall electrical behaviour of an electrochemical cell is often found to be of the form [92]:

$$U_T = U_0 + iR_S,$$  \hspace{1cm} (3.12)

where $U_0$ is the combined cell potential and $R_S$ is the resistance of the system. The applied potential for each cell ($U_C$) can then be calculated as

$$U_C = \frac{U_0}{n},$$  \hspace{1cm} (3.13)
where $n$ is the number of cells.

For comparison with other technologies, the cost of removing 1 kilogram of the pollutant is often used. For an electroscrubber, the power consumption is expected to be the dominating part of the OPEX. Therefore, the overall performance of the electroscrubber can be estimated as the amount of power required for removal of 1 kg of the pollutant ($P^0$):

$$P^0 = \frac{P}{S} = \frac{U_T i}{(y_{\text{in pollutant}} - y_{\text{out pollutant}}) \frac{pG_v}{RT} M_{\text{pollutant}}}.$$  \hspace{1cm} (3.14)

### 3.7 Summary of Electroscrubbers

The concept of electroscrubbing has been introduced together with a short overview of the literature. The scientific field of electroscrubbers is limited. Currently, no commercial applications of the technology is known. However, the high removal rate combined with the consumption of electricity rather than chemicals makes the process interesting for biogas desulfurization.

Different parameters for evaluation of electroscrubbing processes have been introduced. These evaluation parameters allow for comparison of the processes independent of gas flow and concentration.

A list of requirements for the selection of an electroscrubbing process have been presented. These requirements must be taken into account when selecting the active species for a gas cleaning process.
Chapter 4
Electroscrubbing Process Design

There are certain requirements for H\textsubscript{2}S removal upstream second-generation upgrading of biogas. A high removal rate may be considered the most important parameter, as described in Section 1.2.2. For the desulfurization technology to be suitable, the CO\textsubscript{2} should be left in the biogas as the CO\textsubscript{2} is required as carbon source. Other important parameters include flexibility, fast reaction kinetics and no waste generation.

The electroscrubbing process described in this chapter fulfil these requirements. A new active compound, chlorine, was found to perform well on all process requirements. Active chlorine has not been studied before for electroscrubbing purposes.

4.1 Selection of the Active Species

The active compound is the most important parameter in the design of an electroscrubber. In this work, three different active compounds were initially investigated before the final active compound, chlorine, was chosen. The three active compounds investigated were potassium permanganate, bromine and chlorine.

All three elements have active compounds that can oxidise H\textsubscript{2}S. In Figure 4.1, the Pourbaix diagrams of sulfur and the active elements are presented. The Pourbaix diagrams show which forms of elements are thermodynamically stable with water present as a function of pH-value and electrical potential (Eh). The blue color indicates water soluble ions, the black color indicates insoluble solids and the red color indicates water soluble compounds. The light blue lines indicate the stability area of water, i.e. between the light blue lines, water is stable.

From the Pourbaix diagram in Figure 4.1(a), it is observed that at pH-values 0-8, H\textsubscript{2}S can be oxidized to elemental sulfur (S) or sulfate (SO\textsubscript{4}\textsuperscript{2−}). At higher pH-values, HS\textsuperscript{−} is the preferred form of sulfide and it is only oxidized to sulfate. In the Pourbaix diagram, oxidation of sulfide to sulfur is showed with arrow 1 and further oxidation to sulfate is showed with arrow...
2. Both oxidations may happen, however, initially only the first oxidation step will be discussed. The oxidation of sulfide is presented at a pH-value of 1. This value is based on experimental conditions, and will be discussed in detail.

### 4.1.1 Potassium Permanganate

Potassium permanganate (KMnO$_4$) is an oxidizing agent that can be used for removal of H$_2$S [93]. In the first MeGa-StoRE project, KMnO$_4$ had successfully been applied to remove H$_2$S in the biogas down to non-detectable limits. H$_2$S can be removed by KMnO$_4$ by the reaction [93]:

$$3\text{H}_2\text{S} + 2\text{KMnO}_4 = 3\text{S} + 2\text{H}_2\text{O} + 2\text{MnO}_2 + 2\text{KOH} \quad \Delta G_{20°C} = -596 \text{ kJ/mol.} \quad (4.1)$$

The active permanganate compound cannot be regenerated, since MnO$_2$ is an insoluble solid. In other words, once the permanganate (MnO$_4^{-}$) has been reduced to MnO$_2$, electrochemistry cannot practically regenerate it. This makes the process unsuited for an electroscrubber.

In Figure 4.1(b) the Pourbaix diagram of manganese with water is presented. MnO$_4^{-}$ is observed to be a soluble ion that is stable at all pH-values and has a high potential, i.e. oxidation potential. The Pourbaix diagram also shows that for pH-values 0-14, MnO$_4^{-}$ is reduced to MnO$_2$. However, for pH-values 14-15, MnO$_4^{-}$ may be reduced to another soluble ion in the form of manganate (MnO$_2^{-}$), as indicated by the orange circle.

The redox couple, MnO$_4^{-}$/MnO$_2^{-}$ is known from the printed circuit board industry [94]. Here, MnO$_4^{-}$ is used to oxidise epoxy resin in etching baths. The etching baths are operated at sufficiently high pH-values to ensure MnO$_2^{-}$ is formed and not MnO$_2$, when the MnO$_4^{-}$ is reduced. MnO$_4^{-}$ is then regenerated by the reaction$^1$ [94]:

$$\text{MnO}_4^{2-} = \text{MnO}_4^{-} + \text{e}^{-} \quad \text{E}^0 = 0.558 \text{ V.} \quad (4.2)$$

The reaction is shown in Figure 4.1(b) with a blue arrow.

This process is suited for an electroscrubber, as both ions in the redox couple are soluble. A few experiments with regeneration of KMnO$_4$ were performed with equipment borrowed from a local printed circuit board factory. The experiments found that regeneration of MnO$_4^{-}$ could not be achieved under biogas conditions, making it unsuitable for the project.

### 4.1.2 Bromine and Chlorine

Bromine and chlorine have similar chemical properties as both are halogens. This result in both elements have a high solubility in water as halides, see Figure 4.1(c) and 4.1(d). Furthermore, both elements can form diatomic molecules that are highly oxidizing and water soluble. For chlorine, the redox couple is Cl$_2$/Cl$^-$ and for bromine it is Br$_2$/Br$^-$. The overall reactions for removal of H$_2$S are similar, here presented for bromine:

$$\text{Br}_2 + \text{H}_2\text{S} = \text{S} + 2\text{H}^+ + 2\text{Br}^- \quad \Delta G_{20°C} = -179 \text{ kJ/mol,} \quad (4.3)$$

$^1$Electrochemical potential data from *Handbook of Chemistry and Physics 100th Edition* edited by Dr. John Rumble are used throughout the thesis.
with the regeneration steps [95]:

\[ 2 \text{Br}^- = \text{Br}_2 + 2 \text{e}^- \quad \text{E}^0 = 1.07 \text{V}. \] (4.4)

The regeneration steps have also been showed in the Pourbaix diagrams, Figures 4.1(c) and 4.1(d).

Bromine has the advantage over chlorine that under standard pressure and temperature, bromine is a liquid and chlorine is a gas. For a scrubbing solution, a liquid oxidizing species is preferred as it minimizes the risk of the oxidizing agent leaving the desulfurization system. During the initial testing, the bromine formed at the anode was visually confirmed to form a liquid that sank to the bottom of the electrolyte. Chlorine formed a gas, which bubbled through the electrolyte. Keeping the oxidizing species in the scrubber is of key importance to avoid downstream issues.

During testing, bromine and chlorine was found to performed similarly, which is expected based on their similar chemistry. Chlorine was chosen as the oxidizing species for the process since it is the most common of the two elements. This means that chlorine compounds are more has a lower cost and are more widely used. Furthermore, there is more literature on the subject of chlorine as an oxidative species.
4.2 Process Chemistry

Based on the initial testing, chlorine (Cl₂) was chosen as the active compound for the process. Throughout the experiments, an initial electrolyte consisting of water and sodium chloride (NaCl) has been used. The principle of operation is presented in Figure 4.2. The chlorine is generated by electrochemistry as H₂ is formed at the cathode and Cl₂ is formed at the anode, shown in Figure 4.2(c). This process is well known from the chloralkali from which >95% of the chlorine throughout the world is produced [96]. The reactions are:
Cathode reaction [97]:

$$2H^+ + 2e^- = H_2(g). \quad (4.5)$$

Anode reaction:

$$2Cl^- = Cl_2(aq) + 2e^- \quad (4.6)$$

As shown in Figure 4.2(d), the $Cl_2$ formed at the anode will react with water to form HClO [98]:

$$Cl_2(aq) + H_2O = HClO + H^+ + Cl^- \quad (4.7)$$

The electrolyte interacts with the biogas inside the scrubber. The most important interaction between the electrolyte and the biogas is the interaction with hydrogen sulfide. Hydrogen sulfide will dissolve in the electrolyte as [99]:

$$H_2S(g) = H_2S(aq), \quad (4.8a)$$
$$H_2S(aq) = HS^- + H^+ \quad (4.8b)$$

which is shown in Figure 4.2(a). The dissolved $HS^-$ will be oxidized to elemental sulfur by HClO as shown in Figure 4.2(b):

$$HClO + HS^- = S(s) + H_2O + Cl^- \quad \Delta G_{20^\circ C} = -301 \text{ kJ/mol.} \quad (4.9)$$

This reaction has a reaction rate constant (K-value) of $6.35 \times 10^{57}$, which indicates that the reaction greatly favours the right hand side.

This gives the overall equation:

$$H_2S(g) + \text{Electrical energy} = H_2(g) + S(s) \cdot \quad (4.10)$$

The sulfur oxidation is showed by arrow 1 in Figure 4.1(a). The sulfur is insoluble in the electrolyte and will float [100]. This was confirmed in the experiments, even though the density of sulfur is higher than that of the electrolyte. If left in the electrolyte, the elemental sulfur is expected to be further oxidized by HClO (arrow 2 in Figure 4.1(a)):

$$3HClO + S(s) + H_2O = SO_4^{2-} + 3Cl^- + 5H^+ \quad \Delta G_{20^\circ C} = -663 \text{ kJ/mol}, \quad (4.11)$$

If this reaction happens, then the overall reaction will not be Eq. 4.10. Instead, the overall reaction would be:

$$H_2S(g) + H_2O + \text{Electrical energy} = 4H_2(g) + SO_4^{2-} + 2H^+. \quad (4.12)$$

This reaction is unwanted for two reasons:

- It consumes 4 times the electrical energy that Eq. 4.10 consumes
- It dilutes the electrolyte with $H_2SO_4$, lowering the pH-value in the process.

However, the reaction may be avoided. While the oxidation from sulfide to sulfur is considered fast, the oxidation from sulfur to sulfate is slow [101,102]. This allows for removal of the solid sulfur before further oxidation.
Figure 4.2: The overall process flow of the electroscrubber. a) \( \text{H}_2\text{S} \) enters the scrubber and is dissolved in the electrolyte, Eqs. 4.8. b) The dissolved sulfide is oxidized by \( \text{HClO} \) to form elemental sulfur, Eq. 4.9. c) In the electrochemical cell, \( \text{H}_2 \) is formed at the cathode (Eq. 4.5) and \( \text{Cl}_2 \) is formed at the anode (Eq. 4.6). d) \( \text{Cl}_2 \) reacts spontaneously with water to form \( \text{HClO} \), Eq. 4.7. From unpublished work [49].
4.2.1 Reactions between the Electrolyte and other Compounds in the Biogas

While the reaction between the electrolyte and the hydrogen sulfide is the most important, the electrolyte interaction with other compounds in the biogas must also be taken into account:

**Methane**

Generally, CH$_4$ is the valuable compound in biogas and it is therefore important that the desulfurization technology do not remove it from biogas. Thermodynamically, CH$_4$ may react with HClO spontaneously:

$$4 \text{HClO} + \text{CH}_4 = \text{CO}_2 + 2 \text{H}_2\text{O} + 4 \text{HCl} \quad \Delta G_{20^\circ C} = -953 \text{ kJ/mol.} \quad (4.13)$$

However, reaction kinetics prevent this reaction from happening. Throughout the experiments, no difference in concentration of methane in and out of the electroscrubber was measured. Generally, methane has a very low solubility in water and is not expected to interact with the electrolyte [103].

**Carbon Dioxide**

Carbon dioxide is a sour gas, and upon interaction with water it will dissolve as:

$$\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq}), \quad (4.14a)$$

$$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+. \quad (4.14b)$$

which will lower the pH value of the electrolyte. During operation, the system will be saturated with carbonate and an equilibrium achieved. The equilibrium will be dependent on the partial pressure of CO$_2$, and will therefore change if the biogas composition changes.

**Water**

The biogas is expected to be saturated with water when it enters the desulfurization plant. Thus, if the gas is cooled inside the system additional water is expected to be added to the system. This is unwanted, as water would dilute the electrolyte and thus decrease the efficiency of the system. However, if the biogas exiting the system has increased in temperature, it may remove water from the system, which is also unwanted as it would dry the system over time. In practice, the incoming and exiting gas is kept at the same temperature to avoid liquid loss/addition. As this was not convenient for the experiments performed in this project, the amount of electrolyte had to be closely monitored.

**Other Compounds**

As described in Section 1, biogas contains other compounds than H$_2$S that may interact with the electrolyte. These pollutants include ammonia NH$_3$, CH$_3$SH and siloxanes. In theory, if the pollutant can be oxidized by HClO then the system may remove it by oxidation. The removal of other pollutants than H$_2$S has not been investigated in detail.
4.3 Electrolyte Transformation

While the initial electrolyte consists of NaCl dissolved in water, the electrolyte changes during operation. The pH-value has been observed to change during operating throughout the experiments. This change is expected to be dependent on chlorine and sulfur chemistry. Here, the expected reactions are presented for the pH-value, chlorine and sulfur compounds.

4.3.1 Expected pH-value of the Electrolyte

Upon applying current, HClO will form, according to Eq. 4.7. This will increase the oxidation potential of the liquid. The oxidation potential can be measured with a probe submerged in the liquid. Overall, the pH-value is not expected to change upon applying a current. However, once the electrolyte interacts with the biogas, the pH-value is expected to decrease as CO₂ is dissolved in the electrolyte according to Eq. 4.14. Furthermore, if the elemental sulfur is not removed from the electrolyte, it may be oxidized according to Eq. 4.11, which will decrease the pH-value further.

4.3.2 Chlorine Compounds Formed

Active chlorine may exist in several different states. From the Pourbaix diagram of chlorine, Figure 4.1(d), three different active species are observed: chlorine (Cl₂), hypochlorous acid (HClO) and hypochlorite (ClO⁻). In the literature, it is commonly believed that only Cl₂ is formed at the anode and that the other compounds are formed subsequently [104]. In Eq. 4.7, the formation of hypochlorous acid is described and it is observed that at lower pH-values, Cl₂ is favoured, in accordance with the Pourbaix diagram in Figure 4.1(d). Similarly, hypochlorite is formed by dissociation of hypochlorous acid:

\[
\text{HClO} = \text{ClO}^- + \text{H}^+, \quad (4.15)
\]

which is favoured at higher pH-values. These compounds are all 2 valence oxidative active species, i.e. they all discharge by receiving 2 valence electrons [95]:

\[
\begin{align*}
\text{Cl}_2 + 2 \text{e}^- &= \text{Cl}^- & E^0 &= 1.36 \text{V}, \quad (4.16a) \\
\text{HClO} + \text{H}^+ + 2 \text{e}^- &= \text{Cl}^- + \text{H}_2\text{O} & E^0 &= 1.482 \text{V}, \quad (4.16b) \\
\text{ClO}^- + \text{H}_2\text{O} + 2 \text{e}^- &= \text{Cl}^- + 2 \text{OH}^- & E^0 &= 0.81 \text{V}. \quad (4.16c)
\end{align*}
\]

Thus, the three active species have similar reactions with the dissociated HS⁻:

\[
\begin{align*}
\text{Cl}_2 + \text{HS}^- &= 2 \text{Cl}^- + \text{S} + \text{H}^+ & \Delta G_{20^\circ C} &= -279 \text{ kJ/mol}, \quad (4.17a) \\
\text{HClO} + \text{HS}^- &= \text{Cl}^- + \text{S} + \text{H}_2\text{O} & \Delta G_{20^\circ C} &= -302 \text{ kJ/mol}, \quad (4.17b) \\
\text{ClO}^- + \text{HS}^- &= \text{Cl}^- + \text{S} + \text{OH}^- & \Delta G_{20^\circ C} &= -265 \text{ kJ/mol}. \quad (4.17c)
\end{align*}
\]

From the Eqs. 4.16 and 4.17, the individual oxidation potential of the active chlorine species is observed, with the HClO having the highest potential.

Active chlorine exists in several forms different from the compound described in Eqs 4.16. For instance, chlorine dioxide (ClO₂) has been observed to be formed as a by-product during
electrochemical disinfection of drinking water [105]. Trichloride (Cl$_3^-$) have also been reported in the literature [106–109].

In practice, the exact mechanism of oxidation by active chlorine is not as important as the removal of H$_2$S. The most important electrochemical property is the voltage required for the oxidation of chloride to chlorine, i.e. Eq. 4.6, which is well-studied and applied in the chlor-alkali industry on a large scale [110].

**4.3.3 Sulfur Compounds Formed**

Sulfur exists in three different oxidation states at ambient conditions: sulfide (oxidation state -2), sulfur (oxidation state 0) and sulfate (oxidation state +6) [102]. However, due to the slow reaction kinetics of sulfate formation from lower oxidation states, Kelsall et al. [102], argues that a metastable Pourbaix diagram should be implemented to understand the reaction kinetics of the oxidation of H$_2$S. Thiosulfate (S$_2$O$_3^{2-}$) and sulfite (SO$_3^{2-}$) were among the metastable sulfur compounds predicted, which is supported by Couvert et al. [101].

Within the literature of electroscrubbers for H$_2$S removal, the end product of the sulfur differs between sulfate and elemental sulfur. Independent on the active compound, oxidation to sulfate requires 4 times the electrical power of oxidation to sulfur, see Eqs. 4.9 and 4.11. In the literature, several of the electroscrubbers are focused on the recovery of elemental sulfur [41, 42, 54, 58, 80, 111]. The elemental sulfur formed is reported to be gummy and sticky mass which is difficult to recover [42, 54]. The behaviour of elemental sulfur is complex as it may exist in more than $5 \times 10^5$ different forms [112]. The application of the formed sulfur depend on the amount and kind of impurities.

Sulfate is also investigated as end product of H$_2$S removed by electroscrubbers [40, 61–63, 88]. The generation of sulfate will acidify the electrolyte, and the sulfate may increase the conductivity of the electrolyte as well. While the sulfate generation requires additional energy, the lower pH value and higher conductivity may result in higher power efficiency, see Sections 3.2 and 3.6.4.

To reach a steady state of the electroscrubbing system, formation followed by removal of elemental sulfur is expected to be the best case scenario for the process. In this way, the complex chemistry of intermediate sulfur compounds may be avoided, and a by-product, sulfur is formed.

**4.4 By-products from the Process**

The OPEX of the process is dominated by the power consumption. Generally, electroscrubbing processes have been found to have high OPEX which minimizes the commercial interests. However, for second-generation upgrading of biogas, the H$_2$ produced at the cathode (Eq. 4.5) can be used directly in the upgrading process. Thus, both the cathode and the anode reaction of the electroscrubber is used in the process. The H$_2$ produced in the electroscrubber directly replaces H$_2$ that would otherwise have been produced in the electrolysis system by utilization of a similar amount of power. The power consumption of the electroscrubber can be considered net-zero for second-generation biogas upgrading plants. Furthermore, the sulfur produced by
the electroscrubber may have commercial value, and could be sold to create a revenue stream. Combined with the added value of the H$_2$, the electroscrubber may ultimately generate income.

4.5 Summary of the Process Design

An electroscrubbing process for H$_2$S removal from biogas for second-generation upgrading has been described. A new active compound for the electroscrubbing process is used, as chlorine was chosen. Chlorine was found to fulfil requirements described in Section 3.5:

- Cl$_2$ has an oxidation potential high enough for oxidation of sulfide to sulfur
- It was found to have a high reactivity with H$_2$S
- Both compounds in the redox-couple of chlorine are highly soluble in water
- A sodium chloride solution is not expected to degenerate over time under the operating conditions
- There are limited unwanted sides reactions in chlorine electrochemistry
- Chlorine generation by electrochemistry is well-known
- Chloride solutions are not costly
- Chloride is not poisonous to the environment
Chapter 5
Laboratory Experiments

In Chapter 4, chlorine is introduced as a new active compound for electroscrubbers. In this chapter, laboratory experiments performed with the new process are presented. While some of the results are included, the main results from the laboratory experiments are discussed in Chapter 8, where the results will be compared with the campaigns. The laboratory experiments are also described in the manuscript *New Electroscrubbing Process for Desulfurization*, Appendix III.

Currently, there is no literature describing the dimensioning of an electroscrubber. Most of the electroscrubbers in the literature have been based on regular scrubbers in their design. Furthermore, only four electroscrubbers of ∼10 Nm³/h or larger have been described in the literature, with only a few details regarding the actual size and design of the electroscrubber [35,36,79,90]. Thus, direct experimentation was applied to investigate the dimensioning required for the pilot plant electroscrubber.

5.1 Measurement Technologies

Throughout the project, commercially available measurement technologies were used. The commercial equipment was used mainly due to the ease of operation and communication. On both campaigns, the electroscrubbers were remote controlled which required the measurement technologies to be remote controlled as well.

5.1.1 Gas Measurements

The gas concentrations were measured with an MRU SWG 100 stationary biogas analyzer¹. The MRU was equipped with four different gas sensors for H₂S, CH₄, CO₂ and O₂, respectively:

---

¹Referred to as MRU throughout the thesis.
• **H\textsubscript{2}S**
  The H\textsubscript{2}S sensor was a continuous electrochemical gas sensor designed for biogas by IT Dr. Gambert GmbH, type I-43 [113]. It measured within the range of 0-10,000 ppm with a resolution of 1 ppm and an accuracy of ±50 ppm/5% of the reading [114].

• **CH\textsubscript{4} and CO\textsubscript{2}**
  The methane and carbon dioxide were measured with nondispersive infrared sensors (NDIR) between 0-100 Vol.% with a resolution of 0.1 Vol.% and 0.01 Vol.%, respectively, and an accuracy of ±0.3 Vol%/3% of the reading [114].

• **O\textsubscript{2}**
  The oxygen was measured electrochemically in the range of 0-25 Vol.% with a resolution of 0.01 Vol% and an accuracy of 0.2% of the absolute measured value [114].

5.1.2 **Liquid Measurements**

The following measurement devices were used during operation of the electroscrubbers:

• **Electrical Properties**
  The resistance of the electrolyte is continuously measured during operation through the applied potential and the resulting current.

• **pH-Value**
  The pH-value of the liquid was measured with a sensor from Oxyguard.

• **Redox Potential**
  The redox potential was also measured with a sensor from Oxyguard.

5.1.3 **Scanning Electron Microscopy (SEM)**

A Hitachi tabletop SEM model TM3000 equipped with energy dispersive x-ray spectroscopy (EDS) was used for analysis. The SEM was both used for imaging and elemental analysis, as solid samples were analysed with EDS. EDS can be used to analyse the elemental composition of a sample, although not light elements. The analysis provides uncertainties for the measurements, depending on the measurement quality.

5.1.4 **Uncertainties**

Throughout the experiments, the uncertainties have been estimated according to the error analysis described by Taylor [115]. For repeated gas concentration measurements, the standard deviation has been calculated and compared with the uncertainty of the measurement device, and the largest of the two uncertainties have been used. The propagation of uncertainties for the derived evaluation parameters in Section 3.6 have been calculated as according to [115, Eq. 3.47]:

\[
\delta q(x_1, \ldots, x_n) = \sqrt{\left( \frac{\partial q}{\partial x_1} \delta x_1 \right)^2 + \ldots + \left( \frac{\partial q}{\partial x_n} \delta x_n \right)^2},
\]  

(5.1)
where $\delta q(x_1, ..., x_n)$ is the uncertainty an evaluation parameter ($q$) that is a function of several independent parameters ($x_1, ..., x_n$), $\delta x_1$ is the uncertainty of the parameter $x_1$ and $\delta x_n$ is the uncertainty of the parameter $x_n$.

If the uncertainty is estimated to be at least an order of magnitude lower than the last decimal, it has not been included in writing.

For the dynamic data, time has been used without uncertainty. This has been done for two reasons. Firstly, the uncertainty in the time reading is expected to be very low and secondly because the uncertainty of the time reading is not expected to have any effect on the results.

### 5.2 Electroscrubber Design

Two scrubbers were constructed, see Figures 5.1 and 5.2. The liquid distribution inside the scrubbers was performed by a commercial shower head and visually inspected to be satisfactory. The electrochemical cell was implemented at the bottom of the electroscrubber in the electrolyte reservoir. Two carbon electrodes (Ø6 mm) were connected to a Volcraft LSP-1403 80 W switching DC power supply. In Figure 5.1(a), the electrodes are visible in the blue circle.

#### 5.2.1 Choice of Electroscrubber Materials

The laboratory electroscrubbers were constructed using standard waste water connectors with see-through pipes, all made from polymers. A scrubber diameter of 110 mm was used as this had been used prior in the MeGa-StoRE project and is a standard size within the piping industry. The polymer equipment was chosen based on several advantages, including:

- Gas tight equipment as it is used to operate with H$_2$S
- The polymer tubing is unaffected by H$_2$S and the electrolyte
- The components can easily be assembled and dismantled for reconfiguration of the electroscrubbers
- The see through pipes allows for visual inspection of the process
- Low price
- In compliance with the MeGa-StoRE design, see Section 1.4.4

#### 5.2.2 Choice of Packing Material

Uncoated Lightweight Expanded Clay Aggregate (LECA) balls with a density of 210-280 kg/m$^3$ were used as packing material. As a ceramic structure containing mostly silicon and aluminum oxides, the LECA balls did not corrode when in contact with the model biogas or the electrolyte. The LECA balls were observed to show excellent wetting abilities and in Figure 5.3(a) the surface of a LECA ball is shown to have a rather large surface area. Furthermore, the ceramic structure contains iron oxides as highlighted in Figure 5.3(b). Iron oxides are known to react with H$_2$S [116]. The iron oxides may therefore act as an active surface that is regenerated by the active chlorine, having a positive effect on the overall process.
Figure 5.1: (a) The first electroscrubber constructed. It was designed to have the maximum available tower height inside the fume hood with two columns, a spray (the yellow ellipse) and a packed column. The blue circle shows the electrodes. (b) The first electroscrubber was modified as the spray column was removed.
Figure 5.2: The second laboratory electrosruber. It was designed to be more convenient as experiments showed that a tall tower was not necessary to achieve complete removal.

Figure 5.3: (a) SEM image of Lightweight Expanded Clay Aggregate (LECA) balls used for packing in the laboratory electrosrubbers, magnified 1000 times. The LECA balls are observed to have a rather large surface area which results in suitable gas-liquid wetting abilities. (b) The iron oxides on the LECA surface highlighted in blue. The LECA balls are a ceramic material with mostly inert oxides, with the exception of iron oxides.
5.3 Test of Scrubbing Height

Part of the project goal was to remove H$_2$S down to the ppb-range in order to make the biogas suitable for second generation upgrading, see Section 1.3. As discussed in Section 3.3, the purification level of the gas depends on the scrubbing tower height. With the aim of achieving ppb-range of H$_2$S in the purified biogas, the initial scrubbing tower was designed to be as tall as possible. The dimensions of the fume cabinet limited the height of the scrubber to $\simeq$ 1 m. However, in order to achieve a taller scrubber, a co-current spray was installed in the initial version of first electroscrubber, see Figure 5.1(a). This gave the scrubber a combined height of $\simeq$ 2 m.

The liquid distribution between the two columns was controlled via a set of valves. During the initial testing, it was found that the electroscrubber performed best using only the counter-current scrubber. Based on these results, the spray column was removed from the electroscrubber, see Figure 5.1(b).

Further experiments showed that the scrubber height could be reduced. A second electroscrubber was constructed to be smaller than the first for convenience, see Figure 5.2. By varying the gas flow and tower height, it was determined that the scrubbing tower was not required to be taller than a few centimeters. A complete removal of H$_2$S was possible at tested tower heights down to $3.2 \pm 0.2$ cm in the electroscrubber in Figure 5.2.

5.4 Results of Sulfur Removal in the Laboratory

This sections present the initial results from the laboratory. These results were used to estimate the size of a pilot plant capable of cleaning 10 Nm$^3$/h biogas. The major part of the results are analysed in Chapter 8. Only the results required for understanding the design and construction of the first campaign scrubber are included here.

5.4.1 Dynamic Results from the Laboratory

In Figure 5.4, dynamic results from an laboratory experiment is presented. The black squares show the amount of H$_2$S entering the electroscrubber and the red dots show the amount leaving the system. The blue triangles indicate the potential applied to the electrolyte. In other words, the blue triangles show how much power was used in the system. The laboratory electroscrubber in Figure 5.2 was used for the experiment. The experiment was performed with a total gas flow of $200 \pm 10$ L/h and a packing height of $3.2 \pm 0.2$ cm.

Figure 5.4 show that for the first 2 h of the experiment the potential is kept constant at 4.52 $\pm$ 0.05 V. From the red dots, it can be seen that after a run-in time of 40 min. the H$_2$S is completely removed. After 2 h, the applied potential is turned down to 3.89 $\pm$ 0.04 V. The response from the system is observed immediately, as the H$_2$S content in the cleaned gas increases to 360 $\pm$ 50 ppm. After almost 3 h, the potential is turned up to 4.22 $\pm$ 0.04 V and again the response is immediately observed. The H$_2$S content in the cleaned gas decreases as expected and stabilizes at $170 \pm 50$ ppm.

The removal efficiency ($\Delta S$, see Eq. 3.9) is observed to be dependent on the applied potential. This is expected, as a higher applied potential results in a higher current. The current is
used to generate the oxidizing species, and higher currents therefore results in more oxidizing species. The sulfur is removed with the oxidizing species. The removal efficiency of the system was also observed to immediately change when the potential changed. This shows that the system can respond quickly to changes in the biogas composition. These data are representative for all the experiments performed on the laboratory electroscrubbers.

5.4.2 Static Data Analysis

Steady state data points from the laboratory electroscrubbers are presented in Figure 5.5. The removal efficiency ($\Delta S$) is showed as function of the gas flow and the current relative to the $H_2S$ concentration $i/i_{theory}$, see Section 3.6.1.

Figure 5.5(a) shows the effect of $i/i_{theory}$ on the removal efficiency ($\Delta S$). It is observed that an increase in $i/i_{theory}$ results in an increase in the $\Delta S$. The experiments were performed with different gas flows, 200 L/h and 250 L/h. Based on the two pairs at $i/i_{theory} \simeq 2.3$ and $i/i_{theory} \simeq 3.6$, the two gas flows are observed to behave similarly.

In Figure 5.5(b), the effect of the gas flow is showed. Increasing the gas flow decreases the removal efficiency. This is showed for different flows and for different $i/i_{theory}$-values. It is observed, that for a gas flow of 200 L/h, an $i/i_{theory}$-value of $3.5 \pm 0.2$ is sufficient to achieve $\Delta S = 100\%$. From the two arrows in Figure 5.5(b), it is showed how $\Delta S$ can be decreased:
• **Increased gas flow (arrow 1 in Figure 5.5(b))**

   If the gas flow is increased from 200 L/h to 250 L/h, the $\Delta S$ decreases. This indicates that the reaction becomes limited by kinetics or mass transfer inside the scrubbing tower. This will be discussed below.

• **Decreased the applied current (arrow 2 in Figure 5.5(b))**

   If the $i/i_{\text{theory}}$-value is decreased to $2.2 \pm 0.2$, $\Delta S$ decreases. This indicates that there is not enough oxidizing agent in the electrolyte.

The electroscrubber is observed to be limited by two different mechanisms; the amount of oxidizing species and the contact time inside the scrubber.

The amount of the electrolyte is represented as the $i/i_{\text{theory}}$-value. In theory, an $i/i_{\text{theory}}$-value of 1 should be sufficient for complete removal of H$_2$S. At a $i/i_{\text{theory}}$-value of 1, HClO is produced in a 1:1 ratio with H$_2$S. If the current efficiency ($\eta_i$, Eq. 3.8) is 100%, then $i/i_{\text{theory}} = 1$ is enough for a complete removal. Due to unwanted side reactions and reverse discharge reactions (reduction of HClO on the cathode), the expected efficiency is lower than 100%. In Figure 5.5(a), a low $i/i_{\text{theory}}$ value results in a low capacity of the electrolyte and therefore lower $\Delta S$. In Section 8.2, the current efficiency of the electroscrubbers will be discussed in detail.

The gas flow shows the limitations in mass transfer and reaction kinetics. As expected, if the gas flow is too high, the electroscrubber does not have the time to remove all the H$_2$S. From these experiments, it was determined that 0.30 L packing material was required for a gas flow of 200 L/h. This corresponds to a space velocity of:

$$\frac{200 \text{ L/h}}{0.30 \text{ L}} = 667 \text{ h}^{-1}. \quad (5.2)$$

It was assumed, that this value was dependent on the removal reaction and independent on the scrubber design. In other words, the space velocity was for scaling up the electroscrubber.

In Section 8.7, a simple model will be formulated for the determination of the scrubber height.

### 5.4.3 Sulfur Generation

During operation, elemental sulfur was observed to float on the electrolyte, in accordance with theory. A simple filtration device was implemented. Initial experiments indicated that the pressure loss in the filtration system was too high. It was decided not to run the experiments with filtration. The amount of sulfur produced in the experiments were a few grams, and was not observed to affect the overall performance of the electroscrubber.

Sulfur samples were collected from the electrolyte between experiments. In Figure 5.6, a sulfur sample is investigated using SEM. The sample configuration was studied with EDS and found to contain mostly sulfur with significant amounts of oxygen, sodium and chlorine, see Table 5.1. The sodium and chlorine are expected to be trace amounts of the electrolyte found as NaCl in the sample. The EDS analysis supports this as the sodium and chlorine are found in the same areas, see Figures 5.6(d) and 5.6(e). The oxygen was found to be present throughout the sample, see Figure 5.6(e) and could be present in the form of oxidized sulfur. Sulfate could have
Figure 5.5: Steady state data points for the electroscrubber in Figure 5.2, operated with 3.2 cm packing height. (a) The removal efficiency is observed to increase with the $i/i_{\text{theory}}$-value. (b) Increasing the gas flow is observed to decrease the removal efficiency.

Table 5.1: Elemental distribution of the solid sample in Figure 5.6 analysed by EDS. Sulfur is the main component, with oxygen, sodium and chlorine present as well. The almost equal amounts of sodium and chlorine, combined with the mapping in Figures 5.6(d) and 5.6(e), indicates that NaCl is present in the sample. The oxygen most likely comes from residual water in the sample. This distribution is representative for solid samples extracted from all electroscrubbers, both in the laboratory and campaigns.

<table>
<thead>
<tr>
<th>Element</th>
<th>S</th>
<th>O</th>
<th>Na</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic percentage</td>
<td>72 ±3</td>
<td>11 ±1</td>
<td>8.9 ±0.3</td>
<td>8.1 ±0.4</td>
</tr>
</tbody>
</table>

been formed during the experiment or when the sulfur sample was exposed to air. However, the oxygen must likely comes from water still present in the sulfur sample.

The sulfur sample presented in Figure 5.6 and Table 5.1 is representative for the solid samples extracted from all electroscrubbers, both during the laboratory experiments and campaigns. Discussions with Jacob Wagner Jensen, biomass manager at Bigadan and Professor Jørgen Eriksen, Department of Agroecology at Aarhus University, revealed that the sulfur extracted from the electroscrubber could be directly added to the degassed manure leaving the biogas plant without further processing.
Figure 5.6: (a) SEM image of a solid sample extracted from the electroscrubber. An EDS analysis showed that sulfur was the main component with amounts of oxygen, sodium and chlorine present as well, see Table 5.1. The EDS analysis further showed that sulfur (b) and oxygen (c) were present throughout the sample, while sodium (d) and chlorine (e) were localized to a few places. This indicates that the solid sample consists of wet sulfur with NaCl present as well.
5.5 Conclusions of Laboratory Experiments

Overall, the electroscrubbing process was found to remove H$_2$S down to non-detectable limits. Experiments were performed to estimate the parameters to scale up the process. Based on three different scrubbing set-ups, a height of $3.2 \pm 0.2$ cm was found to be sufficient for complete removal of H$_2$S. A space velocity of $667 \text{ h}^{-1}$ was determined, which is used for scaling up the electroscrubber. The sulfur was found to leave the system as elemental sulfur that was floating on the electrolyte. The sulfur samples extracted from the system contained residual water and NaCl, however, of high enough quality to be allowed to enter the degassed manure as fertilizer. Thus, the electroscrubbing process fulfilled the design criteria of removing H$_2$S down to low levels without generating any waste.
Chapter 6

1st Campaign;
Pilot Testing at Nysted Biogas Plant

In this chapter, the design, construction and operation of the first campaign are presented. The main results from the campaign electroscrubber are discussed in detail in Chapter 8 where they are compared with the results from the laboratory and the second campaign. The first campaign is described in the manuscript Pilot Plant Testing of Novel Electro-scrubbing Process for Biogas Desulfurization, Appendix IV.

6.1 Motivation for the Campaign

This campaign was originally not part of the MeGa-StoRE project plan. Beginning in the summer of 2017, the MeGa-StoRE project was planned to perform a combined campaign at the Midtfyn biogas plant. However, three different circumstances made the a stand-alone campaign for the electroscrubber possible and favourable:

- The originally planned campaign at Midtfyn was delayed
- The Midtfyn biogas plant reported low \( \text{H}_2\text{S} \) concentrations in the raw biogas
- The electroscrubbing process was ready for a campaign 2 months prior to the scheduled campaign

The Midtfyn biogas plant used chemical precipitation for desulfurization which resulted in low \( \text{H}_2\text{S} \) concentrations in the raw biogas, as described in Section 2.2. While this desulfurization process was reported to be temporary, no alternative was planned to be implemented within the time-frame of the MeGa-StoRE project. Thus, for the electroscrubbing desulfurization
technology to be tested on biogas with common levels of \( \text{H}_2\text{S} \), another campaign had to be performed. The main targets of this campaign were to test:

- The performance of the electroscrubber on real biogas
- The capacity of the system, both for \( \text{H}_2\text{S} \) concentrations and gas flows
- The elemental sulfur generation and removal
- The flexibility of the system to adjust to the biogas concentration

\[ \text{Figure 6.1: The electroscrubber before departure to Nysted from the front (a) and back (b). The scrubbing tower is the corrugated orange shaft, the white bucket contains the filtration unit and the grey box is the electrochemical cell. The electronics are observed to be directly exposed. The electroscrubber is observed to be contained within two cabinets as per the MeGa-StoRE design criteria, see Section 1.4.4.} \]
6.2 Design and Construction

The design of the electroscrubber was mainly based on the experiments performed in the laboratory, see Chapter 5. The outer dimensions of the electroscrubber were limited by two server cabinets. This was due to the MeGa-StoRE design restrictions, see Section 1.4.

In Figure 6.1, the electroscrubber is presented before departure for the campaign. A piping and instrumentation diagram (P&ID) of the electroscrubber is presented in Figure 6.2. The orange shaft in Figure 6.1 is used as the scrubbing tower where the biogas is cleaned. The biogas is analysed at gas analysis point (GAP) A before it enters the scrubber and at GAP B after.

The blue lines in Figure 6.2 indicate the electrolyte flow. After the electrochemical cell, the electrolyte is pumped into the scrubber. The pump is visible in Figure 6.1(a) in the lower left corner, or the lower right corner in Figure 6.1(b). When the electrolyte leaves the scrubber, it enters a filtration system. The filtration system is placed inside the white bucket in the center of the electroscrubber in Figure 6.1. After filtration, the electrolyte enters the electrochemical cell, visible in the lower left corner of Figure 6.1(b). Redox sensors (RS) are used to measure the oxidizing potential of the electrolyte before and after the electrochemical cell. The pH-value is also measured, as presented in Figure 6.2.

Two major changes were made to the electroscrubber during the campaign: The filtration system was removed and the H$_2$ chimney was relocated. These changes are indicated in Figure 6.2 by showing the initial set-up with dashed lines and the final set-up full lines. The changes to the system will be discussed in Sections 6.3.2 and 6.3.3 below.

![Figure 6.2: Piping and instrumentation diagram of the first campaign electroscrubber. The dashed lines indicate the initial set-up. Changes were made during the campaign and the full lines show the final set-up.](image)

Legend

<table>
<thead>
<tr>
<th>GAP</th>
<th>Gas analysis point</th>
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<td>pH sensor</td>
</tr>
<tr>
<td>RS1</td>
<td>Redox sensor 1</td>
</tr>
<tr>
<td>RS2</td>
<td>Redox sensor 2</td>
</tr>
</tbody>
</table>

- Biogas flow
- Initial electrolyte flow
- Final electrolyte flow
- Initial H$_2$ flow
- Final H$_2$ flow
6.2.1 Scrubbing Tower Diameter

The diameter was chosen based on discussions with the suppliers of the packing material, Jan Dehn from Christian Berner A/S and Giles Cobley from Koch-Glitsch. For small scale experiments, wall-effects within the scrubber cannot be neglected [117]. The wall-effect refers to the fact that packing material tend to divert the liquid flow to the walls of the scrubber which in unwanted as the walls have a smaller surface area than the packing. For larger set-ups, the wall-effects are only limited, as the area increases with \( r^2 \) while the circumference only increases with \( r \). Thus, in order to minimize the wall-effect, pilot plant tests for up-scaling purposes were preferred to have diameters of at least 30 cm within the industry according to Giles and Jan. To satisfy this target, a diameter of 31.5 cm was chosen. This diameter is >30 cm and at the same time is a standard size in the polymer well industry.

6.2.2 Scrubbing Tower Height

The laboratory electroscrubber was found to achieve a complete removal with a space velocity of 667 h\(^{-1}\), see Section 5.4.2. Using this space velocity to estimate the volume for removal of 10 Nm\(^3\)/h with a diameter of 31.5 cm, 15 L of packing material would be required. Ultimately, the first campaign electroscrubber was designed with 39 L of packing material, which was expected to correspond to a biogas flow of 26 Nm\(^3\)/h.

6.2.3 Scrubber Materials

As for the laboratory electroscrubbers, polymers were chosen as the main construction material. This decision was based on the highly corrosive environment inside the electroscrubber. The combination of low pH-values, active chlorine compounds, H\(_2\)S and CO\(_2\) results in an environment only a few metals can resist.

6.2.4 Electrochemical Cell

Dimension stable anodes (DSA) in the form of titanium electrodes with a mixed metal oxide (MMO) surface coating for electrochlorination was purchased from Magneto Special Anodes B. V. The electrodes were operated bi-polar in an undivided electrochemical cell, and had the dimensions 300 mm \( \times \) 350 mm \( \times \) 1 mm with connections, see Figure 6.3(a). 4 electrodes were positioned with an interelectrode distance of 4 cm, as observed in Figure 6.3(b). Only the two outermost electrodes were connected to the power supply.

6.2.5 Gas and Liquid Distribution

The scrubbing tower was filled with 39 L polypropylene Koch-Glitsch FLEXIRING\textsuperscript{®} random packing, nominal size: 38 mm, void fraction 91% and bulk weight 70 kg/m\(^3\). The liquid was distributed using a home made distribution system. A single pump was used as a sealless mag drive pump, model DB5 from Finish Thompson generated a flow of 13 L/min throughout the system.
6.2.6 Remote Operation

The system was operated by changing the applied potential, which was controlled through a PLC. All measurements and control was connected to a PLC with internet connection that allowed for remote control. A webcam was installed allowing for visual inspection of the system while it was remote controlled.

(a) (b)

Figure 6.3: (a) One of the four titanium electrodes coated with MMO used in the electrochemical cell. Two handles for connection purposes are connected to the 300 mm × 350 mm × 1 mm electrode. The connection is observed to be corroded. (b) The electrochemical cell as configured during operation. Four electrodes are positioned with an inter electrode distance of 4 cm, resulting in three electrochemical cells. Elemental sulfur is observed as the yellowish substance sticking to the electrodes and sides of the electrochemical cell.

6.3 Installation and Operation at the Nysted Biogas Plant

Nysted Biogas Plant is owed by Bigadan A/S, and situated at Kettinge, Falster in Denmark. The plant generates 1150 Nm$^3$/h biogas, which is used to generate electricity and heat. Currently, a biological desulfurization system is used to clean the biogas down to approximately 50-80 PPM H$_2$S before the CHP engines. No continues measurements of the H$_2$S content is used. In Table 6.1, the average biogas configuration is presented, as measured throughout the campaign of ∼ 60 h.

6.3.1 Installation

The installation of the electroscurber is shown in Figure 6.4. The shed was part of the former biological desulfurization system and is thus connected to the raw biogas flow. To ensure a gas flow, a side channel blower could be turned on and off. Throughout the experiments, the
Table 6.1: The raw biogas composition at the Nysted biogas plant as measured during the campaign. This biogas composition can be considered common for manure-based biogas plants in Denmark.

<table>
<thead>
<tr>
<th>Gas compound</th>
<th>CH₄</th>
<th>CO₂</th>
<th>H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average value</td>
<td>68 Vol.%</td>
<td>30 Vol.%</td>
<td>1810 ppm</td>
</tr>
<tr>
<td>Maximum value</td>
<td>71 Vol.%</td>
<td>36 Vol.%</td>
<td>6590 ppm</td>
</tr>
<tr>
<td>Minimum value</td>
<td>56 Vol.%</td>
<td>25 Vol.%</td>
<td>160 ppm</td>
</tr>
</tbody>
</table>

combination of pressure loss within the electroscrubber and the pressure generated by the side channel blower resulted in a flow of $5.0 \pm 0.2 \text{Nm}^3/\text{h}$. Unfortunately, the installed capacity of the system was thus only half the targeted value of $10 \text{Nm}^3/\text{h}$ and only $\approx 1/5$ of the expected maximum biogas flow of $26 \text{Nm}^3/\text{h}$.

Figure 6.4: The shed where the first campaign electroscrubber was installed. The wall was reattached during the experiments. The shed was connected to the former biological desulfurization system that was no longer in use; however, could still be connected to the raw biogas stream.

6.3.2 Lesson Learned: Filtration

An oil skimmer was applied as sulfur filter. As no oil skimmers made from polymers were available, the most corrosion resistant model made from chrome plated steel was applied. This decision was made, knowing that the component would have a limited life-time. The oil skimmer was an interesting concept for filtration due to physically separating the sulfur from the
Figure 6.5: (a) A description of the oil skimmer principle, the oil or slurry is continuously separated from the liquid by a belt and a scraper. (b) The corroded oil skimmer following a few hours of operation. Due to the quick failure, no data was collected regarding the oil skimmer principle as filtration system for elemental sulfur removal.

electrolyte, while also running continuously, see Figure 6.5(a). The life-time of the component was greatly overestimated, as the component corroded before significant data was collected on the function of the filter, see Figure 6.5(b). The filtration system was removed as showed in Figure 6.2. Thus, no filtration system was used throughout the experiments and the produced sulfur was left in the electrolyte. The elemental sulfur in the electrolyte may be oxidized according to Eq. 4.11 which was expected to be the reason the pH-value decreased throughout the experiments.

6.3.3 Lesson Learned: Gas Analysis

The initial installation of the gas analysis connection proved to be unfortunate. In Figure 6.1(b), the issue is highlighted in the blue circle. The green arrow indicates the purified gas flow out of the system. Continuous gas analysis is performed by extracted gas via the yellow arrow. However, the ventilation system from the electrochemical cell enters the purified gas stream via the red arrow. The ventilation gas from the electrochemical cell consists of $\text{H}_2$ and diluted the gas measurements. To avoid this, the exit of the $\text{H}_2$ chimney from the electrochemical cell was relocated. In Figure 6.2 this change is showed, as the final set-up has the $\text{H}_2$ entering the scrubber with the raw biogas. Unfortunately, the initial installation of the analysis caused the results from the first 1/3 of the campaign to be invalid.
6.3.4 Lesson Learned: Corroded Connection

The electrochemical cell was connected through two wires that entered the cell through the lid. The connections were covered in order to avoid contact with the liquid and biogas, however, the cathode connection was harmed anyway and failed due to corrosion. In Figure 6.3(a), the electrode with the corroded cathode connection is presented, as the green corrosion product, copper oxide, is observed.

A new connection was implemented for the remaining experiments. Upon decommission, significant corrosion was observed on both connections.

6.3.5 Lesson Learned: Heating Water Accident

During installation of the electroscreening at Nysted, the shed was rearranged which involved removal of piping equipment. The pipes removed belonged to the central heating system of Nysted biogas plant which is in use in the winter. When the central heating system of Nysted biogas plant was started up, the lack of pipes resulted in large quantities of hot water being sprayed onto the system. The electronic devices were damaged, most notable the MRU. Only a single experiment was performed after this, as an external gas analysis was performed.

6.3.6 External Gas Analysis

An external analysis was performed by Danish Gas Technology Centre. The analysis was performed in order to get a more accurate idea of the purification level of the electroscreener.

The analysis was performed by a gas chromatograph equipped with thermal conductivity detection (GC/TCD) and a thermal desorption combined with a gas chromatograph and a mass spectrometer (TD/GC/MS). This analysis allowed for detection of many different pollutants and a more precise measurement of the \( \text{H}_2\text{S} \) concentration.

In Table 6.2, the results from the external analysis is presented. \( \text{H}_2\text{S} \) is observed to be found in a concentration of 221 mg/m\(^3\), corresponding to 160 ppm, in the raw biogas while it is in not detected (ND) in the cleaned biogas. The external analysis was performed after the MRU had been damaged. Thus, the electroscreener was operated with an unknown \( \text{H}_2\text{S} \) concentration during the testing. This was very unfortunate, as one of the scopes of the analysis was to compare the analysis performed by the MRU with the external analysis. Furthermore, the \( \text{H}_2\text{S} \) concentration varied greatly during the campaign, see Table 6.1. Without knowing the concentration of the biogas, the electroscreener was operated with a high applied voltage and resulting current to ensure a complete removal. Again, this proved unfortunate, as the \( \text{H}_2\text{S} \) concentration measured in the raw biogas during the analysis was found to be 160 ppm. This low concentration was later explained as the utilization of chemical precipitation was used for desulfurization during the analysis.
Table 6.2: The external analysis of the raw and cleaned biogas performed by Danish Gas Technology Centre. H$_2$S is observed to be removed down to non-detectable (ND) limits in the cleaned biogas. The siloxanes D$_4$ and D$_5$ are also observed to be present in the biogas and are also removed, although not completely.

<table>
<thead>
<tr>
<th>Gas compound</th>
<th>Unit</th>
<th>Raw</th>
<th>Cleaned</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>mol %</td>
<td>69.81</td>
<td>69.04</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>mol %</td>
<td>28.85</td>
<td>28.23</td>
</tr>
<tr>
<td>N$_2$</td>
<td>mol %</td>
<td>1.04</td>
<td>2.15</td>
</tr>
<tr>
<td>O$_2$ + Ar</td>
<td>mol %</td>
<td>0.29</td>
<td>0.58</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>mg/m$^3$</td>
<td>221</td>
<td>ND</td>
</tr>
<tr>
<td>D4</td>
<td>mg/m$^3$</td>
<td>17</td>
<td>4</td>
</tr>
<tr>
<td>D5</td>
<td>mg/m$^3$</td>
<td>8</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 6.6: Dynamic data from an experiment performed at the Nysted biogas plant. After an initial increase in applied potential, a complete removal of sulfur is observed. The H$_2$S concentration in the raw biogas is observed to change significantly throughout the experiment.

6.4 Main Findings of the First Campaign

In Figure 6.6, dynamic results from an experiment performed during the first campaign are presented. The black squares show the H$_2$S content in the raw biogas, the red dots show the H$_2$S content in the cleaned biogas and the blue triangles show the applied potential.
The H$_2$S content in the biogas is observed to change during the experiment, as it increases from $\sim 1000$ ppm to $\sim 1700$ ppm before decreasing to $\sim 1300$ ppm. During the experiments, changes in the H$_2$S concentration was very common. The changes was usually slower than the values observed in Figure 6.6. One of the conclusions of the experiment is that the raw biogas composition should be monitored periodically. This is required for calculation of the removal efficiency.

Initially, the applied potential is increased until a complete removal of H$_2$S is achieved in Figure 6.6. This is observed to happen after almost 2 h of the experiment. Then, the applied potential is lowered until complete removal is no longer achieved, which happens after 5 h of the experiment.

The experiment shows that increasing the applied potential is linked to increasing the removal efficiency. Furthermore, it is observed that complete removal of H$_2$S can be achieved with the electroscrubber.

The experiment was used to better understand the dynamics of the electroscrubbing system as the continuous change of applied current and biogas concentration resulted in no steady state data points. The results presented here are representative for the experiments performed during the first campaign, although most days had more steady concentrations of H$_2$S in the biogas. The steady state data points achieved during the campaign will be compared with results from the second campaign in Chapter 8.

The main result from the first campaign was the successful removal of H$_2$S from real biogas down to non-detectable limits. The external analysis found that the H$_2$S content was removed down to less than 0.5 ppm, see Table 6.2. However, the external analysis also found chlorinated compounds, mainly Cl$_2$ and HCl, in the cleaned biogas in unknown concentrations.

The external analysis further found that siloxanes, D4 and D5, were present in smaller concentrations as well. The electroscrubber was found to remove these compounds with 76\% (D4) and 75\% (D5) efficiency. Minor amounts of silicon were found in the solid samples, supporting the analyses that D4 and D5 were removed by the electroscrubber.

The electroscrubber proved capable in following the fluctuating concentration of H$_2$S in the biogas as the applied potential was adjusted accordingly. Due to a large pressure drop throughout the system, the gas flow was limited to $5.0\pm0.2$ Nm$^3$/h, and for this value the highest concentration of H$_2$S removed in a single step was 2080 ppm. The oil skimmer implemented as sulfur filter corroded too fast to give an indication if the technology was suitable, see Section 6.3.2. The system was operated for approximately 60 h with no measurable degradation of the main components in contact with biogas with the exception of the filtration unit and the electrode connections. The unprotected electronics were observed to corrode even before the heating water accident, see Section 6.3.5.

6.5 Summary of the First Campaign

The electroscrubbing process was successful in removing H$_2$S down to non-detectable limits. The filtration system failed due to corrosion and another system is required for the removal of the elemental sulfur. The external analysis indicates that the electroscrubber removes sulfur down to very low levels and may thus be suitable for deep desulfurization. Furthermore, Cl$_2$ and HCl was found in the cleaned biogas, which is highly unwanted due to potential downstream
issues. The compounds may have been a result of the system being operated at too high voltage and current. The chlorinated compounds in the purified gas is required to be addressed in future designs. Overall, the main challenges for the electroscrubbing process were determined to be:

- **Reduce** the chlorine compounds in the cleaned gas
- **Identify** a suitable filtration system
- **Optimize** the power consumption
Chapter 7

2nd Campaign;
Pilot Testing at Midtfyn Biogas Plant

In this chapter, the MeGa-StoRE campaign at Midtfyn biogas plant is presented. The description of the desulfurization campaign is discussed. The other results from the MeGa-StoRE project is not included in this thesis.

The main desulfurization results are compared with the first campaign and the laboratory experiments in Chapter 8. This campaign is covered in the manuscript Holistic Biogas Desulfurization within the MeGa-StoRE Project, Appendix V.

7.1 Design and Construction

A completely new pilot plant was designed and constructed for the campaign at Midtfyn biogas plant. The new pilot plant was constructed from scratch in order to implement the lessons learned during the first campaign. An overview of the design and experimental parameters of the equipment for the two campaign electroscrubbers is presented in Table 7.1.

The table shows that the second campaign electroscrubber was constructed to have a slightly higher scrubbing tower. The packing size of the second campaign electroscrubber was decreased in comparison with the first campaign electroscrubber. This was based on visual inspection during the initial testing. The power supply was changed to a model with more suitable parameters. The electrochemical system is preferred to be operated with as few cells as possible to avoid stray currents. Operation with fewer cells require lower potential and higher currents. This was achieved with the new power supply. The amount of electrolyte was significantly increased in the second campaign. This was due to the electrolyte control system, discussed in Section 7.1.3.

A piping and instrumentation diagram (P&ID) of the second campaign electroscrubber is
Table 7.1: Overview of design and experimental parameters for the two campaign electroscrubbers. The two electroscrubbers are observed to be very similar, with the second campaign electroscrubber observed to be slightly larger.

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit</th>
<th>First campaign</th>
<th>Second campaign</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tower height</td>
<td>[cm]</td>
<td>50</td>
<td>80</td>
</tr>
<tr>
<td>Diameter</td>
<td>[cm]</td>
<td>31.5</td>
<td>31.5</td>
</tr>
<tr>
<td>Packing size</td>
<td>[cm]</td>
<td>3.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Gas flows tested</td>
<td>[L/min]</td>
<td>83.3</td>
<td>50-120</td>
</tr>
<tr>
<td>Liquid flow</td>
<td>[L/min]</td>
<td>13</td>
<td>12.5</td>
</tr>
<tr>
<td>Power supply max values</td>
<td></td>
<td>48V/62.5A</td>
<td>12V/200A</td>
</tr>
<tr>
<td>Power consumption</td>
<td>[W]</td>
<td>200-700</td>
<td>100-660</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>0.8-1.2</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Amount of electrolyte</td>
<td>[L]</td>
<td>20</td>
<td>27</td>
</tr>
</tbody>
</table>

presented in Figure 7.1. Figure 7.2 shows a technical drawing of the system and a picture of the realized system is presented in Figure 7.3(a).

These figures show the overall system. The orange shaft in Figure 7.3(a) is the scrubber. When the biogas leaves the scrubber, it enters a heat exchanger, shown in the upper right corner of Figure 7.2. After the heat exchanger, the liquid is condensed from the biogas and collected in the collection tank (CT). The biogas then enters the polishing filter, see the upper right corner of Figure 7.1. From the polishing filter, the biogas enters the compressor.

The electrolyte goes through a loop. It enters the scrubber via a pump, showed in the lower left corner of Figure 7.1. Leaving the scrubber, the electrolyte goes through a bag filter (BF), showed in Figure 7.2. After the bag filter, the electrolyte enters the electrochemical cell and the cycle is ended. The key components will be described in detail in the following sections.

The second campaign electroscrubber was designed to be completely automatic, as part of the MeGa-StoRE design criteria. The automation of the process required a redesign of the electroscrubber and implementation of new components. While the main components remained the same in size and numbers as the first campaign, the new design contained roughly 5 times more electrical components. During the first campaign, the electrical components were exposed to the air at the biogas plant which contains H₂S, resulting in significant corrosion. To avoid this, the electrical components were enclosed in the second campaign installation. This is showed in Figures 7.3(b) and 7.3(c). Here, the electrical connections are showed in three different cabinets.

The design of the electroscrubber was presented to TML Safety Engineering A/S for safety evaluation. Following the minor additions of a ventilation system and operation procedures, TML Safety Engineering a/s approved the system for operation in an ATEX zone 2.
Figure 7.1: Piping and instrumentation diagram of the second campaign electroscrubber. By removing liquid from the cleaned biogas and collecting it in a collection tank, it is possible to adjust the amount of electrolyte in the system.
Figure 7.2: Technical drawing of the electroscrubber for the second campaign. By cooling the purified biogas liquid is removed and collected in the collection tank (CT). The liquid in CT can either be added to the system through automatic valve 1 (AV1) or exiting the container through automatic valve 2 (AV2). The electrolyte level control connection (ELCC) ensures that the liquid level in the system is not increased above a certain level. The bag filter (BF) is view to have a ventilation system and a bypass system for change of the bag filter during operation.
Figure 7.3: (a) The electroscrubber constructed for the second campaign before departure. (b) The main cabinet for electrical components. (c) In order to minimize the amount of wires connecting the electroscrubber with the cabinet, two smaller cabinets are installed on the electroscrubber. The electrical components are observed to be encapsulated in order to avoid corrosion by direct contact with the air at the biogas plant, which contains H$_2$S.
7.1.1 The Electrochemical Cell

A new electrochemical cell was designed and constructed for the second campaign. The new electrochemical cell was designed to enhance the power efficiency by a list of improvements. The improvements included:

- The inter electrode distance was decreased to decrease resistance in the system
- The electrolyte flow through the cell was designed to have a better distribution
- An additional connection to the electrochemical cell was made in order to control the amount of electrolyte
- A smaller cell design and amount of electrolyte was implemented to decrease the amount of stray currents
- The electrodes were connected through the sides of the electrochemical cell to avoid corrosion in the connection
- A new power supply with more suitable operation parameters was implemented, allowing for better process control

In Figure 7.4, the design is presented. The blue arrow indicates the flow of the liquid through the cell. The electrolyte enters the cell through an overflow mechanism designed to distribute the electrolyte evenly. Then, the electrolyte is forced to go under the first electrode holder (EH1), passes in between the electrodes and over the other electrode holder (EH2). Thus, the flow through the active electrochemical cell is forced to be upward and diagonal. The hydrogen evolution at the cathodes is therefore in the same direction as the electrolyte flow. The level of electrolyte within the cell is automatically controlled to not increase beyond the electrodes through the electrolyte level control connection (ELCC). All excess liquid is removed through the ELCC. Too much electrolyte in the electrochemical cell could change the flow through the cell, and is thus unwanted.

The electrical connection to the electrodes was also changed. In the first campaign, the connection to the electrodes failed due to corrosion, see Section 6.3.4. In order to avoid this, the titanium electrodes were connected with a solid titanium rod using titanium nuts and washers. The titanium rod was passed though the side of the electrochemical cell and connected to the copper wires outside the cell.

The H$_2$ produced in the electrochemical cell is mixed with the incoming biogas, see the yellow line in Figure 7.1. Within the H$_2$ chimney, an O$_2$ sensor is installed to monitor oxygen evolution. O$_2$ is highly unwanted in the system for safety reasons. A gas mixture of O$_2$ and H$_2$ may explode. If the O$_2$ does not react with the H$_2$ in the electroscrubber it would react inside the downstream chemical reactor, consuming H$_2$ and generating heat. Besides this sensor, the oxygen content is measured through the MRU and the compressor measures the O$_2$ content downstream the polishing filter.

If O$_2$ is measured in the biogas flow, the container would shut down. This is done by cutting the power. When the power is cut, the normally closed closing valve (CV) will close down, see the upper left corner in Figure 7.1.
Figure 7.4: The electrochemical cell designed for the second campaign. The cell was designed to minimize power consumption. The blue arrow indicates the electrolyte flow through the cell. The electrolyte flow is optimized, as a diagonal upwards flow between the electrodes, achieved by forcing the electrolyte under electrode holder 1 (EH1) and above electrode holder 2 (EH2). The electrolyte level control connection (ELCC) is observed as well, ensuring that the electrolyte level do not increase beyond the electrodes. To the right, the electrochemical cell is observed with four electrodes.

7.1.2 Scrubbing Tower

The main difference in the scrubbing tower was the implementation of a spiral nozzle, see Appendix VI. The previously used, home-made distribution system, was suspected not to ensure a uniform distribution of the electrolyte. A industrial spiral nozzle was chosen instead. The spiral nozzle has no moving parts, limited pressure drop and distributes the liquid evenly throughout the scrubbing tower. The liquid distribution inside the scrubbing tower was tested in the laboratory during construction and found to be satisfying.

The packing material was also changed. Visual inspection during operation indicated that the gas/liquid interaction was not optimized and smaller packing material was thus implemented. The final packing material was 15 mm × 15 mm polypropylene Raschig Pall Rings.

The biogas flow through the system is ensured by the compressor. Under operation, the downstream compressor sucked biogas through the electroscrubber. A valve was used to control the biogas flow though the system.

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The liquid flow is controlled by a regulation valve situated downstream the pump in the lower left corner of Figure 7.1. A flow meter is installed to measure the liquid flow to the scrubbing tower.

### 7.1.3 Electrolyte Control

The water content of the biogas may interact with the electrolyte as discussed in Section 4.2.1. During the first campaign, no noticeable addition or removal of liquid was observed.

However, this could not be assumed to be the case for the second campaign. To ensure the amount of electrolyte is not increased beyond the designed amount, ELCC is directly connected to a water trap. This installation will automatically remove excess electrolyte through a water trap.

To avoid depletion of electrolyte from the system, a gas chiller and condenser are installed downstream the scrubbing tower. This is showed in Figure 7.1. The liquid removed from the purified biogas through the condenser is collected in a collection tank (CT). Automatic valve 1 (AV1) connects the collection tank with the electrochemical cell through the ELCC, see Figure 7.2. Capacitive sensors are mounted to measure the level of electrolyte inside the electrochemical cell.

The electrolyte level is most sensitive next in the sampling tank next to the pump. If the level of electrolyte is decreased beyond a certain point, liquid will be added through AV1. AV1 has been programmed to open for a limited amount of time. A controlled amount of liquid (1 L) will then be added to the electrochemical cell from the collection tank, which will be described below.

The liquid level in the water trap connected to ELCC is also monitored. If the water trap dries out, gas from inside the electrochemical cell can exit the system, which is highly unwanted. The water trap is connected to automatic valve 2 (AV2).

The collection tank contains up to 20 L and is also monitored. If the collection tank is filled up, AV2 opens and exits liquid through pipes to a collection tank outside the container, see Figure 7.2. AV2 has also been programmed to open only for a limited amount of time, in order to ensure that the collection tank is not completely emptied. Sensors monitoring the collection tank is also installed in order to ensure this. When liquid is removed from the collection tank it is not added to the electrochemical cell, as this may lead to dilution of the electrolyte. The liquid collected in the collection tank is not expected to contain a concentration of NaCl similar to the electrolyte.

Two capacity sensors are installed for each point of interest to ensure redundancy in case one of the sensors malfunctions.

### 7.1.4 Filtration System

A bag filter (BF) was installed in order to remove the sulfur, see Figure 7.2. Although this filtration technology proved capable of filtering elemental sulfur from the electrolyte, it is not the final solution. The bag filter do not physically separate the elemental sulfur from the electrolyte. Thus, further oxidation remains possible through Eq. 4.11. Furthermore, bag filtration is a batch operation as the bag requires periodic change. With the rest of the electroscrubbing system designed to be completely continuous and automatic, the change of the bag in the filter
is the only manual operation. In order to ensure continuous operation during the change of the bag filter, manual bypass valves (BV) are installed to allow the electrolyte to bypass the filtration unit.

In Figure 7.1, this is illustrated. BV1, BV2 and BV3 is used for the filtration system. During regular operation, BV1 and BV3 are open, while BV2 is closed. This ensures that the electrolyte enters the filter. When the bag filter is changed, BV1 is closed, BV2 is opened and BV3 is closed. Then, ventilation to the filter is opened (not showed in Figure 7.1). This procedure was developed together with TML Safety Engineering, in order to ensure the container remained an ATEX zone 2.

### 7.1.5 Chlorine Compounds

Addressing the chlorine species in the purified gas was among the most important topics in the new design. The exact amount of the chlorinated species was yet to be determined and it was decided to investigate this in detail during the campaign. It was believed, that the chlorinated compounds originated from the overconsumption of power during the analysis and that under normal operational conditions the amount of chlorinated compounds would be low. It was further expected, that optimal operation conditions could be found, where the H\textsubscript{2}S would be removed down to a certain level without being completely removed by avoiding overconsumption of power. If the chlorinated compounds originate from overconsumption of power, operation with insufficient power might avoid the chlorinated compounds in the purified gas. If the chlorinated compounds could be avoided by deliberately not completely removing the H\textsubscript{2}S, this would be preferable over having to remove chlorinated species. A series of experiments were prepared with the gas analysis laboratory at Danish Technological Centre in Aarhus in order to find the optimum operational conditions, minimizing the concentration of H\textsubscript{2}S and chlorinated species.

### 7.1.6 Polishing System

As the purified biogas was used in the methanation unit, a polishing filter was installed downstream the electroscrubber. The polishing filter was used to remove trace amounts of H\textsubscript{2}S and other pollutants. The polishing system consists of two filters filled with activated carbon, see Figure 7.5. Activated carbon impregnated with KOH was found to be the best suitable option as it can operate without the addition of oxygen and can remove both H\textsubscript{2}S and chlorinated compounds such as HCl. The activated carbon was installed in two filters connected with a system of valves in order to be able to change one of the filters during operation. The implementation of a polishing filter enables experiments with the electroscrubber during operation of the methanation unit, as the activated carbon could remove any remaining H\textsubscript{2}S in the purified biogas. The electroscrubber can also be completely bypassed if necessary.

### 7.1.7 Piping and Instrumentation Diagram

In Figure 7.1, a P&ID of the electroscrubber is presented. The P&ID has been modified to give more clarity. The main modifications is the simplification of the polishing system, described in Section 7.1.6. Other omissions include:
Figure 7.5: (a) The two polishing filters containing activated carbon impregnated with KOH. The compressor is observed next to the polishing filters. (b) At set of valves were used to ensure that the polishing filter could be changed during operation.

- Manual valves for removing the electrolyte
- Water traps on all connections to and from the electrochemical cell
- Ventilation for the filtration system

Two sets of bypass valves (BV) are implemented in the electroscurber. The first bypass system consists of BV1, BV2, and BV3 and enables the filtration to be bypassed during operation. The second bypass system consists of BV4, BV5, and BV6. This system enables a bypass of the whole electroscurbing system. Under normal operation, BV4 and BV6 are open, while BV5 is closed. To bypass the electroscurber, BV5 is opened while BV4 and BV6 is closed.

An automatic closing valve (CV) is installed upstream the electroscurber. This valve will close if the power is cut to the container, as it is only open when a potential is applied. The alarms mounted in the container will cut the power if e.g. a fire or large amounts of CH$_4$ is detected.

There are three different gas analysis points (GAP) showed in the biogas flow. In this thesis, the results presented are from GAP A and GAP B. These measurements points give the raw biogas concentration and the cleaned biogas concentration before polishing. GAP C was used periodically to ensure the activated carbon in the polishing filter remained active. If H$_2$S is detected in GAP C, the activated carbon should be changed.

Two pressure sensors (PS) are also showed in Figure 7.1. The sensors were mounted and the wires connected, however, the control software was not updated to include the data from the sensors.
7.2 Installation and Operation at the Midtfyn Biogas Plant

The Midtfyn biogas plant (Figure 1.1) uses first-generation upgrading to produce biomethane for the natural gas grid, see Section 1.2.1. The plant is operated by Nature Energy, a project partner of the MeGa-StoRE project, see Section 1.4.

In Figure 7.6(a), the MeGa-StoRE and H\(_2\)-container are presented and the connection to the biogas plant showed. The MeGa-StoRE container was connected directly to the digestion tank in order to provide raw biogas for the experiments. The cleaned and upgraded biogas was returned to the digestion tank.

![Figure 7.6: (a) The two containers of the MeGa-StoRE project at the Midtfyn biogas plant. The white container was producing H\(_2\) by alkaline electrolysis while the dark blue container purified the biogas and converted it to CH\(_4\). (b) Upon installation, the pipes connecting the containers with the biogas reactor were leak tested.](image)

7.2.1 H\(_2\)S Concentration in the Biogas

Midtfyn biogas plant started producing biogas in 2016. Unfortunately, the biological desulfurization system implemented was unsuitable due to the amount of O\(_2\) present in the purified biogas. Instead, iron chloride was used for H\(_2\)S removal. Thus, when the campaign arrived at the Midtfyn biogas plant, the H\(_2\)S concentration in the raw biogas was measured to be 0-40 ppm. Although expected, this was unfortunate for the experiments with the electroscrubber. Such low concentrations of H\(_2\)S would not result in meaningful data for biogas desulfurization. A biogas with 0-40 ppm H\(_2\)S may be considered cleaned for all practical applications of today.

A new biological desulfurization system was installed at the Midtfyn biogas plant during the campaign. When the new system was installed, iron chloride was no longer added to the feedstock and the H\(_2\)S concentration in the raw biogas increased to 1000-1600 ppm.
7.2.2 Gas Measurements by the MRU

Following the first campaign, the MRU was fixed and an additional H$_2$S sensor installed. The new H$_2$S sensor had a lower detection limit and higher accuracy making it better suited for measurement of the H$_2$S concentration in the purified gas. The MRU is programmed to switch between the two sensors, high and low, depending on the H$_2$S concentration in the measured biogas. Upon operation, it was found that H$_2$ interacted with the new H$_2$S sensor. When the purified biogas exits the electroscrubber, it contains H$_2$ roughly in the same concentration as the H$_2$S that enters the electroscrubber. The H$_2$S low sensor measured at least some of the H$_2$ as H$_2$S. This was determined, as the electroscrubber was unable to remove even small concentrations of H$_2$S and that the H$_2$S concentration increased with increasing applied current. The opposite had been the case throughout the laboratory experiments and the first campaign. Furthermore, the polishing filter also proved incapable of removing small concentrations of H$_2$S, even immediately after the activated carbon had been changed. The H$_2$S low sensor was removed from the MRU and operation with the H$_2$S high sensor was resumed.

7.2.3 Gas Measurements by the Protea

An alternative gas measurement device was also employed. A Protea portable high-resolution multicomponent Fourier transform infrared spectroscopy analyser\(^1\) was used for precise measurements. The equipment and personnel was borrowed from DTU Center for Energy Resources Engineering (CERE). The Protea was employed in order to obtain more precise measurements and to ensure that data was obtained even if the MRU did not provide any. Unfortunately, H$_2$S has a very weak infrared signal, which results in large uncertainties [118]. Discussions with the supplier revealed that the detection limit of H$_2$S could be as high as 30-50 ppm for a newly configured and calibrated equipment, depending on the other gases present. 50 ppm was used as uncertainty for the detection limit, as the equipment was new and freshly calibrated.

The Protea equipment provided both better and faster analysis of the biogas. The Protea equipment averaged over 10 scans of the gas before compiling an analysis. During operation, at least 4 analyses were performed for each data point. The procedure during for data acquisition was the following:

- Analysis of the purified gas until stable, at least 4 times 10 scans
- Data point obtained
- Protea equipment set to measure the raw biogas
- Change of an operating parameter, e.g. applied potential
- Stabilization of measured electroscrubbing parameters, i.e. redox potential and current
- Protea equipment set to measure the purified biogas (end of cycle)

Thus, the data points were alternating between the raw and purified biogas.

\(^1\)Referred to as Protea
7.2.4 Installation Safety and ATEX

The MeGa-StoRE container was designed to be an ATEX zone 2. This is the least dangerous of the ATEX zones. It can only be achieved if there is no risk of an explosive atmosphere during normal operation [119]. Furthermore, explosive atmospheres should not be present more than 10 hours per year. To ensure the MeGa-StoRE container fulfilled these criteria, all the components had to be gas tight. Upon installation on site, some of the components in the gas cleaning system was found to leak. The components were leak tested using a portable H2 sniffing leak detector. Two components were found to leak:

- **The filtration system**
  Additional latches were installed and successfully gas tightened the unit

- **The polishing system**
  Additional latches were also installed, however, a small leak remained. The leak resulted in a local concentration of $\approx 40$ ppm CH$_4$ and was monitored during operation.

7.2.5 Time of Operation

The MeGa-StoRE container and the hydrogen container was installed at the Midtfyn biogas plant in mid October of 2018, see Figure 7.6(a). The second campaign was present at the Midtfyn biogas until early May 2019. Different circumstances resulted in only limited amount of time for desulfurization experiments. A short breakdown of the circumstances are:

- **October 2018 - March 2019**
  The application of iron chloride resulted in too low H$_2$S concentration in the biogas (0-40 ppm).

- **March 2019 - mid April 2019**
  The purified biogas concentration could not be measured due to the MRU having various issues.

- **Mid April 2019 - end April 2019**
  Installation and initialization of the Protea equipment.

The experiments were halted as the biogas plant was scheduled to expand. Ultimately, the experiments were continued until a few days before construction started on the same spot as the containers had been located. Unfortunately, the limited amount of time for testing meant that the experiments regarding the amount of chlorinated species could not be performed. However, the results obtained by the gas analyses performed by the Protea were of higher quality than previous experiments.

7.2.6 Dilution Incident

During operation of the electroscrubber, a large, unknown, amount of liquid was suddenly added to the electroscrubbing system. The liquid is expected to originate from the piping system connecting the containers with the biogas reactors, see Figure 7.6(b). As described in Section 1.1,
biogas is produced at elevated temperatures and under humid conditions. Thus, when the biogas leaves the fermentation tank and is cooled, liquid is removed from the gas. During operating of the MeGa-StoRE container, the piping equipment connecting the container with the biogas reactor was regularly emptied. It is believed, that an unknown amount of liquid collected in the connection pipes formed a plug and was injected into the electroscrubber. Unfortunately, the liquid also entered the Protea analysis equipment which was damaged. Following the incident, the electroscrubber was operated for an additional 3 h before the experiments were terminated. No gas analysis was performed after the incident.

![Figure 7.7: The electrical properties during the dilution incident.](image)

In Table 7.2, a comparison of the electrolyte before and after the dilution is presented. The start values of the mass and chloride concentrations are based on the electrolyte mixed 4 days of operation prior to the incident. Following the incident, the electrolyte was emptied from the system and weighted to estimate the mass. The chloride concentration in the diluted electrolyte

<table>
<thead>
<tr>
<th>Dilution</th>
<th>Mass</th>
<th>Resistance</th>
<th>Chloride concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>32.4 ± 0.1 kg</td>
<td>0.120 ± 0.003 Ω</td>
<td>182 ± 3 g/L</td>
</tr>
<tr>
<td>End</td>
<td>40.7 ± 0.05 kg</td>
<td>0.155 ± 0.003 Ω</td>
<td>140 ± 6 g/L</td>
</tr>
<tr>
<td>Factor</td>
<td>1.26 ± 0.05</td>
<td>1.29 ± 0.03</td>
<td>1.30 ± 0.06</td>
</tr>
</tbody>
</table>

*Table 7.2: Dilution parameters of the electrolyte from the second campaign. Based on all three measurable parameters, a dilution factor of ≃ 1.3 is obtained. This corresponds to 8 L of water added to the electrolyte.*
is based on an analysis performed by Force Technology, see Table 7.3, which will be covered in Section 7.2.7. The resistance of the electrolyte was measured continuously during the incident, and may be assumed to be the most precise measurement. It is assumed that the electrical resistance depends linearly on the concentration of the electrolyte.

The dilution factor based on all three parameters is \( \simeq 1.3 \), which corresponds to the electrolyte being diluted by 8 L of water with no chloride content, a density of 1.0 g/mL and a high electrical resistance.

In Figure 7.7, the electrical properties are showed during the dilution incident, as the blue line show when the dilution happened. As expected, the electrical properties of the system was changed. The dilution meant that the electrolyte had a higher resistance. The applied potential that was kept constant at 4.15 ± 0.05 V during the dilution incident. The resulting current was observed to change from 43.1 ± 0.3 A before the dilution to 33.2 ± 0.3 A directly after the dilution. The potential was kept constant and over the course of 3 h, the resulting current was increased to 35.4±0.3 A. The effect of the dilution on the gas cleaning is not known due to the damage to the Protea equipment. It is expected that the removal efficiency decreased as the applied current decreased.

Based on the dilution incident, an estimation of the run-in time of the electrolyte can be made. The liquid added to the electroscrubber is observed to continuous increase in conductivity after the incident. This is expected until the fresh liquid is saturated with components from the from the biogas and electrolyte. From Figure 7.7, the run-in time of a fresh electrolyte can be estimated to be in the order of a few hours. 3 h after the incident, the conductivity still increases although only slowly, which indicates that the run-in time is almost done. The conductivity is directly linked to the amount of ions in the electrolyte and it is expected to be lower as the total amount of NaCl is not changed.

### 7.2.7 External Liquid Analysis

An external liquid analysis was performed of the electrolyte to get a better understanding of the composition after use. In Table 7.3, the results from the external liquid analysis performed by Force Technology is presented. Unfortunately, the analysis was performed on the electrolyte after the dilution incident, see Section 7.2.6.

Both sulfur and sulfate are observed to be present in the electrolyte, proving that the bag filter was not successful in removing the sulfur from the electrolyte. Sulfate is expected to be present in the electrolyte due to oxidation of sulfur according to Eq. 4.11. The bag filter does not physically separate the elemental sulfur from the electrolyte, which allows the electrolyte to oxidise the sulfur. However, the elemental sulfur measured in the liquid sample was unexpected, as the sample was taken downstream the bag filter and no visible sulfur was present.

The mineral acidity refers to the amount of sulfuric acid (H\(_2\)SO\(_4\)) and hydrochloric acid (HCl), while the total acidity takes the organic acids into account as well. For this process, the acidity is expected to come from the oxidation of sulfur according to Eq. 4.11 and the difference between the total acidity and the mineral acidity may be assumed to be carbonate formed by dissolved CO\(_2\) by Eq. 4.14.

The data from the liquid analysis can be used in the modelling of the electrolyte development.
Table 7.3: Liquid analysis of the electrolyte from the second campaign electroscrubber, after dilution, see Section 7.2.6. A high acidity is observed, corresponding to a pH-value of 0.85. Sulfate is also observed in the electrolyte, as expected. However, sulfur is also observed which was not expected and indicates that the bag filter did not remove all sulfur particles from the electrolyte.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Result ± 4</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total acidity</td>
<td>142</td>
<td>mmol/L</td>
</tr>
<tr>
<td>Mineral acidity</td>
<td>110</td>
<td>mmol/L</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>4.2 ± 0.7</td>
<td>g/L</td>
</tr>
<tr>
<td>Sulfate (SO$_4^{2-}$)</td>
<td>13 ± 1.3</td>
<td>g/L</td>
</tr>
<tr>
<td>Chloride (Cl$^-$)</td>
<td>140 ± 6</td>
<td>g/L</td>
</tr>
</tbody>
</table>

7.3 Main Findings of the Second Campaign

This section presents dynamic results from the second campaign is presented. The static data from the campaign is analysed together with the laboratory and first campaign electroscrubber in Chapter 8. In Figure 7.8, dynamic results from an experiment performed during the second campaign electroscrubber are presented. As described in Section 7.2.3, the data points alternate between the raw (black squares) and purified (red dots) biogas. The blue triangles show the applied potential. The experiment was performed with a raw biogas flow of 105 L/min.

Initially, the a potential of 4.70 ± 0.05 V is applied. This results in the H$_2$S being removed down to 440 ± 40 ppm in the purified gas. The applied potential is then turned up to 5.1 ± 0.05 V, and the removal efficiency is observed to increase as the purified gas stabilizes with a H$_2$S concentration of 80 ± 30 ppm. The applied potential is once more turned up, this time to 5.20 ± 0.05 V, which results in a complete removal of the H$_2$S. Following this result, the applied potential is turned down to 4.15 ± 0.04 V, where a complete removal of H$_2$S is also achieved. It is expected that turning the potential further down would result in an incomplete desulfurization. It should be noted that the H$_2$S concentration in the raw biogas decreases throughout the experiment. This is taken into account when comparing the static data in Chapter 8.

Figure 7.8 show that the electroscrubber reacts fast to the changes in applied potential. The applied potential was changed 0.4 V after 16 min. of the experiment and the H$_2$S concentration in the purified gas is stabilized within 30 min. of the experiment. For a smaller change in potential, the stabilization is even faster. After 38 min. of the experiment, the potential is changed 0.2 V, and the stabilization time is within 9 min. During the change of the potential, the raw biogas is measured as described in Section 7.2.3. When the cleaned biogas is analysed after 47 min. of the experiment, no amount of H$_2$S is measured.

Based on the stabilization times of the system, is can be concluded that the electroscrubber may be quickly adjusted to changes in the H$_2$S concentration. Within 9 min. of experiment, the liquid is cycled through the system 4.17 times, as the circulation time is 2.16 min. The flexibility is an important feature that current desulfurization technologies such as chemical precipitation and biological desulfurization do not have.

Following the first campaign, three areas were highlighted as requiring additional research. While all three areas were addressed, all require even further research:
Figure 7.8: Dynamic results from an experiment performed during the second campaign. The utilization of the Protea equipment resulted in faster and more precise measurements. An increase in the applied potential is observed to increase the removal efficiency, and the stabilization time after a change in applied potential is observed to be in the order of 15 min.

- **Chlorine compounds**
  Due to limited time for experiments, the amount of chlorine compounds in the purified gas remains unknown. Analysis of the electrolyte did indicate that it is not rapidly depleted from chloride, see Section 7.3.1.

- **Filtration**
  A new filtration system was implemented that proved capable of removing sulfur from the electrolyte. However, the solution is not final, as the elemental sulfur remains in contact with the electrolyte and the process is not continuous.

- **Power consumption**
  The new electrochemical cell design decreased the resistance in the system. As the current efficiency remained the same, this corresponds to an overall reduction in power consumption. It should be noted, that the initial electrolyte concentration was also increased, from 200 g/L to 300 g/L NaCl which also decreases the resistance.
7.3.1 Chlorine Compounds

Chlorine compounds in the purified biogas was one of the main concerns before the campaign was initiated. Chlorinated compounds in the purified biogas is unwanted for several reasons. Among these are the depletion of the active compound from the electrolyte. No measurable difference in the chloride concentration was observed, when taking the dilution factor into account, see Table 7.2. Calculation of the dilution of the electrolyte was based on three parameters, one of which was the chloride concentration. Of the three parameters, the resistance of the system is expected to be the most accurate. The resistance of the system gives a dilution factor of $1.29 \pm 0.03$, which indicates that there is no loss of chloride from the electrolyte.

Any chlorine compounds in the purified biogas is expected to have been removed by the activated carbon. The activated carbon impregnated with KOH was analysed before and after utilization. The sulfur content had increased to $14 \pm 0.6$ wt.% of the activated carbon while the chlorine content had increased to $1.2 \pm 0.1$ wt.%. This indicates that chlorinated species were present in the purified biogas. The activated carbon was used for a prolonged period of time. This includes early experiments where the MRU gave wrong readings, see Section 7.2.2. The incorrect measurements of the gas resulted in operation with high applied currents, which may have resulted in the excess chlorine compounds in the purified gas.

7.4 Summary of the Second Campaign

An optimized electroscrubber was designed, constructed and operated during the second campaign. The electrochemical was redesigned in order to minimize power consumption, while the scrubbing tower was optimized to ensure a high removal efficiency. Furthermore, the electroscrubbing system was designed to be completely automatic, with the exception of the periodic change of the bag filter.

Sulfur was found to be removed by the bag filter. However, the filtration system required further optimization. A analysis of the electrolyte showed that sulfur and sulfate was present. This indicates that the bag filter did not completely remove the sulfur from the electrolyte, and that the sulfur is oxidized further.

Chlorine was found in the activated carbon after use. This indicates that chlorine species did leave the system, even though there was no difference in chloride concentration measured. The result could come from early experiments where the system was operated with too high currents due to malfunction of the MRU.
Chapter 8

Results and Discussion

Results from all experiments, both campaigns and laboratory, are presented and discussed here. The calculations of the parameters for comparison can be found in Section 3.6. The main results from the laboratory experiments, the first and second campaign have also been discussed in their respective manuscripts: New Electroscrubbing Process for Desulfurization (Appendix III), Pilot Plant Testing of Novel Electroscrubbing Process for Biogas Desulfurization (Appendix IV) and Holistic Biogas Desulfurization within the MeGa-StoRE Project (Appendix V).

8.1 Removal Efficiency

The removal efficiencies, $\Delta S$, for both campaigns and the laboratory experiments are compared with the relative current ($i/i_{\text{theory}}$) in Figure 8.1. The first campaign (red dots) and the second campaign (black squares) are observed to have similar behaviour. The laboratory campaign (blue triangles) is showing similar behaviour as the campaign electroscrubber, although it is at lower $i/i_{\text{theory}}$-value.

In the following sections, the performance of the electroscrubbers will be compared. The campaign electroscrubbers will be analysed together based on their similar performance.

8.1.1 Campaign Removal Efficiency

Both campaigns are observed to have increasing removal efficiency for increasing $i/i_{\text{theory}}$ until a value of $i/i_{\text{theory}} = 5.6 \pm 0.2$ is achieved. This $i/i_{\text{theory}}$-value represents a change in behaviour of the electroscrubbers. The behaviour of the campaign electroscrubbers can be divided into two cases:
• **Case 1:** $i/i_{\text{theory}} < 5.6 \pm 0.2$
  Limitation by capacity of the electrolyte.

• **Case 2:** $i/i_{\text{theory}} > 5.6 \pm 0.2$
  Limitation by the kinetics and mass transfer of the scrubber.

These cases will be discussed below.

For $i/i_{\text{theory}} < 5.6 \pm 0.2$ (Case 1), the electroscrubber is observed to increase in efficiency with increasing $i/i_{\text{theory}}$. This indicates, that the cleaning of the biogas is limited by the capacity of the electrolyte. It seems like there is not enough oxidizing species to completely remove $\text{H}_2\text{S}$. An $i/i_{\text{theory}}$-value of $5.6 \pm 0.2$ would seem to be required for complete removal of the $\text{H}_2\text{S}$ based on Figure 8.2. This value is significantly higher than the theoretical value of $i/i_{\text{theory}} = 1$. For $i/i_{\text{theory}} = 1$, current is applied to generate 1 $\text{HClO}$ for 1 $\text{H}_2\text{S}$. In theory, this should be enough for a complete removal of $\text{H}_2\text{S}$. Potential explanations for the lower current efficiency will be discussed in Section 8.2.

For $i/i_{\text{theory}} > 5.6$ (Case 2), the removal efficiency is observed to stagnate for both campaigns. For the first campaign, steady and high removal efficiencies are achieved, although a 100% is only achieved for 1/5 data points. For the second campaign, the removal efficiency is observed to be 100% for 10/11 data points. It may be assumed that for $i/i_{\text{theory}} > 5.6$, there is sufficient applied current for complete removal of sulfur. In other words for $i/i_{\text{theory}} > 5.6$, there is enough $\text{HClO}$ for removal of $\text{H}_2\text{S}$. Other factors are therefore limiting $\Delta S$ during the first campaign. These factors are expected to include gas flow and liquid distribution.

One of the improvements for the second versus the first campaign electroscrubber was the implementation of a spiral nozzle for liquid distribution, see Section 7.1.2 and Appendix VI. During the first campaign, a home-made liquid distribution system was used. In the second campaign, a spiral nozzle was used for liquid distribution, see Section 7.1.2. It is expected that the spiral nozzle improved the liquid distribution. The spiral nozzle was tested and found to distribute the liquid in a satisfying manner, see Appendix VI. No experiments were performed regarding the distribution by the home-made system.

The packing material was another difference between the two campaigns. Both campaigned used raschig rings. The first campaign contained nominal size of 3.8 cm, while for the second campaign the nominal size was 1.5 mm, See Table 7.1. These improvements may have resulted in an overall mass transfer in the second campaign scrubbing tower.

The design change of the electrochemical cell is not assumed to have had effect on the higher removal efficiency at higher $i/i_{\text{theory}}$-values. If the optimized electrochemical cell had had a positive effect on $\Delta S$, it would be expected to be observed at lower $i/i_{\text{theory}}$-values as well.

### 8.1.2 Laboratory Removal Efficiency

Figure 8.1 also shows results from the laboratory experiments. $\Delta S$ is also observed to increase with $i/i_{\text{theory}}$. However, the laboratory data reaches a 100% removal rate at $i/i_{\text{theory}} = 3.5 \pm 0.5$, well before the campaign electroscrubbers. The data from the laboratory electroscrubber may be assumed to be limited by the capacity of the electrolyte, i.e. similar to Case 1 for the
Figure 8.1: The removal efficiency ($\Delta S$) of the electroscrubbers as a function of the applied current with respect to the theoretical current ($i/i_{\text{theory}}$). For all experiments, an increase in $\Delta S$ is observed for increasing $i/i_{\text{theory}}$ until a certain value where a complete or steady high removal of H$_2$S is obtained. For the laboratory experiments, the complete removal is obtained at $i/i_{\text{theory}} = 3.5 \pm 0.5$, while for the campaigns the value is $i/i_{\text{theory}} = 5.6 \pm 0.2$.

campaign electroscrubbers. This is argued, as an increase of the applied current results in an increase in removal efficiency.

The LECA balls as packing material has the benefit of iron oxides present in the surface, see Figure 5.3(b). The iron oxide (e.g. Fe$_2$O$_3$) may go through a cycle where it is reduced to iron sulfide (FeS):

$$\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{S} = 2\text{FeS} + 3\text{H}_2\text{O} + \text{S}\quad \Delta G_{20^\circ\text{C}} = -76.0\text{ kJ/mol}, \quad (8.1)$$

and then oxidized by HClO:

$$2\text{FeS} + 3\text{HClO} = \text{Fe}_2\text{O}_3 + 3\text{Cl}^- + 3\text{H}^+ + 2\text{S}\quad \Delta G_{20^\circ\text{C}} = -692\text{ kJ/mol}. \quad (8.2)$$

This in-situ regeneration of an active adsorption surface could be part of the explanation why the LECA packing performs well.

The low porosity of the LECA packing is expected to result in a large pressure drop. During the laboratory experiments, this was not measured as the gas was fed directly from a 10 bar
system. However, during the campaigns, the pressure drop of the system became important. Therefore is the LECA packing not expected to be a suitable packing material for larger scale implementations.

8.2 Current Efficiency

The overall current efficiencies, $\eta_i$ (Eq. 3.8), for both campaigns and the laboratory experiments are shown as a function of the current densities ($J$) in Figure 8.2. The results from laboratory experiments are showed in the insert graph.

Figure 8.2 shows that the current efficiency for the campaign scrubber were between $6.3 \pm 1.5\%$ and $18.9 \pm 0.9\%$. These values were obtained when operating the electroscrubbers between 1.7 A/m$^2$ and 6.1 A/m$^2$. For the laboratory electroscrubber, the numbers were significantly different. Here, $\eta_i$ between $29 \pm 2\%$ and $35 \pm 3\%$ were obtained for $J$ between 14 A/m$^3$ and 41 A/m$^2$.

Since the current efficiency is similar for both campaigns, it may be concluded that the changes made between the two electroscrubbers have had little effect on $\eta_i$. This indicates that the parameters which have not been changed are the most important for the current efficiency. The unchanged, or almost unchanged, parameters that are expected to influence the current efficiency are:

- **A membrane**
  Neither campaigns had a membrane implemented

- **The electrodes**
  Dimensional stable anodes of titanium coated with mixed metal oxide for both campaigns

- **Electrolyte concentration**
  200 g/L (first campaign) and 300 g/L (second campaign)

- **Liquid flow through the system**
  12.5 L/m (first campaign) and 13 L/m (second campaign)

These are discussed in the following paragraphs.

An ion exchange membrane to limit the reverse discharge reaction is believed to be the most important parameter, see Section 3.6.2. The membrane would limit the reverse discharge reaction, where the active compound generated at the anode is discharged at the cathode. Such a membrane would also allow a complete separation of the electrolyte into an anolyte and a catholyte each operated with separate pumps. This would make it possible to optimize the reactions separately and may improve the current efficiency significantly.

The electrodes used for the electroscrubbers are all well-suited. While the DSA used during the campaigns are the best suited, graphite is also a widely used anode material for electrochlorination [120]. Operating using a single cell removes the possibility of stray currents that may lower the efficiency of the campaign electroscrubbers, although this is only expected to result in a few % lower efficiency.

The electrolyte concentration and liquid flow can also be optimized. Overall, a high concentration of the electrolyte is expected to have a beneficial effect. High concentration of NaCl
ensures high conductivity of the electrolyte which lowers the power consumption. The high chloride concentration is also required to avoid O$_2$ formation. From a thermodynamically point of view, O$_2$ should be formed at the anode instead of Cl$_2$ [95]. However, due to reaction kinetics, Cl$_2$ formation is favoured over O$_2$ formation, when Cl$^-$ is present in the electrolyte. The liquid flow in the electrochemical cell should be high enough to ensure that Cl$^-$ is always present at the anode surface. An optimized flow velocity at the anode surface may be achieved by operation with separate pumps.

Generally, the $\eta_i$ is observed to be significantly higher for the laboratory electroscrubber than for the campaign electroscrubbers. The main explanation by the higher current efficiencies in the laboratory is expected to be the pure gas. In the campaigns, raw biogas is used that contains several different pollutants. The laboratory experiments were performed on synthetic biogas with no pollutants except H$_2$S. As discussed in Section 4.2.1, these other pollutant may also be removed by the electroscrubber. This would consume some of the oxidizing compounds in the electrolyte. The removal of other pollutants would decrease $\eta_i$, since $\eta_i$ only takes sulfur removal into account. The first campaign electroscrubber was found to remove the siloxanes
D4 and D5 from the biogas. D4 and D5 requires respectively 8 and 10 times the amount of oxidizing species than H$_2$S requires for oxidation [121]. The removal of D4 and D5 will therefore have affected $\eta_i$ significantly. The same may be assumed to have been the case at the second campaign.

From the literature and industry, higher current efficiencies are reported. It is expected that higher current efficiencies may be achieved when the electroscrubber is optimized as discussed above. However, the electrochemical cell for a biogas electroscrubber may not have as high efficiency as for other applications. Biogas contains many different impurities. The desulfurization system is usually situated just downstream the fermentation tank. The liquid in the desulfurization system is therefore expected to contain a lot of impurities. A highly optimized electrochemical cell may be damaged by these impurities. The electrochemical cell of a biogas electroscrubber has to be robust in order to withstand operation with impurities. A robust design may have a lower current efficiency than a highly optimized design. The electrochemical cell of a biogas electroscrubber may therefore have a lower efficiency than for other applications.

Overall, optimization of the current efficiency is possible. An ion-membrane is expected to increase the current efficiency significantly.

### 8.3 Electrolyte Development

The electrolytes in the electroscrubbers were under constant development. As described in Section 4.2.1, the different compounds in the biogas interacts with the electrolyte in different ways. All electroscrubbers were operated without actively controlling the pH-value.

When the electroscrubbers were initiated, the pH-value of the electrolyte was immediately observed to decrease. This is expected, as the CO$_2$ interacts with the electrolyte and forms carbonic acid, see Eqs. 4.14. The pH-value, however, decreases beyond what can be expected from interaction with CO$_2$. All electrolytes reached a steady state pH-value of $\approx 1$.

None of the electroscrubbers physically separated the elemental sulfur from the electrolyte. Acidification through oxidation of elemental sulfur to sulfate may therefore be assumed to be the explanation of the lowering of the pH-value, see Eq. 4.11.

At lower pH-values, the Cl$_2$ to HClO ratio is expected to be higher, resulting in a higher partial pressure of Cl$_2$. A higher partial pressure of Cl$_2$ could result in Cl$_2$ leaving the electroscrubber in the cleaned gas. However, a lower pH-value is expected to result in a higher HCl concentration. The HCl increases the solubility of Cl$_2$ [96]. Overall, better understanding of the effect of the electrolyte on the purified gas is required. This could be achieved either by development of a thermodynamically model or a series of experiments.

Operating the electroscrubber without adding chemicals for pH-control is preferable. Since the overall reaction do not affect the pH-value, see Eq. 4.10, optimization of the electrochemical cell and filtration system may result in the equilibrium pH-value depending mainly on the CO$_2$. However, the equilibrium pH-value of $\approx 1$ obtained by the electroscrubbers is favourable. The low pH-value has beneficial effects on the power consumption, see Section 3.2.
8.4 Electrical Properties

The electrical properties (voltage, current and resistance) of the electroscrubbers are important parts of the overall performance. Figure 8.3 shows the applied potential plotted as a function of the resulting current for both the laboratory experiments and the two campaigns. All data from the experiments are plotted, together with the stable data points. The green arrow indicates that a shift to the right is an increase in conductivity. This is preferable in order to lower the power consumption.

The black squares in Figure 8.3 show all the electrical data collected from the laboratory experiments, while the red squares show the static data from the same data set. The red squares are observed to almost cover all the black squares.

The blue circles show all the electrical data from the first campaign electroscrubber, with the orange circles showing the static data of this data set. Here, the blue circles are observed to be spread out significantly more than the orange circles. This is explained, as the first campaign electroscrubber was often adjusted and therefore opened. Every time the electroscrubber was opened, a run-in time was required before the system was stable. During the run-in, the conductivity of the electrolyte increased. In Figure 8.3, an increase in conductivity results in a shift to the right. The static points are therefore generally to the right of the bulk of the data.

The purple triangles show all the measured data from the second campaign electroscrubber, with the golden triangles showing the static data of this data set. As for the first campaign electroscrubber, the static data is generally observed to be to the right of the bulk data. The explanation is the same as for the first campaign electroscrubber, as a run-in time increases the conductivity.

The electrochemical cells in Figure 8.3 are observed to behave fairly linearly, as expected from Eq. 3.12. The linear dependency indicates that the electrochemical cells has an ohmic behaviour, where the slope is the resistance of the system. A linear fit have been made to the static data points and the results are presented in Table 8.1.

In Table 8.1, the laboratory electroscrubber is observed to have a lot higher resistance ($\Omega$) than both the campaign electroscrubbers. The resistance of the campaign electroscrubbers was significantly reduced by the implementation of suitable electrodes with large surface areas. The large resistance of the laboratory electroscrubber is assumed to be explained by the small electrodes.

The electrical properties are further optimized between the two campaign electroscrubbers. The design of electrochemical cell of the second campaign electroscrubber was given special care, as described in Section 7.1.1. The main objective of the optimization of the cell was to decrease the power consumption by decreasing the resistance. This was achieved by decreasing the inter electrode distance and having the electrolyte flowing the same direction as the $H_2$ bobbles. Having the same flow direction makes sure that the electrolyte at the surface of the electrodes is changed more often. Furthermore, the electrolyte concentration was also increased in the second campaign. These changes may be assumed to explain the lower resistance of the second campaign electroscrubber when compared with the first campaign.

The cell potential, $U_C$ is also observed to change between the electroscrubbers. Generally, a low $U_C$ is preferred in order to minimize the power consumption. Due to the higher resistance of the laboratory electroscrubber, $U_C$ is approximately twice as high as $U_C$ for the campaigns.
Again, the second campaign electroscrubber is observed to have the lowest $U_C$, which may be explained by the optimized electrochemical cell.

**Figure 8.3:** The correlation between applied potential and resulting current for the electroscrubbers. For each electroscrubber, all data points have been plotted together with the steady state data points. A linear fit have been made to the steady state data points and the results are shown in Table 8.1. All electroscrubbers are observed to have ohmic behaviour.
8.5 Power Efficiency

The power efficiency is perhaps the most important overall parameter of the electroscrubber. This is the case, as the OPEX of the electroscrubber is directly dependent on the power consumption. In the following section, the method of calculation of the power efficiency ($\eta_P$) is performed by comparison with the industry. The power efficiency of the electroscrubbers will then be calculated and compared in the section thereafter.

8.5.1 Calculation of the Power Efficiency

$\eta_P$ is calculated when comparing the power consumption of the electroscrubber with an ideal value. The theoretical current can be found by utilization of Faraday’s law, see Eq. 3.4. However, the theoretical potential depends on several process parameters, as discussed in Section 3.2. $\eta_P$ has therefore been calculated by comparison with numbers from the industry.

Production of Cl$_2$ from low pH electrolysis has been reported to consume 1.400 kWh pr. kg. Cl$_2$ [96]. Assuming a 100% reaction rate between Cl$_2$ and H$_2$S, the ideal power consumption per kg of H$_2$S ($P^0_{\text{industry}}$) can be calculated as

$$P^0_{\text{industry}} = 1.400 \text{ kWh per kg } \text{Cl}_2 \times \frac{M_{\text{Cl}_2}}{M_{\text{H}_2\text{S}}} = 2.908 \text{ kWh per kg of } \text{H}_2\text{S}, \quad (8.3)$$

where $M_{\text{Cl}_2}$ and $M_{\text{H}_2\text{S}}$ refer to the molar mass of Cl$_2$ and H$_2$S, respectively. The power efficiency can then be calculated

$$\eta_P = \frac{P^0_{\text{industry}}}{P^0}, \quad (8.4)$$

where $P^0$ is the power consumption per kg of H$_2$S for the electroscrubber, see Eq. 3.14.

These calculations will be used in the following section to evaluate the performance of the electroscrubbers.

8.5.2 Power Efficiency of the Electroscrubbers

In Figure 8.4, the power efficiency is showed for the electroscrubbers as a function of the removal efficiency. The three electroscrubbers are observed to have similar power efficiencies ($\sim 10\%$). The laboratory electroscrubber achieves the highest power efficiency (point A in Figure 8.4), as
η_P = 16 ± 1.7\% is achieved at ΔS = 74 ± 6\%. The power efficiency at ΔS = 100\% is of specific interest. An optimized electroscrubber for second-generation upgrading would have a high η_P at ΔS = 100\%. Of the electroscrubbers investigated in this project, the second campaign electroscrubber is observed to have the highest η_P at 13.4 ± 0.9 \% for ΔS = 100 ± 4\% (point B in Figure 8.4). This corresponds to a power consumption of 22 ± 1.5 kWh per kilogram of H₂S.

The current efficiency was significantly higher for the laboratory experiments than for the campaign electroscrubbers. However, the high resistance of the laboratory electroscrubber results in the overall power efficiency being similar to the campaign electroscrubbers.

High removal efficiencies are usually much more energy intensive than lower removal efficiencies. This is not observed for the electroscrubber. Generally, no apparent correlation between η_P and ΔS is observed, as η_P is similar to 10\% for all ΔS.

Optimization of the power efficiency is expected to happen by utilization of a suitable membrane. It is expected, that an ion-exchange membrane would result in higher current efficiencies while also increase the resistance of the system. However, due to the significance of the current efficiency, it may be assumed that a membrane would increases the power efficiency.

![Figure 8.4: The power efficiency (η_P) of the electroscrubbers. A maximum value of 16 ± 1.6\% is achieved in the laboratory (Point A) and 13.4 ± 0.9\% during the campaigns (Point B). The superior electrical properties of the campaign electroscrubbers are observed to partly compensate for the higher current efficiency of the laboratory electroscrubbers. The second campaign electroscrubber is observed to have the highest η_P at ΔS = 100 ± 4\% (Point B).](image-url)
8.6 Sulfur Filtration

Since the first elemental sulfur became visible during the laboratory experiments, 4 different filters have been tested. None of these proved successful. As discussed in Section 7.1.4, the bag filter implemented for the second campaign electroscrubber is not the final solution. The bag filter does not physically separate the elemental sulfur and the electrolyte. Two filters for physical separation have been tried, and both failed:

- **A cyclone filter** was tested in the laboratory where it did not prove capable in removing the sulfur. Instead, the particles removed from the electrolyte was the corrosion product formed as the cyclone filter started to corrode.

- **The oil skimmer filtration system** for the first campaign was successfully tested to remove different compounds that resembled the sulfur from water. However, upon operation in contact with biogas and the electrolyte, the oil skimmer corroded before any data on the performance was collected.

It should be noted that several of the filtration technologies suitable for this process, e.g. drum filters or band filters, were not available in suitable material or sizes for a pilot plant, within the time frame of the project.

It is expected that the implementation of a suitable filtration system could benefit the overall OPEX of the process. While the sulfur recovered from the biogas is can be fed into the degassed manure, there are also other possibilities. Should the purity allow it, sulfur is a valuable chemical compound with many applications. It could therefore be sold as a by-product from the cleaning process. Furthermore, the discussion with Professor Jørgen Eriksen from Department of Agroecology at Aarhus University revealed that the sulfur produced from an electroscrubber may be considered organic. Organic fertilizers with high content of sulfur are highly priced, and thus even with a low purity the sulfur generated may be valuable.

8.7 Model of Scrubber Height

In this section, a simple model for determination of the scrubber height will be constructed. The aim of the model is to estimate an scaling up of the electroscrubber. The model will be based on the calculation of a scrubber height from the Height of a Transfer Unit (HTU) and the Number of Transfer Units (NTU).

8.7.1 Height of a Conventional Scrubber

The scrubber height \( h \) can be calculated based on the Height of a Transfer Unit (HTU) times the Number of Transfer Units (NTU) [122]:

\[
h = NTU \times HTU.
\]

(8.5)

When the mass transfer from the gas to the scrubbing liquid is low, the molar gas flow \( (G_M) \), the molar liquid flow \( (L_M) \) and the overall gas phase mass transfer coefficient \( (K_g) \) can be assumed to be constant. For these conditions, both the equilibrium line and operating line, see Figure
8.5(b), are straight [122]. The NTU and HTU can be calculated under these assumptions as [122]:

\[
NTU = \frac{y_i - y_u}{\Delta y_m}, \quad (8.6a)
\]

\[
HTU = \frac{G_M}{AaK_g}, \quad (8.6b)
\]

where \(y_i\) is the mole fraction of the pollutant in the gas at the inlet of the bottom of the scrubber (see Figure 8.5(a)), \(y_u\) is the mole fraction of the pollutant in the gas at the outlet of the top of the scrubber, \(A\) is the cross sectional area of the scrubber, \(a\) the specific surface area of the packing material, \(G_M\) is the total molar gas flow and the log mean concentration difference \(\Delta y_m\) is given by [122]:

\[
\Delta y_m = \frac{(y_i - y_i^*) - (y_u - y_u^*)}{\ln(y_i - y_i^*) - \ln(y_u - y_u^*)}, \quad (8.7)
\]

where \(y_i^*/u\) is the mole fraction of the pollutant in the gas that is in equilibrium with the liquid at the bottom (i) or the top of the scrubber (u). Thus, the difference, \(y_i - y_i^*\), corresponds to the driving force of the mass transfer at the bottom of the scrubber and vice versa for \(y_u - y_u^*\). The values \(A, a, G_M, y_i\) and \(y_u\) are either given, e.g. \(G_M, y_i\) and \(y_u\), or part of the design of the scrubber, e.g. \(A\) and \(a\). \(K_g\) is calculated as [123]:

\[
K_g = \frac{1}{m Ek_l + \frac{1}{k_g}}, \quad (8.8)
\]

where \(k_{l/g}\) is the mole fraction mass transfer coefficient in the liquid (l) or the gas phase (g), \(E\) is the enhancement factor and \(m\) is the equilibrium constant, given by \(y = mx\) where \(x\) is the mole fraction of the of the pollutant in the solution, see Figure 8.5(b). The enhancement factor, \(E\), indicates the improved performance of an reactive solvent when compared with an non-reactive solvent. A reactive solvent has \(E \gg 1\), and this is expected to be the case for electroscrubbers. The enhancement factor is a well developed concept that has been a subject in several text books, including Danckwerts [123] and Astarita [124].

### 8.7.2 Estimation of the Mole Fraction Gas Side Mass Transfer Coefficient

An approximation of \(k_g\) is obtained by using the method derived in Absorption Towers by Morris and Jackson [125], as presented in Kemiske enhedsoperationer by Kiorboe et al. [122]. Several different methods for calculations of \(k_g\) exist. This includes models far more complicated that what have been used here. Initial calculations and assumptions indicated that the more advanced models were not required to give a fair estimation of the height. The implementation of more complicated models was therefore not applied. According to Morris and Jackson, \(k_g\) can be calculated [122,125]:

\[
k_g = k_{cg} \rho_g \frac{M_g}{M_g}, \quad (8.9)
\]
Figure 8.5: Scrubbing mechanism with linear operating and equilibrium lines. (a) A gas flow $G$ enters at the bottom of the scrubber with a concentration $y_i$ of the pollutant and leaves the scrubber in the top with a concentration $y_u$. Likewise, a liquid flow $L$ enters at the top of the scrubber with a concentration of the pollutant $x_i$ and leaves at the bottom with a concentration $x_u$. (b) Graphical overview of the scrubbing process with linear operating and equilibrium line. The slope of the equilibrium line is observed to be the equilibrium constant, $m$.

where $M_g$ is the molar mass of the gas, $\rho_g$ is the density of the gas and $k_g$ is the mole fraction mass transfer in the gas phase. $k_g$ can be calculated as:

$$k_{cg} = 0.04C_g Re^{-0.25} Sc^{-0.5} \frac{v}{x_{Bm}}$$

where $C_g$ is the gas film factor, $x_{Bm}$ is the logarithm of the average fraction of the solvent (B) in the liquid film, $v$ is the superficial gas velocity, $Re$ is Reynold’s number and $Sc$ is Schmidt’s number. The superficial gas velocity is given by:

$$v = \frac{G_V}{A}$$

where $G_V$ is the gas volume flow. $Sc$ is given by:

$$Sc = \frac{\eta_g}{D_{cg}\rho_g}$$
where $\eta_g$ is the viscosity of the gas and $D_{cg}$ is the diffusion coefficient of the gas phase. Reynold’s number is given by:

$$Re = \frac{d_h v \rho_g}{\eta_g},$$

(8.13)

where, $d_h$ is the hydraulic diameters of the packing material given by:

$$d_h = \frac{4 \epsilon}{a},$$

(8.14)

where $\epsilon$ is the porosity of the packing material.

### 8.7.3 Calculation of the Electroscrubber Height

$K_g$ for the laboratory electroscrubber is calculated under several assumption. It is assumed that $L$, $G$ and $K_g$ are constant. The oxidation of HS$^-$ is reported as fast and has a high K-value, see Section 4.2. Therefore, the concentration of the pollutant, i.e. HS$^-$, in the liquid may be assumed to be $\sim 0$ [128]. The high reactivity may be assumed to result in a high enhancement factor $E$.

The equilibrium between H$_2$S in the gas phase and in the liquid phase for the given oxidative system is expected to result in very low $m$-values. The partial pressure of the H$_2$S is very small for any concentration in the liquid phase. This is equivalent to a very small $m$-value.

For a large $E$ and a small $m$, $K_g = k_g$ according to Eq. 8.8. This is in accordance with Ramm’s rule [122]. $K_g$ is then calculated as $k_g$ using Eq. 8.9. The physical parameters used for the calculation of $k_g$ are presented in Table 8.2.

Under these assumptions, the height of the laboratory electroscrubber is estimated to be $22.8 \pm 0.3$ cm.

There are two main conclusions from this scrubber height:

- This is a very low scrubber height
- It fits fairly with the experimentally predicted height of $3.2 \pm 0.2$ cm

The scrubber height is calculated based on Eq. 8.5. The input values are given in Table 8.2. If the equation is split up into separate values according to Eq. 8.6a, $NTU = 3.3$ and $HTU = 6.95 \pm 0.09$ cm is achieved. The $NTU = 3.3$ is a consequence of the large driving force in the reaction. The electrolyte is assumed to have a very low concentration of the pollutant ($\sim 0$). Therefore, $NTU = 3.3$ is obtained. The $HTU$ depends on $K_g$ and physical parameters.

The scrubber has been designed with a fairly large diameter when compared with the gas flow, which is part of the reason why the $HTU$ is small. While the estimated height is small, it fits well with practise. In the laboratory experiments, a scrubber height of $3.2 \pm 0.2$ cm was successfully operated to have a removal efficiency of 100%. The estimated height is in the same order as the experimental. Although the estimated value is higher, both values are very small scrubber heights.
Table 8.2: Parameters for approximation of the scrubber height. Parameters for the LECA as packing materials has been obtained by a combination of assuming the LECA packing as random packing of spheres and assumptions based on values from Kiørboe et al. [122].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar gas flow</td>
<td>$G_M$</td>
<td>mol/s</td>
<td>$(2.3 \pm 0.1) \times 10^{-3}$</td>
<td>Measured</td>
</tr>
<tr>
<td>Molar liquid flow</td>
<td>$L_M$</td>
<td>mol/s</td>
<td>$1.2 \pm 0.1$</td>
<td>Measured</td>
</tr>
<tr>
<td>Radius of scrubber</td>
<td>$r$</td>
<td>m</td>
<td>$55.0 \times 10^{-3}$</td>
<td>Supplier information</td>
</tr>
<tr>
<td>Gas density</td>
<td>$\rho_g$</td>
<td>kg/m$^3$</td>
<td>1.1</td>
<td>[126]</td>
</tr>
<tr>
<td>Gas viscosity</td>
<td>$\eta_g$</td>
<td>Pa s</td>
<td>$12.3 \times 10^{-6}$</td>
<td>Calculated as 70% CH$_4$ and 30% CO$_2$ based on numbers from [95]</td>
</tr>
<tr>
<td>Porosity</td>
<td>$\epsilon$</td>
<td>Fraction</td>
<td>0.38</td>
<td>Based on data from poured random packing of spheres [127].</td>
</tr>
<tr>
<td>Diameter of packing material</td>
<td>$D_p$</td>
<td>m</td>
<td>0.025</td>
<td>Measured</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>$a$</td>
<td>m$^2$/m$^3$</td>
<td>149</td>
<td>Calculated as $a = \frac{6(1-\epsilon)}{D_p}$ [127].</td>
</tr>
<tr>
<td>Start concentration</td>
<td>$y_i$</td>
<td>Mole fraction</td>
<td>$(1330 \pm 70) \times 10^{-6}$</td>
<td>Model biogas concentration</td>
</tr>
<tr>
<td>End concentration</td>
<td>$y_u$</td>
<td>Mole fraction</td>
<td>$50 \times 10^{-6}$</td>
<td>Detection limit of the MRU</td>
</tr>
<tr>
<td>Equilibrium end concentration</td>
<td>$y_u^*$</td>
<td>Mole fraction</td>
<td>$5 \times 10^{-9}$</td>
<td>$y_u^* \ll y_u$, factor used: 10000</td>
</tr>
<tr>
<td>Equilibrium start concentration</td>
<td>$y_i^*$</td>
<td>Mole fraction</td>
<td>$1.33 \times 10^{-7}$</td>
<td>$y_i^* \ll y_u$, factor used: 10000</td>
</tr>
<tr>
<td>Logarithm of the average fraction of the component B in the liquid film</td>
<td>$x_{B_m}$</td>
<td>Unit less</td>
<td>1</td>
<td>Assumed value due to low concentrations of the pollutant</td>
</tr>
<tr>
<td>Gas film factor</td>
<td>$C_g$</td>
<td>Unit less</td>
<td>2.5</td>
<td>Assumed</td>
</tr>
<tr>
<td>Diffusion coefficient of the gas phase</td>
<td>$D_{cg}$</td>
<td>m$^2$/s</td>
<td>$2.42 \times 10^{-5}$</td>
<td>Assumed to be the same as water vapour in air, data from [95].</td>
</tr>
<tr>
<td>Molar mass of gas</td>
<td>$M_g$</td>
<td>g/mol</td>
<td>27.2</td>
<td>Calculated from density, assuming ideal gas behaviour</td>
</tr>
</tbody>
</table>
8.8 Comparison with other Technologies

The electroscrubbing technology was developed to purify biogas for second-generation upgrading, see Appendix I. The utilization of this electroscrubbing process for desulfurization of biogas has several advantages over current desulfurization technologies. A comparison of the technologies is presented in Table 8.3 and described in detail below.

Table 8.3: Comparison of the desulfurization technologies, including the electroscrubbing technology. Compared with the biological scrubbing, the electroscrubbing technology is observed to perform better or equally well on all parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Electroscrubbing</th>
<th>Biological scrubbing</th>
<th>Activated carbon</th>
<th>Chemical precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAPEX</td>
<td>Medium</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>OPEX [€/kg H₂S]</td>
<td>0.87 (Non-optimized)</td>
<td>1</td>
<td>13-22</td>
<td>4.3</td>
</tr>
<tr>
<td>Oxygen in purified gas</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Purification level</td>
<td>Non-detectable</td>
<td>≈ 100 ppm</td>
<td>Non-detectable</td>
<td>≈ 100 ppm</td>
</tr>
<tr>
<td>Flexibility/agility</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Waste generation</td>
<td>None</td>
<td>None</td>
<td>Yes</td>
<td>None</td>
</tr>
</tbody>
</table>

8.8.1 CAPEX

The electroscrubber will require a scrubbing tower of much smaller size than the biological scrubber. The experiments indicate that the required size of the electroscrubber is between 1/5 and 1/10 of a biological scrubber. This will save a significant amount expenses during construction, making the new process cheaper than biological desulfurization in CAPEX. Chemical precipitation and activated carbon require very low capital investments when installed and will be have a lower CAPEX than the electroscrubber.

8.8.2 OPEX

The OPEX of the electroscrubber is dominated by the power consumption. In Figure 8.6, the OPEX of the electroscrubber is presented for different scenarios. The color indicates the price per kilogram of sulfur removed. In the price/color scale, the OPEX of biological desulfurization has been included, as Thiopaq® has reported the OPEX of their process to be 1 euro per kilogram of H₂S [18]. This is commonly used when comparing the OPEX of H₂S removal technologies. The return of investment have not been included in the figure, since the exact CAPEX remains unknown.

The power efficiency is calculated as described in Section 8.5. The highest achieved value for the second campaign electroscrubber is included as the horizontal dotted line efficiency of

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current system in the Figure 8.6. An expected optimized efficiency of 70% is included as indicated by the horizontal dotted line at $\eta_p = 70\%$. The electrochemical cell of the electroscrubber is not expected to reach high efficiency. The explanation is that there are a lot of impurities in the biogas as described in Section 8.2.

The three blue circles with letters in Figure 8.6 refer to the three different cases. These cases represent the second campaign electroscrubber and two future, optimized electroscrubbers:

- **Case A:**
  The second campaign electroscrubber. The power efficiency is $13.4\pm0.9\%$ and the Danish electricity price for biogas plants were reported to be 0.04 euro per kWh. This gives a price per kilogram removed sulfur of 0.87 euro, as seen by the color grading.

- **Case B:**
  The projected OPEX of an optimized demonstration electroscrubber. The power efficiency is increased to 45% due and the electricity price remains the same. A price of 0.26 euro per kilogram sulfur removed, which corresponds to 26% of the Thiopaq® price.

- **Case C:**
  A fully developed electroscrubber operated in Germany. Further optimization of the process gives a power efficiency of 70%. The electricity price for the biogas plant is 0.08 euro/kWh. This gives a price of 0.33 euro per kilogram of sulfur removed.

Comparing Case A, B and C shows that the electroscrubbing process has a great potential for optimization and commercialization. Depending on the electricity price, a profitable area has been highlighted inside the dotted lines in Figure 8.6. The diagonal bottom line corresponds to the OPEX of the biological scrubber. This is assumed to be independent of electricity price.

The industrial electricity price of Germany has been plotted in Figure 8.6 as well. This shows that a power efficiency of $\sim 30\%$ would result in the electroscrubber having the lowest OPEX for $>10.000$ biogas plants [1, 129]. These calculations have been performed without taking the production of by-products into account. The $\text{H}_2$ and sulfur produced may lower the OPEX of the electroscrubber further.

### 8.8.3 Oxygen

Throughout the experiments, no addition of $\text{O}_2$ to the purified biogas has been detected for any of the electroscrubbers. This is a major advantage when compared with biological desulfurization. The addition of air to the biological scrubber results in residual $\text{O}_2$ in the purified biogas, which is highly unwanted for both first- and second-generation upgrading, see Appendix I. Activated carbon suffer from the same issue with $\text{O}_2$ in the purified gas if operated at maximum capacity. Chemical precipitation has the same benefit as the electroscrubber, as no $\text{O}_2$ is required to purify the biogas.

### 8.8.4 Purification Level

The electroscrubbers have been found to remove the $\text{H}_2\text{S}$ down to non-detectable concentrations, which is at least below 30-50 ppm, and may even be as low as $< 0.5$ ppm, see Table
6.2. Desulfurization with chemical precipitation and biological scrubbing result in H$_2$S concentrations of $\sim 100$ ppm. This is sufficiently purified for utilization of biogas in CHP engines or first-generation upgrading. Higher removal efficiency is thus not required for biogas plants with the utilization technologies of today, although the lower H$_2$S content in the biogas is expected to result in lower corrosion rates throughout the utilization systems.

For second-generation upgrading, removal down to 10-100 ppb is required [13,14]. Currently, only activated carbon is capable of achieving such low concentrations [4]. It is expected that activated carbon will be used as polishing filter independently of the bulk desulfurization system for second-generation biogas upgrading [26]. The high removal efficiency of the electroscrubber is an advantage as it would lower the OPEX of the polishing filter for second-generation upgrading.

8.8.5 Fluctuating Biogas Flow

Electroscrubbers are easily adjusted in capacity through the applied potential and resulting current. During both campaigns, the electroscrubbers were found to respond to changes within
10 min. and stabilize within $\sim 20$ min. The stabilization time is expected to be highly dependent on the amount of electrolyte and electrolyte flow and could thus increase when the process is scaled up. However, even a scaled up electroscrubber is expected to have a short reaction time, which is a great advantage. Biological scrubbers cannot be adjusted, while chemical precipitation generally has a retention time of $\sim 24$ hours. Activated carbon do not require adjustment to fluctuations in the H$_2$S concentrations.

A flexible desulfurization system is highly advantageous. Unwanted downtime of the biogas plant can be avoided with a flexible H$_2$S removal system.

### 8.8.6 Waste Generation

The electroscrubber does not generate any waste. The H$_2$ can be collected and the sulfur can be collected, according to the description in Section 5.4.3. The by-products may even be a source of income.

Biological scrubbers and chemical precipitation do not generate any waste either. Activated carbon requires periodic changes which generate sulfur containing waste. For impregnated activated carbon, the sulfur containing spent material may be toxic and has to be deposed accordingly, which increases the OPEX further.

### 8.9 Summary of the Discussion and Results

All the electroscrubbers proved capable of removing H$_2$S down to non-detectable limits.

Overall, the results from the two campaigns are observed to give similar results. The most significant changes are the higher removal efficiency and the better electrical properties. The laboratory results show that higher current efficiencies are possible at lower relative currents. This indicates that an optimization of the current efficiency is possible.

The second campaign electroscrubber was found to have the highest power efficiency during a complete removal of H$_2$S. The removal efficiency of $13.4 \pm 0.9\%$ corresponds to a power consumption of $22 \pm 1.5$ kWh per kilogram of H$_2$S. With a reported price of 0.04 euro per kWh at biogas plants, this power efficiency corresponds to a OPEX of $0.87 \pm 0.06$ euro per kilogram of H$_2$S. This is cheaper than the current desulfurization technologies.

A simple model was derived to calculate the scrubber tower height. The estimated height was in fair agreement with the experimental results.

A comparison with the commercially available desulfurization technologies show that the electroscrubbing technology is competitive on several other parameters as well. The electroscrubbing technology is already found to have certain qualities as a biogas desulfurization system, including no O$_2$ in the purified gas, no waste generation, high purification level and high flexibility.
Chapter 9

Conclusions

In this chapter the overall conclusions of the project are presented. The conclusions are based on observations from both the two campaigns, the laboratory experiments and process design.

It has been shown that electrochemically generated active chlorine compounds can be used for selective $\text{H}_2\text{S}$ removal from biogas. $\text{CH}_4$ and $\text{CO}_2$ are not removed in the process. No oxygen is present in the purified gas. $\text{H}_2\text{S}$ is removed down to non-detectable concentrations in a single step. The process is flexible and can be adjusted to the $\text{H}_2\text{S}$ flow. Calculations show that the process is competitive in price.

The $\text{H}_2\text{S}$ is oxidized to elemental sulfur that floats on the electrolyte. The dried sulfur has been found to be $72 \pm 2\%$ pure, containing trace amounts of the electrolyte when air-dried. The elemental sulfur may be used in the degassed manure as fertilizer without further purification. The fertilizer may be considered to be organic. If the elemental sulfur is not physically separated from the electrolyte, it will be further oxidized to sulfate. The oxidation to sulfate acidifies the electrolyte. The pH-value initially decreases until a value of $1.0 \pm 0.2$ is reached. Even though $\text{H}_2\text{S}$ is a sour gas, the electroscrubbers if found to have a high removal efficiency at low pH-values. This is assumed to be explained by fast reaction kinetics and high reaction constant.

Optimization of the electrochemical cell resulted in an increase in power efficiency, as the resistance of the system was greatly decreased. The current efficiency did not increase with decreasing resistance and is expected to be highly dependent on a suitable membrane system. For the campaigns, an $i/i_{\text{theory}}$-value of $5.6 \pm 0.2$ has been found to have a removal rate of 100%. For $i/i_{\text{theory}} > 5.6$, a steady high removal rate was found during both campaigns, as the optimized system had a removal rate of 100% in 10/11 experiments. For the laboratory experiments, a $i/i_{\text{theory}}$-value of $3.5 \pm 0.5$ was required for a removal rate of 100%.

An overall power efficiency of $16 \pm 1.6\%$ was achieved in the laboratory and $13.4 \pm 0.9\%$ in the campaign. This results in an OPEX competitive with the current technologies, depending on the electricity price.
Electroscrubbers are suitable for biogas desulfurization. Especially when the biogas is utilized for upgrading. For first-generation upgrading, the main advantages are the O$_2$-free purified biogas and the flexibility in operation. For second-generation upgrading, the main advantages also include high removal efficiency and H$_2$-production.

The overall conclusion is that the novel electroscrubbing process for gas cleaning is an interesting process both from a scientific and a commercial point of view. Electroscrubbing remains a small scientific field with many possibilities to be investigated. The electroscrubbing process is also of commercial interest, as the OPEX is competitive with current technologies.
Chapter 10
Future Work

The electroscrubbing process for removal of H$_2$S from biogas have been developed from idea to pilot plant testing during this project. However, there still is a great potential for future work with this and other electroscrubbing processes.

A new project, Biogas Electro Clean (BE-Clean) has been formulated based on the results from this project. The aim of the BE-Clean project will be to further develop the electroscrubbing process and demonstrate it on a commercial level. The BE-Clean project partners have applied for funding at the Energy Technology Development and Demonstration Program (EUDP), a Danish funding programme.

The suggested development and demonstration project will continue the work performed in this project. Some of the project tasks have been included here.

10.1 Chlorinated Species and Parameter Analysis

Currently, the chlorinated species in the purified biogas is the biggest challenge for the process. It is not known what the concentration is and if the compounds can be avoided by optimizing the operation of the electroscrubber. A series of experiments were prepared for the second campaign, which unfortunately could not be performed due to the limited window for experiments. These experiments will have a high priority in any future projects.

During both campaigns, the maximum biogas flow was limited by the pressure drop throughout the installation. Thus, the electroscrubbers were not capacity tested. The largest biogas flow used during the second campaign was 120 L/min. The expected capacity is in the order of 600 L/min. The electrolyte flow is adjustable in the second campaign electroscrubber. This allows for investigation of the effect of gas versus liquid flow. Overall, it would be preferable to perform an in-depth parameter analysis of the second campaign electroscrubber before designing and constructing the next electroscrubber. The parameters that could be investigated
include packing, gas flow, liquid flow, electrolyte concentration, temperature etc.

10.2 Electrochemical Properties of the System

The MMO coated DSA for Cl₂ production was operated at low current densities throughout the project. A better understanding of the electrochemical properties of the surface is required for optimal operation of the electrochemical cell. Electrochemical impedance spectroscopy of the active surface could reveal underlying chemical processes.

10.3 Filtration System

A suitable filtration system has yet to be successfully implemented. Continuous and physical removal of the elemental sulfur from the electrolyte is required. Another restriction is that the filter should be gas tight. The elemental sulfur floats on the electrolyte and the filtration therefore has to take place before the water trap. Filtration systems such as belt filter and a rotatory drum filter may be suitable. Within this project, these filters were not found in both proper materials and fitting size.

10.4 Thermodynamic Model of the Electrolyte

In order to gain a better understanding of the electrolyte development, a thermodynamic model is under development. The model is based on the Extended UNIQUAC model, which have been developed for thermodynamic modelling of electrolyte systems. The model will be an important tool in understanding the solubility and molecular interaction in the electroscrubbing process. The electrolyte is important to understand in order to develop the electroscrubbing process. Currently, the development of the electrolyte is not described in detail. For continuous operation of the process, steady state conditions are required, which can be found by the model. Part of the model goal is also to find the optimal electrolyte composition.

10.5 Scrubber Model

For future and larger electroscrubbers, better understanding of the process parameters are required for modelling the scrubbing tower size. The model for the scrubbing tower dimensions will also include parameters from the thermodynamic model. The scrubbing tower dimensions are important for the commercialization of the process. The expenses for construction of the scrubbing tower are approximately half the total CAPEX for biological desulfurization [130]. The same may be expected to be the case for the electroscrubbing process.

10.6 Removal of Other Pollutants

This project has investigated removal of H₂S from biogas. During the first campaign, an external analysis showed that siloxanes, D4 and D5, were also removed to a certain extend.
From a thermodynamic view, there are several pollutants that may be removed by oxidation, both from biogas and other gasses. However, the reaction kinetics must also be taken into consideration, as observed with CH$_4$ that is not removed, although it is thermodynamically possible.

In the literature, electroscrubbers have been widely used for removal of NO$_x$ and SO$_2$, see Table 3.1. NO$_x$ and SO$_2$ are pollutants that are found in flue gas from e.g. power plants and maritime engines. In the electroscrubbing literature, SO$_2$ have been found to be more easily removed than NO [35,82,83,90]. Thermodynamically, both SO, SO$_2$ and NO may be removed by HClO:

\[
\begin{align*}
\text{HClO} + \text{SO}_2 + \text{H}_2\text{O} &= \text{H}_2\text{SO}_4 + \text{HCl} \quad \Delta G_{20^\circ C} = -260 \text{ kJ/mol,} \\
2 \text{HClO} + \text{SO} + \text{H}_2\text{O} &= \text{H}_2\text{SO}_4 + 2 \text{HCl} \quad \Delta G_{20^\circ C} = -528 \text{ kJ/mol,} \\
3 \text{HClO} + 2 \text{NO} + \text{H}_2\text{O} &= 2 \text{HNO}_3 + 3 \text{HCl} \quad \Delta G_{20^\circ C} = -314 \text{ kJ/mol,}
\end{align*}
\]

(10.1) (10.2) (10.3)

However, experiments are required in order to evaluate the reaction kinetics of the process.
Chapter 11

Bibliography


[113] IT Dr. Gambert GmbH. H2S - Industrial Sensor / Type I-43.


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Appendix I

The Potential of Biogas; the Solution to Energy Storage
Energy storage will be essential for balancing the renewable energy systems of tomorrow, especially if excess electricity from wind and solar power requires immediate utilization. The use of biogas as a carbon source can generate carbon dioxide-neutral carbon-based energy carriers, such as methane or methanol. The utilization of biogas today is limited to the generation of heat/power or biomethane (first-generation upgrading); both processes disregard the potential of the coproduced carbon dioxide during the fermentation process. By using renewable energy, biogas upgrading systems can convert carbon dioxide into hydrocarbon-based high-energy-density fuels, which can replace fossil-based fuels for applications in which they are hard to decarbonize. The possibilities for the future utilization of biogas are discussed, and the terminology for “second-generation upgrading” is introduced to help research and development within this field. It is believed that second-generation upgrading of biogas will have a huge potential for dynamic energy storage.

Biogas

The market share of renewable energy resources is increasing.\(^1\) In particular, wind and solar power has increased tenfold globally from 2004 to 2014.\(^2\) Consequently, energy storage has become a growing challenge.\(^3\) Several technologies have been proposed to assist in the need for energy storage, for example, pumped storage hydroelectricity, compressed air energy storage, swing wheel storage, and large-scale batteries.\(^4\) Nevertheless, efficient energy storage still remains a huge issue.

Biogas has the potential to become the preferred solution to energy storage of the future. It is produced from the anaerobic breakdown of different biological feedstocks and generally consists of around 60% CH\(_4\) and 40% CO\(_2\), with approximately 2000 ppm H\(_2\)S as the main impurity. Independent of the downstream application of biogas, it is necessary to remove H\(_2\)S owing to the corrosion and health issues involved. The majority of biogas plants produce combined heat and power (CHP), whereas a very small number (around 2% of all plants) produce biomethane.\(^5\) For biomethane production, CO\(_2\) has to be removed from biogas to ensure sufficient energy density to allow for injection into the natural gas grid. This is called biogas upgrading and CO\(_2\) is a waste product from this process.

Future biogas upgrading technologies will need to consider CO\(_2\) in biogas as an additional carbon source, which could be used to increase the energy density in connection with efficient energy storage. In this way, electrical energy could be stored as either CH\(_4\) or liquid organic molecules through catalytic upgrading by using renewable hydrogen (H\(_2\)) from electrolysis to convert CO\(_2\) into liquid fuel through, for example, the Fischer–Tropsch process.

Within the EU alone, biogas energy production was 654 PJ in 2015\(^6\) and it continues to grow.\(^7\) The biogas energy potential within Europe is estimated to be as high as 2.3\(\times\)10\(^7\) PJ by 2030.\(^8\) This corresponds to 15% of the total energy used for transportation in the EU in 2015,\(^9\) and if biogas is further upgraded by using renewable H\(_2\), this share could be even higher.

We believe that the use of biogas could be a key enabler for closing the carbon cycle. This would allow industries such as aviation and long-distance transportation,\(^10\) which are not easily decarbonized, to be converted into a sustainable future operation that use green carbon-neutral fuel resources. However, these future applications of biogas lack a general term, and we therefore propose to use the term “second-generation upgrading” to describe those technologies that use CO\(_2\) in biogas as the carbon source.

Upgrading Today: First-Generation Upgrading

Today, biogas upgrading refers to the process of extracting CH\(_4\) (biomethane) from biogas.\(^11\) This process is necessary to make biogas suitable as a fuel for vehicles or injection into the
natural gas grid.[13] Biomethane is known for its low carbon footprint, which can even be negative,[14] making it highly attractive for several industries such as the agricultural sector, the chemical industry, and so on. Presently, industrial upgrading of biogas is solely first generation. The four main first-generation upgrading technologies are as follows: 1) chemical scrubbing, 2) water scrubbing, 3) membrane separation, and 4) pressure swing adsorption. There are other emerging technologies; however, these four are the market drivers.

First-generation upgrading seeks to remove CO₂ as a waste product, although efforts are underway to create high-value food products from CO₂ through chemical scrubbing. CO₂ could also be used for energy storage by combining it with hydrogen from electrolysis, driven by renewable electricity from wind or solar power. Unfortunately, chemical scrubbing is quite energy intensive and there is no need to use a pure CO₂ stream to convert it into synthetic hydrocarbon (HC) during the upgrading of biogas. Removing the need for chemical scrubbing would significantly improve the overall energy efficiency of existing biogas upgrading systems.[16]

First- versus Second-Generation Upgrading

We believe the time has come to introduce the term “second-generation upgrading” as an alternative to the existing “first-generation upgrading”.

Second-generation upgrading refers to those technologies that utilize biogas as a carbon source for storing energy. First-generation upgrading uses methods that only focus on the removal of CO₂ from biogas, whereas second-generation upgrading technologies actively use CO₂ to produce more carbon-containing energy carriers.

Although the two generations of biogas upgrading have several technical and scientific differences, the most significant distinction between first- and second-generation upgrading is:

1) First-generation upgrading does not utilize the CO₂ of the biogas
2) Second-generation upgrading uses the CO₂ as a carbon source

Significant research is being performed into second-generation biogas upgrading[17] (according to our terminology), although the current terminology does not allow first- and second-generation technologies to be distinguished. Moreover, completely different technologies are required for second-generation upgrading. The main differences are listed in the following sections.

Carbon Dioxide Utilization

Second-generation upgrading makes use of CO₂ as an additional carbon source for energy storage. It is closely linked to carbon capture and utilization (CCU) technology, which is currently highly promoted as necessary to reach zero-CO₂ policies.[18] It has become clear that a renewable energy supply alone is insufficient to achieve a CO₂-neutral society and, therefore, renewable energy should be supplemented by CO₂ storage or reuse. CCU allows for a lowering of the carbon footprint to a certain extent, with the need to use additional energy for the overall process.

Conversely, second-generation biogas upgrading does not require energy-expensive carbon capture. CO₂ present in the biogas is directly converted into hydrocarbon-containing molecules, thus, enabling a better overall energy efficiency.[16]

Maturity of Second-Generation Upgrading Technology

In our view, the current terminology on biogas upgrading constrains economic support by favoring simpler first-generation technology. New terminology would allow a clearer focus on the energy-storage possibilities of biogas and could help accelerate additional and necessary research and development into second-generation upgrading technologies.

First-generation upgrading is presently in use, whereas second-generation upgrading technologies remain in the demonstration phase. There is a clear need for innovative and cost-efficient technology development within second-generation upgrading as it requires more expensive and complicated equipment compared with first-generation upgrading. The most promising technologies for second-generation upgrading are discussed below.

Biogas as a Carbon Source: Second-Generation Upgrading

The conversion of CO₂ into biofuel or further conversion into synthetic fuel through Fischer–Tropsch catalytic synthesis is a research area that receives a lot of attention.[16] Herein, we propose catalytic methanation, methanol synthesis, and biological conversion. Methanation and methanol production as biogas second-generation upgrading are visualized in Figure 1, which also shows how present-day technology emits CO₂; whereas, the application of forthcoming second-generation technology uses energy in the form of H₂ to produce biofuels.

The need for renewable H₂ is common to all second-generation upgrading technologies discussed herein. Renewable H₂ is produced through electrolysis of water, mainly alkaline solutions.[16] Furthermore, this technology is characterized by both high efficiency and quick response time, which are of utmost importance to the storage of renewable energy. Although flexible storage of excess energy as H₂ is a possibility, storage of the energy as either CH₄ or liquid organic molecules allows further utilization of the liquid infrastructures already constructed for storing additional energy. CH₄ can be stored and distributed in the natural gas grid and liquid organic molecules can be implemented in the transportation infrastructure. These applications also deviate from those of renewable H₂ as the energy volumetric density of carbon-based storage is much higher than that of H₂.[16]
Catalytic Methanation

Methanation of biogas produces CH₄ by using CO₂ contained in the raw biogas. The Sabatier reaction is used for this catalytic methanation process for converting CO₂ into CH₄ as follows [Eq. (1)]:

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta G_{\text{300 K}} = -61.1 \text{ kJ mol}^{-1}
\] (1)

This process was first discovered by Sabatier in 1913 and is most notably used today on the international space station to produce water.²¹ Traditionally, the reaction is catalyzed over high-surface-area nickel catalysts with both high selectivity and activity.²² Desulfurized biogas could be used as a direct feedstock for the Sabatier reaction with CH₄ acting as an inert diluent. This can be beneficial for the exothermic reaction owing to the heat-distributing and -absorbent properties of CH₄ which can avoid catalyst runaways.²³

The final product of the first-generation upgrading process (biomethane) needs to have a low H₂S content. Depending on the gas-grid regulations, the requirement is usually below 4 ppm.²⁴ However, for catalytic upgrading the restrictions are far more demanding because H₂S causes irreversible poisoning of the catalysts used for CO₂ reduction.²⁵,²⁶ Bartholomew found that H₂S concentrations as low as 1 to 10 ppb might result in considerable reduction of the catalyst activity²⁷ since the active surface sites react readily with H₂S through a deactivation reaction [Eq. (2)].²²

\[
\text{H}_2\text{S} + \text{NiO} \rightarrow \text{NiS} + \text{H}_2\text{O} \quad \Delta G_{\text{300 K}} = -48.5 \text{ kJ mol}^{-1}
\] (2)

Thus, the H₂S content in desulfurized biogas should be kept as low as possible for catalytic conversion of biogas to achieve a long catalyst lifetime.

Catalytic methanation is highly suitable for energy storage and is driven by H₂ from electrolysis using renewable energy. Also, the CH₄ produced can be easily stored in the natural gas grid. Much ongoing research is investigating the possibility of implementing catalytic methanation at biogas plants.²⁸-³¹ However, so far only few demonstration plants have been reported.³²,³³ The largest demonstration plant is the E-gas facility by Audi in Werlte, Germany,³⁴ which operates with the off-gas from a nearby first-generation upgrading biogas facility.

Chemoautotrophic Biogas Upgrading

In a biological-upgrading approach, microorganisms use CO₂ as the carbon source and reduce it to biomethane. The energy input for this reduction can be provided by reducing compounds such as H₂, which can provide the necessary electrons for the conversion. H₂ can be used by archael hydrogenotrophic methanogens to convert CO₂ into CH₄. Hence, coupling excess electricity with biomethanation through electrolysis appears to be a very attractive solution.

The biological upgrading approach has several technological advantages compared with thermochemical-based technologies. One of the inherent advantages is that the process occurs under mild temperature conditions (in the range of 30 to 60 °C, that is, meso or thermophilic) and close to atmospheric pressure. This is beneficial not only with respect to technology safety but also for the overall economy of biomethanation.³⁵ Moreover, the process is facilitated by hydrogenotrophic methanogens, which are abundant microorganisms found in biogas plants. Mixed cultures can be used to facilitate the conversion process, which means that sterile conditions are not required. Chemoautotrophic biogas upgrading methods have been validated at both laboratory and pilot scales.

Photosynthetic Biogas Upgrading

Another discussed approach is based on the symbiotic interactions between oxygenic photosynthetic, lithoautotrophic, and heterotrophic microorganisms (such as microalgae and cyanobacteria). Presently, these microorganisms represent the only biotechnology organisms capable of simultaneously removing multiple biogas pollutants such as CO₂ and H₂S.³⁶ This novel biogas-upgrading biotechnology relies on photosynthetically driven fixation of CO₂ coupled with the removal of CO₂ and other impurities in biogas, while nutrients are captured (N, P)³⁷,³⁸ Nevertheless, despite clear advantages, this approach
still has several unsolved technical challenges and remains in the proof-of-concept phase. Several projects are currently trying to develop relevant upgrading technologies, such as the EU Horizon 2020 funded projects INCOVER and URBIOFIN.\[39,40\] The efficiency and sustainability of these technologies still remain to be shown and, in particular, evaluated under industrially relevant conditions.

In addition to those mentioned above, new emerging technologies are continuously appearing in the literature. These include fermentative technologies in which microorganisms are able to produce dicarboxylic acids by capturing CO2 along with the conversion of sugars, which provide the reducing equivalents. One very well-developed approach is the production of biosuccinic acid along with biogas upgrading.\[41\] Biosuccinic acid is a chemical platform that has a wide range of applications. Today, succinic acid is mainly produced from petrochemicals.

### Syngas Conversion into Liquid Organic Molecules

Another second-generation upgrading process would be the conversion of biogas into liquid organic molecules. The process may be divided into two steps: syngas production and synthesis of organic compounds such as methanol. In the first step, CH4 and CO2 in the biogas are reformed to carbon monoxide (CO) and H2 in a combination of different reforming processes [Eqs. (3) and (4):]

- Steam reforming:
  \[
  \text{CH}_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta G_{850 \cdots °C} = -57.8 \text{ kJ mol}^{-1}
  \]  
  (3)

- And dry reforming:
  \[
  \text{CH}_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta G_{850 \cdots °C} = -58.8 \text{ kJ mol}^{-1}
  \]  
  (4)

Olah and coworkers have tested a similar process for methanol production from pure CH4.\[42\] They combined steam and dry reforming in a 2:1 ratio in a single process called bi-reforming [Eq. (5):]

\[
3 \text{CH}_4 + 2H_2O + CO_2 \rightarrow 4CO + 8H \quad \Delta G_{850 \cdots °C} = -174 \text{ kJ mol}^{-1}
\]  
(5)

Bi-reforming yields syngas with the correct stoichiometric ratio for methanol production, although it requires a CH4 to CO2 ratio of 3:1. Most biogas plants have a CH4 to CO2 ratio of around 2:1, which does not allow for a direct implementation of the bi-reforming process. Instead of a 2:1 ratio of steam to dry reforming, the biogas composition is better suited for a 1:1 ratio of steam to dry reforming [Eq. (6):]

\[
2 \text{CH}_4 + CO_2 + H_2O \rightarrow 3CO + 5H_2 \quad \Delta G_{850 \cdots °C} = -117 \text{ kJ mol}^{-1}
\]  
(6)

This process, termed as “bio-reforming” (our own terminology), requires additional H2 to obtain the correct stoichiometric ratio between CO and H2. For methanol synthesis, the required CO to H2 ratio is 1:2 [Eq. (7)].\[43\]

\[
\text{CO} + 2H_2 \rightarrow \text{CH}_3\text{OH} \quad \Delta G_{298 \cdots °C} = 26.8 \text{ kJ mol}^{-1}
\]  
(7)

This allows for energy storage similar to the methanation process, because the H2 added to the synthesis could be produced by a wind turbine or solar energy; thus, enabling green hydrogen formation through electrolysis.

Similar to the methanation process, both steam and dry reforming use a nickel catalyst.\[44\] Hence, deep upstream desulfurization is required as also described for catalytic methanation above.

A liquid organic compound, such as methanol, is not only much easier to store than upgraded CH4 but also has a higher commercial value. Presently, most of the methanol produced in the world is made from fossil fuels,\[45\] although biomethanol is already produced through the gasification of biomass.\[46\] The list of applications for a low-carbon-footprint organic compounds are many, including fuel for airplanes, polymer production, and formaldehyde synthesis.\[47–49\]

### Flexible Solutions

Flexibility is essential for effective energy storage. Regularly turning the technology on and off is required to follow the fluctuations of green electricity based on solar cells and wind turbines. Ideally, the storage system should switch from storing (i.e., using electricity) to producing electricity, in much the same way as batteries or hydropower.\[20\] Second-generation biogas upgrading has a different goal because the main objective is to replace fossil fuels in hard to decarbonize applications.

Because biogas production is continuous, the application of biogas should also be continuous. Nevertheless, not all second-generation biogas upgrading technologies have this opportunity.

Catalytic methanation favors continuous operation owing to the applied temperatures and it will need to be shut down if the H2 supply fluctuates or stops. However, methanol synthesis allows for a much more flexible production.

As described above, to reach the correct stoichiometric composition of syngas produced from biogas, additional H2 is required. Should the H2 supply stop, however, methanol production would not stop but simply reduce the production. Under the assumption that the production efficiency does not change, approximately 80% of the methanol production would remain. In case of too little hydrogen inflow, the produced methanol would contain an additional amount of CO, which is not desired, and a gas cleaning system would need to be implemented if the methanol production plant was designed in this way. A benefit of the continuous production of methanol is the ability to deliver methanol according to contract, even though no excess energy might be available for the
hydrogen generation required to reach the optimal CO to \( \text{H}_2 \) ratio of 1.2.

However, for better overall use of carbon, a more complicated system could be implemented, in which excess carbon can be stored. For storage, CO\(_2\) would be preferred over CO and, thus, a CO\(_2\)-capture system upstream of the reforming process may be the best solution. The stored CO\(_2\) can therefore be blended with biogas if the storage of electricity is required to increase methanol production as CO\(_2\) can react with \( \text{H}_2 \) directly to form CO in the reverse water–gas-shift reaction [Eq. (8):

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \hspace{0.5cm} \Delta G_{250}^{\circ} = 19.5 \text{ kJ mol}^{-1} \tag{8}
\]

Or reacted directly to form methanol [Eq. (9):\(^{[43]}\)]

\[
\text{CO}_2 + 3 \text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \hspace{0.5cm} \Delta G_{250}^{\circ} = 46.3 \text{ kJ mol}^{-1} \tag{9}
\]

A second-generation biogas upgrading system for methanol production designed according to these guidelines would have three modes of operation (see Figure 2):

1) Normal mode: The system upgrades all carbon in the biogas to methanol by adding \( \text{H}_2 \) from electrolysis. Electricity is stored in additionally synthesized methanol.
2) Production mode: Storing CO\(_2\) for later use. Methanol production is approximately 80% of that obtained in normal mode and no electricity is used or stored in synthesized methanol.
3) Power mode: Adding CO\(_2\) from gas storage into biogas for higher methanol yield. Electricity is stored in additionally synthesized methanol. Methanol production is higher than that obtained in normal mode.

This system could enable complete utilization of carbon, continuous methanol production, and flexibility during electricity consumption. The ultimate performance would be achieved in combination with additional CO\(_2\) sources for converting CO\(_2\) into methanol instead of releasing it into the atmosphere.

**Outlook**

Biogas is an unusual renewable energy resource with several different aspects: 1) It is part of the waste management system. Biological waste can be used directly in the reactor. 2) Biogas contributes to a lowering of the carbon footprint, which enables green agricultural production. 3) It may even be considered a carbon-capture technology because much of the carbon “caught” in the biogas reactor would otherwise have been released into the atmosphere.

Biogas has much unused potential and could prove central to the interconnected energy infrastructures of the future, as highlighted in Figure 3. Biogas is already a large industry that continues to grow. The present upgrading technologies, that is first-generation upgrading, are implemented at a commercial level. The increasing market share indicates that the industry is open for new technologies.

The use of biogas as a medium for energy storage by adding \( \text{H}_2 \) (produced by (green) electrolysis) is receiving interest across Europe, and a few projects are currently focused on this idea. The Sabatier reaction, methanol synthesis, and biological conversion are all used today at a commercial level. Although efforts have to be made to adapt these technologies to biogas, it should be possible to implement this within a relatively short timeframe.

We believe that a common terminology will help to promote research and development within second-generation biogas upgrading. Furthermore, with many of the technologies required for implementation already available we hope that, with this increased promotion, second-generation upgrading could help to ease the green energy transition within the next
Biogas could be the nexus of three different energy infrastructures. Upon using biogas for the storage of renewable energy, the carbon content enables utilization within both the natural gas grid and as a versatile fuel in the transportation infrastructure.

10 years by utilizing upgraded biogas in difficult to decarbonize industries.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: biogas · carbon source · energy storage · environmental chemistry · sustainable chemistry

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Appendix II

A Review of Electroscrubbers
A Review of Electroscrubbers, with Special Focus on H₂S Removal

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#Abstract

This review covers all the scientific literature within the field of scrubbers with electrochemical regeneration of the active compounds, i.e. electroscrubbers. There are 54 publications, including patents, within this field that use 15 different elements as the active compound. The applications are mostly focused on removal of H₂S or NOx/SO₂, however, other pollutants such as CH₃SH, NH₃ or VOCs have also been tested. Generally, the electroscrubbers are found to have a high removal rate and efficient regeneration of the active compounds. In this review, a list of general guidelines for designing an electroscrubber is given, compiled partly from requirements found in the literature. Furthermore, several quantities enabling comparison across parameters and experimental conditions. H₂S removal receives a special interest as the literature behind the different elements is reviewed closely.

List of symbols:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>c</td>
<td>Concentration</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant (96487 C)</td>
</tr>
<tr>
<td>ϕₑlectronal</td>
<td>Faraday efficiency of the electrochemical cell</td>
</tr>
<tr>
<td>ϕoverall</td>
<td>Overall efficiency of the electroscrubber</td>
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<td>Efficiency of the scrubber</td>
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<td>G</td>
<td>Gas flow</td>
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<td>i</td>
<td>Current [A]</td>
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<tr>
<td>iₜheory</td>
<td>Theoretical minimum current</td>
</tr>
<tr>
<td>Mpollutant</td>
<td>Molar mass of pollutant</td>
</tr>
<tr>
<td>npollutant</td>
<td>Amount of pollutant [mol]</td>
</tr>
<tr>
<td>ntheory</td>
<td>Theoretical amount of moles</td>
</tr>
<tr>
<td>p</td>
<td>Pressure</td>
</tr>
</tbody>
</table>
1. Introduction

The introduction of flue gas cleaning of from fossil-fired power plants resulted in economical and health benefits throughout Europe [1]. Common pollutants formed in fossil-fired power plants are nitrogen oxides and sulfur dioxide (NOx/SO2) that will create harmful acidic rain if not removed. Today, gas purification is implemented in the industry for several different applications such as odor control, flue gas desulfurization and emission control. Gas purification by absorption of the impurity into a liquid is the most commonly applied purification technology [2]. Generally, this process is performed in a scrubber in order to maximize the interaction between the polluted gas and the scrubbing liquid. As described by Arthur Kohl in his book *Gas Purification*, the complexity of the purification process often arises from the reuse of the active compound that is used for the removal [2]. For oxidative scrubbers, the regeneration of the chemical has often been performed by air, i.e. oxygen. Oxidation by air has the advantage of using a free chemical of the regeneration, although the disadvantages includes slow oxidation kinetics. The main alternative is regeneration by electrical energy, i.e. electrochemistry. The disadvantage all electrochemical regeneration processes suffer is the cost of electrical power. This cost has so far made the electrochemical regeneration too expensive, and thus it has not been used in the industry, with a single known exception.

In the late 1920s, Franz Fischer patented the first gas purification process with electrochemical regeneration [3]. The process used an alkaline iron cyanide solution to selectively oxidize hydrogen sulfide (H2S) from a water gas [4]. As described by Dr. Thau in 1932, this process was implemented in a full scale at the Hamburg Gas Plant [4]. Franz Fischer is known for his work with Hans Tropsch in the development of the Fischer-Tropsch process, converting a syngas to liquid organic compounds [5]. Gas purification was key in this process, as the H2S is poison for the catalyst [6]. Therefore, for a
successful implementation of the Fischer-Tropsch process, the syngas has to be completely purified and this may be the reason Franz Fischer developed a new desulfurization process.

The gas plant in Hamburg was decommissioned in 1938 and since then, electrochemical regeneration of the active component in gas purification has been limited to the laboratory [7]. Recently, electrification of the industry has receive interest as the environmental aspect if the industry is increasing in importance [8]. Electricity is a reliable and clean energy source that results in zero local emission. Regeneration of chemicals by electrochemistry has the advantage of fast kinetics and a closed loop cycle. Furthermore, electrochemistry in the form of batteries, fuel cells and electrolyzes is growing in importance as it is expected to be central in the society of the future [9]. Therefore, now may be the time that electrochemical regeneration of the active compound for gas purification can challenge the conventional purification technologies.

In this paper, a review of gas purification with electrochemical regeneration of the liquid is performed. Effort has been made to find all scientific papers and patents within this field. The review do not include direct oxidation/reduction, as only processes with a mediator is included.

2. Electroscrubbers

Gas purification systems with electrochemical regeneration consists of two main parts; an electrochemical cell and a scrubbing tower. In Figure 1, the basic principle is presented. An electrochemical cell generates a chemical compound that is used in a scrubbing process to purify gas. Once the liquid has been used in the scrubber, it is pumped back into the electrochemical cell for regeneration. Throughout the literature, different names have been used to describe this technology. In this paper, the name electroscrubber will be used. The name was introduced by Govindan et al. in 2012 and gives a clear indication of the technology [10]
In Table 1, an overview of the electroscrubbers found in the literature is presented. In total, 54 publications have been found within the subject. Table 1 is limited to include papers and patents that describe processes involving gas treatment with an active component that is electrochemically regenerated. Thus, direct electrochemical treatment and regeneration by other mechanisms are not included. The table has been constructed in order to highlight the amount of different compounds used and the pollutants targeted. H$_2$S and NOx/SO$_2$ are the pollutants receiving the most interest, as 10 and 8, respectively, different active compounds have been tested for oxidation of these species. Methyl mercaptane (CH$_3$SH) is also receiving great interest, especially in combination with H$_2$S removal. The volatile organic compounds (VOC) that have been tested include acetaldehyde (CH$_3$CHO), trichloroethylene (C$_2$HCl$_3$), tetrafluoromethane (CF$_4$), carbon tetrachloride (CCl$_4$) and trimethylamine (N(CH$_3$)$_3$).

Table 1 also includes a few instances where the active compound is generated at the cathode instead of the anode, i.e. the purification process reduces instead of oxidizes the pollutant. There is even a paper, where both the anode and cathode generate active compounds for removal of pollutants [11]. However, most of the papers uses the anode to generate an oxidizing species for removal of the pollutant.

2.1 Patents

Table 1 includes patents, although the inclusion is limited to patents that clearly state the processes and applications they cover. The first patent from 1932 by Fischer, clearly states the use of an alkaline iron cyanide solution for removal of H$_2$S [3]. This patent is easily included in the table. Other patents
have broader scopes, such as the 1968 patent by Keller and the 1989 patent by Weinberg et al. [12], [13]. Keller lists 20 different redox couples that may be applied for the application of removing either H$_2$S or CH$_3$SH, although only 8 different active compounds [12]. Weinberg et al. include all redox couples and combinations thereof in their patent, which also has a very broad list of applications [13]. In these cases, only the chemicals and applications described in the examples of the patents are included in Table 1.

Table 1: Overview of the different electroscrubbers found in the literature. The applications are focused on oxidative scrubbers with a suspended transition metal used to remove H$_2$S, NOx/SO$_2$ and VOC. Other active compounds are also used such as halogens are also used.

<table>
<thead>
<tr>
<th>Active Element</th>
<th>H$_2$S</th>
<th>CH$_3$SH</th>
<th>NOx/SO$_2$</th>
<th>VOC + NH$_3$ Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>[15]–[17]</td>
<td></td>
<td></td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
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</tr>
<tr>
<td>V</td>
<td>[12], [22], [23]</td>
<td>[21]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td>[21]</td>
<td>[13]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>[3], [4], [24]–[29]</td>
<td>[21]</td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>[30], [31]</td>
<td>[11], [30], [31], [33], [34]</td>
<td>[11], [35], [36]</td>
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<td></td>
<td></td>
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<td>[37], [38]</td>
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<tr>
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<td>[50]</td>
<td>[10], [51]–[55]</td>
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</tr>
<tr>
<td>I</td>
<td>[12], [56]–[58]</td>
<td>[12]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>[59]</td>
<td></td>
<td>[60], [61]</td>
<td>[13]</td>
<td></td>
</tr>
</tbody>
</table>

3. Overall Considerations for Electroscrubbers

It is not easy to find the exact match between electroscrubbers and pollutant. In the literature, both Keller and Kalina et al. present characteristics and requirements for a successful electroscrubbers [12], [57]. The two lists are combined and few extra points are added to give the following list of overall requirements of the electroscrubbers:

- High enough oxidation potential to remove the targeted pollutant
- High reactivity with the targeted pollutant
- Solubility of both reduced and oxidative form
- Stability under operating conditions
- No unwanted side reactions
- Well-known electrochemistry
- Chemical cost
- Environmental friendly

Some of the parameters may be estimated with thermodynamics, as Pourbaix diagrams provide a lot of the important information required. From the Pourbaix diagram, the oxidation potential of the active compound can be determined and thus compared with the required potential to remove the pollutant. From the list of active compounds in Table 1, the transition metals is observed to be well represented (Ti, V, Cr, Mn, Fe, Co, Ni, Co), however, it is not clear why e.g. Zn is not used. This is clearly observed from the Pourbaix diagram, as Figure 2 compares the Pourbaix diagrams of iron and zinc. In Figure 2a, iron is observed to have a redox couple Fe(III)/Fe(II) in a pH range from 0 to 2. Both Fe(III) and Fe(II) exist as soluble ions in this pH-range, meaning that when Fe(II) is oxidized it does not form a solid, and the vice versa. For Zink this is not the case. As observed in Figure 2b, Zink do not have a soluble redox couple at any pH-values. Generally, the redox couple is required to be soluble in water. From the literature presented in Table 1, only a single paper uses a non-aqueous electrolyte, however, it is concluded that the high viscosity of the system makes it unsuitable for practical applications [28].

Figure 2: Pourbaix diagrams of iron and zinc. a) The Pourbaix diagram of iron shows a redox couple of Fe(III) and Fe(II) at low pH-values. b) For zinc, no potential redox couple are found, as zinc do not exist in two different oxidations states as soluble ions.

The electrochemistry of the system is a very important prerequisite for the successful application of the electroscrubbers as the operating expenses (OPEX) depends mainly on the electrical energy consumption. Information regarding the redox couples may be found in the scientific literature, as most redox couples have well known electrochemistry. The scientific literature will generally provide an overview of which electrodes that can be used to counter the unwanted side reactions.
The reactivity of the compound and the pollutant greatly affects the capital expenditure (CAPEX) of the system, as the scrubbing tower size depends on the reactivity of the compounds. Data on the reactivity may be found in the scientific literature, however, direct experimentation may be required for determination of the reactivity of the specific system.

The chemical cost is also important for practical applications. While the system reuses the chemicals, periodic changes of the chemicals are expected. High-cost compounds may thus increase the OPEX.

Environmental considerations have to be taken into account when designing an electroscrubber. An example of an element that is not suitable for electroscrubbers due to environmental considerations is arsenic. Several different desulfurization process using As has been developed, however, their use was limited due to legislation regarding the use of As [2].

4. Experimental Electroscrubbers

Experimental investigation of how the electrochemical and the scrubbing process interact are very important for the implementation of electroscrubbers. Direct application of conventional scrubbers and electrochemical cells may not be viable as electroscrubbers have other requirements.

In Table 2, the experimental publications within the field of electroscrubbers, are presented. Table 1 includes both patents and small scale laboratory processes, and in Table 2 only the publications where a scrubbing tower is connected to an electrochemical cell are included. In order to compare the size of the experiments, the scrubbing tower dimension are showed together with the gas and liquid flow through the system.

4.1 Pilot Scale Electroscrubbers

Overall, the organic pollutants, mainly H₂S and CH₃SH, are tested in concentrations from 5-100 ppm and gas flows of 0.2-70 l/min. NOx and SO₂ removal is tested on a similar scale, with most experiments performed within the laboratory with concentrations of 100-400 ppm at gas flow rates of 2-50 l/min. There are, however, a few exceptions, where electroscrubbers are tested on a larger scale, on real biogas and on an industrial scale [4], [10], [19], [20], [61], [62]. These will be covered below.

4.1.1 The Fischer Process

Iron in higher oxidations states has been used for removal of H₂S [63]. Due to the small amounts of the dry oxide being present as fine dust in the purified gas, a wet scrubbing process was developed [4]. The process used a solution of iron cyanide for desulfurization with electrochemical regeneration and was patented by Fischer in 1932 [3]. The process was tested on water gas at the Hamburg Gas Plant as a 500 Nm³/h purification plant was constructed in 1929. Thau reports that 4 kWh are required for the recovery of 1 kg sulfur, which is noted to be of high purity [4]. Hydrogen was formed at the cathode, however, it was simply added to the water gas instead of being collected and sold as a
separate product. The process was found to be less expensive than the utilization of dry oxides for purification under the condition that the sulfur could be sold as high purity [4].

4.1.2 Removal of NOx and SO2 at Pilot Scale

Aurousseau et al. investigated the Ce(IV)/Ce(III) redox couple for removal of NOx and SO2 with electrochemical regeneration [64]–[66]. Based on these studies, Hoffman et al. erected a pilot plant capable of cleaning 100 Nm³/h waste gas from a glass making factory [61]. The process was found to remove >99% of the SO₂, while the removal efficiency for NO remained <33% [61]. The electrochemical cell was found to have a Faraday efficiency of >92% in the production of Ce(IV) [61]. The amount of active compound required for the oxidation of SO₂ was found to be below the theoretical value of 2 Ce(IV) per SO₂, which was explained by a side-reaction of oxidation by air [61]. It was concluded that the future success of the process was hindered by the investment cost of the electrochemical cell.

4.1.3 Removal of NOx and SO2 at Semi pilot Scale

Removal of NOx and SO₂ by electroscrubbing the Ag(II)/Ag(I) redox couple was studied extensively in the laboratory to establish the potential of the process [51]–[55]. Following these studies, Govindan et al. constructed a semipilot scale system to investigate the durability of the process [10]. Due to the high price of the active compound (Ag), the feasibility of the process is linked to the durability of the electrolyte. In this analysis, it was found that altering the current (5 min on/5 min off) resulted in the most sustainable generation of Ag(II) [10]. The removal rate of SO₂ was found to be >99% and while the removal rate of NO remained <90% [10].

4.1.4 Electroscrubber for Deep Desulfurization

Following small-scale laboratory studies, Villadsen et al. investigated Cl as the active compound for H₂S removal from biogas [19], [20]. The process was developed as part of a methanation of biogas project. Methanation by the Sabatier process requires a nickel catalyst that is highly sensitive to H₂S, with concentrations as low as 10-100 ppb reported to damage the catalyst [67]. Thus, an electroscrubber with high removal rate was designed and constructed for the pilot plant test of the methanation. The process was found to have a current efficiency of 18% with a removal rate of the H₂S >99%.

4.1.5 The ISPRA Mark 13A Process

The Mark 13A process was designed for production of H₂ and sulfuric acids (H₂SO₄) from waste gas streams containing SO₂ and was patented in 1979 [46]. Before a larger pilot plant was constructed for testing, a bench scale plant was developed [42], [44], [68]. The process uses Br as the active compound and is different in the sense that removal of the pollutant is not the main focus. Instead,
focus is on the production of H₂ and H₂SO₄. The removal efficiency of the Mark 13A process is therefore not investigated, as the SO₃ content in the purified gas is kept at 200 ppm to avoid excess amounts of active Br [42]. A pilot plant capable of purifying 32.000 Nm³/h waste gas from a refinery was constructed to validate the process [47], [62]. The current efficiency of the pilot plant was determined to be 30-50% which was significantly lower than the bench scale testing. However, 90% of the 4.5 g SO₂/Nm³ was removed, and the H₂ and H₂SO₄ produced were found to be of acceptable quality. Overall, the process was estimated to generate revenue under the assumption that the products, H₂ and H₂SO₄ could be sold [47].

4.2 Parameters for Comparison

Direct comparison of the electroscrubbers is not straightforward. From Table 1, it is observed that several different active mediators are used with each their own process chemistry. Two active compounds may be similar in performance due to the first having great electrochemical properties and poor interaction with the pollutant while the second active compound has the opposite properties. Table 2 shows that even for the same application, i.e. H₂S removal, several different experimental configurations exist.

The gas mixture used for the experiments is also an important parameter. In Table 2, the amount of the pollutants are observed to be of comparable concentrations, however, some of the experiments are performed with inert gasses, while others are not. The most common gas to mix with is air, which is highly unwanted when assessing the performance of an active oxidizing compound. In conventional liquid redox sulfur recovery (LRSR) processes, air is used for regeneration of the oxidizing compound. For oxidizing electroscrubbers air should therefore not be mixed with the pollutant. If this is not possible to avoid, the effect of the oxygen partial pressure should be included in the studies. Overall, it is recommended that inert gasses be used as carrier gasses. Alternatively, the carrier gas could be modelled after the targeted application.

So far, there is not a standard method for comparison of electroscrubbers across different experimental conditions. Below, parameters for comparison of electroscrubbers are presented.

4.2.1 Faraday Efficiency of the Electroscrubber

As showed in Figure 1, electroscrubbers consist of two distinct processes, the electrochemical and the scrubbing process. The overall efficiency of an electroscrubber (\(\varphi_{\text{overall}}\)) is a combination the efficiencies of the two processes:

\[
\varphi_{\text{overall}} = \varphi_{\text{electrochemical}} \cdot \varphi_{\text{scrubber}}
\]

Eq. 1

where \(\varphi_{\text{electrochemical}}\) is the Faraday efficiency of the electrochemical cell and \(\varphi_{\text{scrubber}}\) is the chemical efficiency in the scrubber. In the literature, the electrochemical efficiency, i.e. the Faraday
efficiency, is often calculated, see e.g. [15], [61]. The Faraday efficiency is calculated as the concentration of the active compound measured (c) compared with the amount of active compound expected from the theoretical expression (n_{theory}), where n_{theory} is calculated by Faraday’s law [69]:

$$ n_{theory} = \frac{it}{ZF} \quad \text{Eq. 2} $$

where I is the current, t is time, z is the overall reaction valency and F is Faraday’s constant (96487 C) [69]. This is used to compare with the measured concentration of the active compounds (c) to find the Faraday efficiency [15], [61], [69]:

$$ \varphi_{electrochemical} = \frac{cv}{it} zF \quad \text{Eq. 3} $$

where V is the volume of the liquid with the active compound.

### 4.2.2 Current Comparison

From Faraday’s law, it is possible to calculate the theoretical current (i_{theory}) required for removal of the pollutant as:

$$ i_{theory} = \frac{n_{pollutant} zF}{t} = \frac{y_{pollutant} pG}{RT} zF \quad \text{Eq. 4} $$

where y_{pollutant} is the concentration of the pollutant, n_{pollutant} is the amount of pollutant, p is the pressure of the polluted gas, G is the gas flow, R is the gas constant and T is the temperature.

Under constant current conditions, i_{theory} can be used to compare the applied current as i/i_{theory}, and this quantity can be used to evaluate performance parameters across different parameters. This is especially important when operating with real gas concentrations where the pollutant concentration may vary over time; even the controllable parameters are kept constant.

### 4.2.3 Overall Current Efficiency

Ultimately, the overall current efficiency of the system is of great interest as it is used to calculate the OPEX of the electroscrubber. For steady state conditions, the overall current efficiency of an electroscrubber may be calculated directly from the amount of pollutant removed in the system per time (P):

$$ \left( y_{pollutant}^{(in)} - y_{pollutant}^{(out)} \right) \frac{pG}{RT} M_{pollutant} = P \quad \text{Eq. 5} $$

This quantity is compared with the applied current to find the current efficiency of the system

$$ \eta = \frac{P}{i} = \frac{\left( y_{pollutant}^{(in)} - y_{pollutant}^{(out)} \right) \frac{pG}{RT} M_{pollutant}}{i} \quad \text{Eq. 6} $$
The value of $I$ shows directly how much pollutant is removed per applied ampere per time. Combined with cell potential and electricity prices, the sign value can be used to directly calculate the OPEX.

### 4.2.4 Removal Efficiency

For the scrubbing process, the removal efficiency is often calculated.

$$\Delta P = \frac{y_{\text{pollutant}}^{\text{in}} - y_{\text{pollutant}}^{\text{out}}}{y_{\text{pollutant}}^{\text{in}}}.$$  \hspace{1cm} \text{Eq. 7}

The removal efficiency refers to the difference in pollutant concentration in and out of the scrubber. While this parameter is easily calculated, it is not directly suitable for comparison. For instance, the removal efficiency may be high while the overall efficiency of the electroscrubber is low if large amounts of active mediators are used to remove a small amount of pollutant. On the other hand, an electroscrubber may have a high overall efficiency but a low removal efficiency if the applied current is low.

In order to compare removal efficiencies across different parameters such as gas flow or concentration, the removal efficiency should be compared with $i/i_{\text{theory}}$. This will allow for direct comparison.

The removal efficiency is, however, important and may be studied separately from the overall efficiency of the electroscrubber. Several potential applications of the electroscrubbers, mainly syngas cleaning, have high requirements for the amount of pollutant present in the purified gas.

### 4.3 Process Control

In the literature, three different methods of controlling the electroscrubbers is provided: constant current, pulsed current and a liquid set-point. Constant current is applied in the greater part of the experiments and has a scientific advantage for comparison when other parameters are changed [30]–[32], [50], [59]. Pulsed current, e.g. 1 A for 5 min., is used during experiments where a constant current would generate too much of the active component [35], [36], [38], [40]. Lastly, Gendel et al. controlled the process by continuous measurement of the concentration of the active component in the electrolyte, keeping the concentration within a defined concentration range [25].

Govindan et al. investigated the effect of different forms of applied current and found that a 10 min cycle with 5 min current and 5 min without current had the best effect on the regeneration of the active compound [10].

### 5. H₂S Electroscrubbers
H$_2$S may be considered the most important pollutant within electroscrubbers. H$_2$S removal has been studied with the most different active compounds and in the most publications as can be seen in Table 1. Furthermore, the first and industrial application of electroscrubbers were applied for H$_2$S removal [4]. H$_2$S removal by electroscrubbers will therefore be reviewed in detail.
Table 2: Experimental conditions for electroscrubbers found in literature. The table includes all publications which provided details regarding experiments where a scrubber was combined with electrochemical regeneration. Overall, the experiments have been limited to laboratory testing with low concentrations of the pollutants. Concentration refers to the total concentration of the both parts of the redox couple in the active electrolyte.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S, CH₃SH, NH₃, N(CH₃)$_3$, CH₃CHO</td>
<td>Co</td>
<td>30</td>
<td>5</td>
<td>15</td>
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<td>50-100</td>
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<td>0.75</td>
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<tr>
<td>H₂S</td>
<td>Co</td>
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<td>2.5</td>
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<td>10</td>
<td>2</td>
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<td>10-100</td>
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<td>10</td>
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<td>5-15</td>
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<td>10</td>
<td>30-70</td>
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<td>0.2</td>
<td>10</td>
<td>3</td>
<td>0.01</td>
<td>[36]</td>
</tr>
<tr>
<td>C₂Cl₄</td>
<td>Ni</td>
<td>40</td>
<td>5.5</td>
<td>1</td>
<td>0.2-0.8</td>
<td>15-50</td>
<td>3</td>
<td>0.05</td>
<td>[38]</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Ni</td>
<td>40</td>
<td>5.5</td>
<td>1.25</td>
<td>2.8</td>
<td>100-400</td>
<td>3</td>
<td>0.03-0.05</td>
<td>[37]</td>
</tr>
<tr>
<td>NOₓ, SO₂</td>
<td>Ag</td>
<td>120</td>
<td>5</td>
<td>9.8</td>
<td>10</td>
<td>100-400</td>
<td>2</td>
<td>0.1</td>
<td>[55]</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Fe</td>
<td>46</td>
<td>11</td>
<td>1.35-2</td>
<td>3.63-4.56</td>
<td>700</td>
<td>0.92</td>
<td>0.001</td>
<td>[15]</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Ag/Ce</td>
<td>120</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>400</td>
<td>2</td>
<td>0.01-0.1 (Ag) 0.5-1.0 (Ce)</td>
<td>[53]</td>
</tr>
<tr>
<td>NOₓ, SO₂</td>
<td>Ag</td>
<td>80</td>
<td>5</td>
<td>10</td>
<td>5-50</td>
<td>100-400</td>
<td>1-4</td>
<td>0.1</td>
<td>[52]</td>
</tr>
<tr>
<td>NOₓ, SO₂</td>
<td>Ag</td>
<td>120</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>100-400</td>
<td>2</td>
<td>0.1</td>
<td>[51]</td>
</tr>
<tr>
<td>NOₓ, SO₂</td>
<td>Ag</td>
<td>120</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>100-400</td>
<td>2</td>
<td>0.1</td>
<td>[51]</td>
</tr>
<tr>
<td>NOₓ, SO₂</td>
<td>Ag</td>
<td>95</td>
<td>15x15 (square)</td>
<td>60</td>
<td>250-1000</td>
<td>200-400</td>
<td>25</td>
<td>0.1</td>
<td>[10]</td>
</tr>
<tr>
<td>NOₓ, SO₂</td>
<td>Ce</td>
<td>200</td>
<td>40</td>
<td>10-35</td>
<td>367-1667</td>
<td>250-600</td>
<td>53.3-83.3</td>
<td>0.009</td>
<td>[61]</td>
</tr>
</tbody>
</table>
H$_2$S is naturally formed in reducing environments where also biogas and natural gas is formed [70]. Due to the corrosive nature of H$_2$S, it has to be removed before any downstream applications of the gasses. Furthermore, the toxicity and smelliness of H$_2$S dictates that off-gasses containing H$_2$S must also be purified.

### 5.1 Process Chemistry of H$_2$S Electroscrubbers

In Table 3, the process chemistry and electrochemical set-up of the different experimental publications are presented. The processes follow the same overall process, which may be presented with a model oxidizing redox couple (Me$^{3+}$/Me$^+$) as follows.

First, the H$_2$S is oxidized to form elemental sulfur.

$$H_2S + Me^{3+} = 2H^+ + S + Me^+$$  \[ Eq. 8 \]

The active oxidizing species is then regenerated at the anode:

$$Me^+ = Me^{3+} + 2e^-$$  \[ Eq. 9 \]

While hydrogen is formed at the cathode:

$$2H^+ + 2e^- = H_2$$  \[ Eq. 10 \]

Giving the overall reaction:

$$H_2S = H_2 + S.$$  \[ Eq. 11 \]

However, if the sulfur is further oxidized to sulfate:

$$S + 3Me^{3+} + 4H_2O = H_2SO_4 + 6H^+ + 3Me^+$$  \[ Eq. 12 \]

Which results in the overall reaction:

$$H_2S + 4H_2O = H_2SO_4 + 4H_2$$  \[ Eq. 13 \]

and thus an acidification and consumption of water as electrical energy is used to generate sulfuric acid from water and sulfur.

### 5.2 End Product

H$_2$S may be considered a unwanted combination of two valuable chemicals, i.e. hydrogen and sulfur [57]. Recovery of sulfur from H$_2$S can be achieved through other processes, e.g. the Stretford or Claus process [2]. However, hydrogen is not easily recovered. Using electroscrubbers, both the hydrogen and the sulfur may be recovered.

Part of the publications within electroscrubbers for removal of H$_2$S has a great focus on recovery of the H$_2$ and S [22], [25], [28], [48], [56], [57]. Elemental sulfur may be removed from the electrolyte.
by filtration, as the oxidation from sulfide to sulfur is fast, while the oxidation from sulfur to sulfate is slow [71]. Other publications focus on the formation of sulfate (SO$_4^{2-}$) instead [30–32], [50], [59]. Sulfate is highly soluble in aqueous solutions and may increase the conductivity. The issue of sulfate formation, however, is the extra consumption of chemicals and acidification.

5.3 pH

In 10/13 of the experimental conditions in Table 3, the H$_2$S is removed using an acidic electrolyte. Considering that H$_2$S is an acidic gas, the convention would be to use alkaline scrubbers [26], [57], [72]. However, the electrochemical considerations are advantageous at low pH-values which results in an overall advantage at low pH-values [26]. This is due to the Nernst Equation, from which the equilibrium potential ($E_{\text{Eq}}$) is expressed as [69]:

$$E_{\text{Eq}} = E^0 + \frac{RT}{zF} \ln \left( \frac{[\text{Ox}]}{[\text{Red}]} \right)$$

Eq. 14

Where $E^0$ is the standard potential for the redox reaction and [Ox]/[Red] is the ratio between the activity of the oxidizing and the reducing compounds. Under acidic conditions, [Red] is high which results in a low overall equilibrium potential. Therefore, low pH-values result in lower potentials required for the electrochemical regeneration and therefore lower OPEX. Several of the redox-couples are also limited to certain pH-values due to thermodynamics, such as iron as can be observed in the Pourbaix diagram in Figure 2a. Furthermore, K. Kim et al. studied the effect of the pH on the removal efficiency from pH = 5 to pH = 0.8 and found that the lowest pH-value gave the best results [48].
Table 3: Overview of the publications of electroscrubbers for H$_2$S removal. Most of the experiments are performed with an ion-exchange membrane and under acidic conditions, with Fe as the most widely used active compound. Overall, the removal rate of H$_2$S is found to be very high, with several applications removing H$_2$S down to non-detectable concentrations (>99%).

<table>
<thead>
<tr>
<th>H$_2$S reaction</th>
<th>Electrochemical reaction</th>
<th>Anode</th>
<th>Membrane</th>
<th>Cathode</th>
<th>Condition</th>
<th>Removal rate</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2K_2Fe(CN)_6 + 2K_2CO_3 + H_2S = 2K_2Fe(CN)_6 + 2K_2CO_3 + S$</td>
<td>$2K_2Fe(CN)_6 + 2K_2CO_3 = 2K_2Fe(CN)_6 + 2K_2CO_3 + H_2$</td>
<td>Not published</td>
<td>Not published</td>
<td>Not published</td>
<td>Alkaline</td>
<td>Not published</td>
<td>[3], [4]</td>
</tr>
<tr>
<td>$I_2 + H_2S = 3I^- + 2H^+$</td>
<td>$3I^- + 2H^+ = I_2 + H_2$</td>
<td>Graphite</td>
<td>Nafion 390 or Nafion 117 or Raipore R1035</td>
<td>Platinum on Ti</td>
<td>Acidic</td>
<td>&gt;99%</td>
<td>[57]</td>
</tr>
<tr>
<td>$3H_2O + IO_3^- = 3S + 3H_2O + I_2$</td>
<td>$I_2 + 3H_2O = IO_3^- + 3H_2$</td>
<td>Graphite</td>
<td>Nafion 390 or Raipore R1035</td>
<td>Platinum on Ti</td>
<td>Alkaline</td>
<td>&gt;99%</td>
<td>[56]</td>
</tr>
<tr>
<td>$H_2S + 2H^+ + 2VO_4^{2-} = 2VO_5^{2-} + S + 2H_2O$</td>
<td>Platinum on Ti</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Acidic</td>
<td>&gt;90%</td>
<td>[22]</td>
<td></td>
</tr>
<tr>
<td>$2Fe(III)-IL + H_2S = 2Fe(II)-IL + S + H_2$</td>
<td>Platinum</td>
<td>Ion-exchange</td>
<td>Platinum</td>
<td>Acidic</td>
<td>&gt;98%</td>
<td>[28]</td>
<td></td>
</tr>
<tr>
<td>$PdO_2(VI)O_4 = H_2S = S + 2H^+ + 2H_2O$</td>
<td>Not published</td>
<td>Carbon cloth</td>
<td>Nafion 117</td>
<td>Carbon cloth</td>
<td>Acidic</td>
<td>95%</td>
<td>[48]</td>
</tr>
<tr>
<td>$H_2S + 8Co(II) + 4HCl + SO_2 + 8Ce(III) = 2Ce(IV) + H_2$</td>
<td>Pt-coated Ti</td>
<td>Nafion 324</td>
<td>Ti</td>
<td>Acidic</td>
<td>&gt;99%</td>
<td>[50]</td>
<td></td>
</tr>
<tr>
<td>$H_2S + 8Ag(I) + 4H_2O = 8Ag^{+} + SO_2 + 10H^+$</td>
<td>Not published</td>
<td>Pt-coated Ti</td>
<td>Nafion 324</td>
<td>Ti</td>
<td>Acidic</td>
<td>98%</td>
<td>[30]-[32]</td>
</tr>
<tr>
<td>$H_2S + 2Fe^{3+} = 2Fe^{2+} + S + 2H^+$</td>
<td>$2Fe^{2+} + 2H^+ = 2Fe^{3+} + H_2$</td>
<td>Graphite cloth</td>
<td>Nafion 117</td>
<td>Platinized graphite cloth</td>
<td>Acidic</td>
<td>&gt;99%</td>
<td>[24]</td>
</tr>
<tr>
<td>$H_2S + 2FeCl_3 = 2Fe^{3+} + 2H_2O + S + 2H^+$</td>
<td>RuO$_2$ coated Ti</td>
<td>None</td>
<td>Ti</td>
<td>Acidic</td>
<td>&gt;90%</td>
<td>[25]</td>
<td></td>
</tr>
<tr>
<td>$H_2S + 2FeCl_3 + 3FeCl_2 + 3HCl + S$</td>
<td>2FeCl$_3 + 3FeCl_2 + 2H_2O = 2FeCl_3 + 2FeCl_2 + 2HCl + S$</td>
<td>Carbon</td>
<td>Carbon fiber cloth</td>
<td>Acidic</td>
<td>&gt;99%</td>
<td>[26]</td>
<td></td>
</tr>
<tr>
<td>$H_2S + 2Fe(III)[EDTA]^2+ = 2Fe(II)[EDTA]^2+ + 2H_2$</td>
<td>Carbon cloth</td>
<td>Carbon cloth</td>
<td>Tokuyama A201</td>
<td>pH 7-10</td>
<td>Not published</td>
<td>[29]</td>
<td></td>
</tr>
<tr>
<td>$HClO + H_2S = S + H_2O + 1H^+$</td>
<td>$2H^+ + 2Cl^- = H_2 + Cl_2$</td>
<td>Ti with MMO</td>
<td>None</td>
<td>Ti with MMO</td>
<td>Acidic</td>
<td>&gt;99%</td>
<td>[18]-[20]</td>
</tr>
</tbody>
</table>
5.4 Electrochemical Cell

Generally, the electrochemical cell is operated as a separate loop, with a pump supplying the active compound from the electrochemical cell to the scrubbing solution reservoir. Most set-ups in Table 3 uses an ion-exchange membrane that separates the catholyte and anolyte. In this way, only the anolyte interacts with the gas in the scrubber, as the catholyte is pumped to and from another reservoir.

The electrodes are made from either carbon, titanium, platinum or a combination. The low pH-value of most of the experiments limits the amount of electrode materials. For the cathode, an electrode with low hydrogen over potential is required, which are common as hydrogen production is an optimized process. The choice of anode depends on the active compound, with platinized titanium or carbon a widely used option.

5.5 Removal Efficiency

The electroscrubbers for desulfurization generally achieve a high removal rate of H$_2$S. Several experiments remove H$_2$S down to non-detectable limits, which is presented as >99% in Table 3. A reason for the high removal rate may be the explained by a high active compound to H$_2$S rate. Kalina et al. used an active compound to H$_2$S ratio of 5-25 during their acidic experiments and of at least 1.4 during the alkaline experiments [56], [57]. Pillai et al. performed experiments with lower removal efficiencies and found that the removal rate was increased by increasing the ratio of the active compound to H$_2$S [59]. In their paper they find this can be done both by changing the gas or liquid flow or by changing the concentration [59].

5.6 Active Compounds

7 different active compounds have been tested in the literature of electroscrubbers for H$_2$S removal. Furthermore, Govindan et al. and Pillai et al. tested the removal performance of their electrolyte (6 M and 3 M nitric acid, respectively) [50], [59]. Here, it was found that H$_2$S was removed even without active compounds present, although with a much lower removal efficiency. The presence of a mediator greatly increases the removal efficiency in both papers [50], [59].

5.6.1 Fe

Fe is the most widely used active compound as 5 different research groups have investigated desulfurization with Fe(II)/Fe(III) [4], [24]–[26], [28]. Iron oxides are well known to react with H$_2$S and Huang et al. used an acidic aqueous solution of Fe(II) and Fe(III) to remove H$_2$S [24]. Mizuta et al. and Gendel et al. used an electrolyte where the iron was mixed with chloride [25], [26]. Gendel et al. explained that the addition of chloride hinders the unwanted oxygen generation at the anode, as chlorine formation is favored [25]. Fischer patented a process where the Fe is suspended by cyanide in order to allow larger quantities of iron to be suspended in the aqueous electrolyte [3]. Guo et al.
developed the only non-aqueous electrolyte used in electroscrubbers [28]. The electrolyte was an iron-based imidazolium chloride ionic liquid, however, the high viscosity made the process unsuitable for practical purposes [28].

Kim et al. suspended their iron redox couple using ethylenediaminetetraacetic acid (EDTA) as chelating agent [29]. Fe(III)EDTA had previously been used for removal of H$_2$S with regeneration by air, however, the EDTA had stability problems during the regeneration process due to hydroxyl radicals [73].

### 5.6.2 V

Vanadium redox couples are used in the Stretford process to remove H$_2$S, where air is used for regeneration. Huang et al. investigated an electrochemical regeneration of the vanadium oxide used for desulfurization [22]. VO$_2^+$ as an oxidizing agent has the advantage that it is not capable of oxidizing the sulfur to sulfate [22]. Thus, using VO$_2^+$ as the active compound will result in not electrical energy wasted on forming sulfate as in eq. 12.

### 5.6.3 Ce

Pillai et al. investigated Ce as active compound because it was previously found to be highly effective in removal of organic waste materials [59], [74]. It was found, that low gas flows and low H$_2$S concentrations were required for high removal efficiency [59].

### 5.6.4 Ag

As an alternative to Ce, Govindan et al. investigated Ag for desulfurization [50]. Ag was found to be able to remove both H$_2$S and CH$_3$SH as both pollutant were removed down to non-detectable concentrations [50]. The main issue with Ag, however, is the high cost price which results in a requirement for complete reuse and low concentration of the electrolyte.

### 5.6.5 Co

Co has the advantage over Ce and Ag that it operates well at low temperature [32]. Govindan et al. therefore investigated Co as the active compound for removal of H$_2$S and other odor gasses [31], [32]. The process was found to be a highly sustainable green methodology as the anode material was optimized for lower power consumption and no trace elements were found in the downstream gas [30].

### 5.6.6 I

Kalina et al. investigated the use of iodine oxidants under both acidic and alkaline conditions [56], [57]. While the alkaline conditions are more conventional, the electroscrubber was found to require more than twice the applied voltage when compared with the acidic conditions [56]. Thus, the process
under acidic conditions was patented [58]. In both cases, the iodine based oxidizing agent were reported to oxidize H$_2$S only to elemental sulfur and not further [56], [57].

5.6.7 Mo

H$_2$S removal by heteropoly molybdphosphate (HPMo) or other heteropoly compounds have previously been investigated with air for regeneration [75], [76]. Kim et al. investigated HPMo as a more robust alternative to their previous attempts with iron based EDTA solution [29], [48]. Kim et al. finds that the lowest tested pH-value of 0.8 results in the highest efficiency of the system [48].

5.6.8 Cl

Removal of H$_2$S by using Cl as the active compound is well known [71], [77], [78]. Villadsen et al. [18]–[20] investigated H$_2$S removal with Cl operating under acidic conditions. The main advantages of Cl include the high solubility, well-known electrochemistry and chemical cost. The process was tested on real biogas and found to have a removal efficiency of >99%.

6. Summary

The scientific field of electroscrubbers are currently limited to less than 60 publications that were all reviewed in this paper. A list of requirements and general considerations for electroscrubbers were compiled based on the literature and with a few new points.

For future work with electroscrubbers, several calculated parameters were presented that will allow the comparison across parameters and experimental conditions.

Special interest was given to removal of H$_2$S in this review. Desulfurization by electroscrubbing has been tested with several different active compounds and under different conditions. Contrary to conventional gas sweetening, acidic conditions are favored in the literature due to increased electrochemical properties.


Z. Guo et al., “Nonaqueous System of Iron-Based Ionic Liquid and DMF for the Oxidation of


[63] M. Yumura and E. Furlmsky, “Comparison of CaO, ZnO, and Fe2O3 As H2S Adsorbents at


with heteropoly compound.”


Appendix III

New Electroscrubbing Process for Desulfurization
New Electroscrubbing Process for Desulfurization

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Abstract

A new process for removing sulfur from gas using electricity is presented. The process combines electrochemical production of active oxidizing species with an oxidative scrubber for desulfurization. Reactions for the electrochemical cell and the scrubbing tower are presented and a scrubbing set-up with a continuous electrolyte recirculation is validated on synthetic biogas. The test show that a gas flow of 200 l/h with 1320 ppm H\textsubscript{2}S can be removed down to non-detectable levels in a single step, using 3.46 times the theoretical current. Sulfur is extracted from the system and has traces of NaClO. Sulfur compounds are poison for most heterogeneous catalysts, thus for carbon utilization, the carbon gas source has to be desulfurized. The process that has been have developed allows for the utilization of carbon sources with any sulfur concentration, such as biogas, coke oven gas, off-gas etc.
1. Introduction

The renewable energy sector is booming and especially the biogas industry is growing [1]. Each year new biogas plants are constructed worldwide. In Europe alone there were 17,783 biogas plants in 2017 with more than 10,000 situated in Germany [2]. As compared to other renewable energy sources, as e.g. solar and wind energy, biogas does not suffer from fluctuating and unstable production rates, which makes it even more suitable as a main constituent in a fossil-free society.

Biogas consists roughly of 60% methane (CH₄) and 40% carbon dioxide (CO₂) with several impurities. The main impurity is hydrogen sulfide (H₂S) with levels of several thousand ppm. However, siloxanes and methyl mercaptane are also often found to a lesser extent in the biogas [3]. H₂S is both flammable, toxic and corrosive [4]. Thus, independently of the downstream application, the H₂S content of the biogas has to be minimized.

Traditionally, biogas has been used in a combined heat and power engine for localized energy production. However, within the last decade, biogas upgrading has found its way to the market. Today, state-of-the-art upgrading of biogas refers to extraction of CH₄ from biogas [5], [6]. This type of CH₄ is named biomethane [7] and is a renewable energy resource with many applications.

Future applications of biogas may differ significantly from current state-of-the-art commercially available technologies. Recently, the term ”second generation biogas upgrading” has been suggested to distinguish between traditional biogas upgrading technologies and upcoming upgrading technologies and processes [8].

Using biogas as the main carbon source is currently being investigated as second generation technology for energy storage [9]–[14]. Central to these applications is the reduction of CO₂. Generally, there are three main methods for reducing CO₂, i.e. biological, electrochemical and thermochemical. All technologies have requirements to the H₂S level in the biogas.
The decentralized nature of biogas plants favors the need for desulphurization technologies with local regeneration and without waste generation. Regeneration could be performed in-situ either by air, e.g. biological desulfurization and the Lo-Cat process [15], by heat, e.g. chemical scrubbers or by electricity.

Among the desulfurization technologies used today, only the biological desulfurization technology fulfills these requirements. However, one large drawback from biological desulfurization is the residual oxygen found in the cleaned gas [16]. For biogas plants with first generation upgrading facilities, this is a large issue, as the maximum allowed oxygen content can be as low as 100 ppm for biomethane [17]. Finally, another drawback of the biological cleaning system is also very slow response time when it comes to fluctuating H2S levels.

Applying electro-assisted scrubbers to biogas could be beneficial when included in second generation biogas upgrading technologies. However, a water-based electrolyte would have to take the rather large amount of CO2 in the biogas into account. CO2 will be dissolved into the electrolyte and affect the pH-value. Generally, the pH-value is expected to reach a steady state level below neutral, due to the acidic properties of CO2. Therefore, an electro-assisted scrubbing process operating at moderately low pH values would be preferred for biogas applications.

This paper reports the results of a new and novel process which can be regenerated in-situ and does not generate waste. The aim is to develop a cheap, stable and robust process that selectively removes H2S down to the very low ppm levels, while leaving the CO2 in the biogas. Together with a suitable electrolyte system, electrochemical and scrubbing reactions are suggested. The electrolyte system is tested on a lab-scale electro-scrubber set-up interfaced with a gas mixture mimicking a real biogas.

Patent is pending.

The process is an electrochemically assisted scrubbing system. The solvent selectively oxidizes the H2S content of the biogas into free sulfur. The process applies continuous solvent recirculation, which is
regenerated in an undivided electrochemical cell. In Figure 1, the mechanism is presented. The electrolyte comprises an aqueous solution and the electrochemical mechanism is (Figure 1c):

**Anode** [18]:

\[ 2\text{Cl}^- = \text{Cl}_2(aq) + 2\text{e}^- \quad \text{Eq. 1} \]

**Cathode:**

\[ 2\text{H}^+ + 2\text{e}^- = \text{H}_2 \quad \text{Eq. 2} \]

Following the formation, chlorine reacts with water to form hypochlorite (Figure 1d) [19]:

\[ \text{Cl}_2(aq) + \text{H}_2\text{O} = \text{HCl} + \text{HClO} \quad \text{Eq. 3} \]

Within the scrubber, the biogas interacts with the liquid. CH₄ has been assumed to be inert and is in the experiments considered interchangeable with other similar inert low-soluble gasses such as N₂ or higher hydrocarbons. The CO₂ is expected to saturate the liquid over time due to CO₂ dissolution:

\[ \text{CO}_2(g) = \text{CO}_2(aq) \quad \text{Eq. 4} \]

\[ \text{CO}_2(aq) + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+ \quad \text{Eq. 5} \]

The hydrogen sulfide is expected to dissolve and dissociate (Figure 1a) [20]:

\[ \text{H}_2\text{S}(g) = \text{H}_2\text{S}(aq) \quad \text{Eq. 6} \]

\[ \text{H}_2\text{S}(aq) = \text{HS}^- + \text{H}^+ \quad \text{Eq. 7} \]

And subsequently being oxidized by hypochlorite (Figure 1b):

\[ \text{HS}^- + \text{HClO} = \text{S} + \text{H}_2\text{O} + \text{Cl}^- \quad \text{Eq. 8} \]

The overall reaction is thus
\[ \text{H}_2\text{S} + \text{electrical power} = \text{H}_2 + \text{S} \]  
Eq. 9
Figure 1: The reactions in the electro-scrubber. a) Hydrogen sulfide enters the scrubber and is dissolved and dissociated (Eq. 6 and 7). b) The dissociated sulfide is oxidized by hypochlorite (Eq. 8). The elemental sulfur formed is insoluble in the electrolyte. c) The electrochemical cell forms chlorine at the anode (Eq. 1) and hydrogen at the cathode (Eq. 2). d) The chlorine formed reacts with water to form hypochlorite (Eq. 3).
2. Materials and Methods for the Developed Electrochemically Scrubber System

2.1 Scrubbing System

A scrubbing system was constructed using standardized tubing devices and equipment based on an internal diameter of 110 mm. The tower and liquid container were made from PMMA (Plexiglas) allowing for visual inspection of the liquid flow and electrochemical cell under operation. A water circulation pump with a brushless motor capable of 5.5 m lift was used together with a showerhead which resulted in a liquid flow of 1.26 L/min. evenly distributed within the scrubbing tower. Simple uncoated Lightweight Expanded Clay Aggregate (LECA) balls with a density between 210 and 280 kg/m³ were used as packing material with suitable gas-to-liquid wetting abilities.

2.2 Electrochemical Cell

The undivided electrochemical cell was positioned in the bottom of the scrubber unit and consisted of two graphite electrodes from Frederiksen Scientific A/S, with a diameter of 6 mm and a total length of 250 mm. 150 mm of the electrodes were inside the reactor and 100 mm outside for connection purposes. No degradation of the carbon electrodes were observed during the experiments. The voltage and current were applied by a Voltcraft LSP-1403 80 W switching DC power supply. An electrolyte consisting of 1 L of demineralized water mixed with 200 g NaCl was used within the system.

2.3 Gas Flow

The gas flow rate was determined by a combination of two mass flow controllers (MFC). The H₂S containing gas was controlled by a Brooks SLA5851 MFC, and the CO₂ was controlled by an MKS GE50A025503BN010 MFC. All gasses were supplied by Strandmøllen. The gas compositions entering and exiting the system were measured with an MRU SWG 100 stationary biogas analyzer, where the CO₂ is measured between 0-100% with an uncertainty of ± 0.3% using NDIR, H₂S is measured
electrochemically between 0-10,000 ppm with an uncertainty of ± 50 ppm and O₂ is also measured electrochemically, although between 0-21% with an uncertainty of 0.2%. For each setting, at least 4 measurements were made. The standard deviation was used as uncertainty in case it was larger than the uncertainty of the analysis equipment. The pH-value was determined using standard pH-strips with four zones. The same liquid was used throughout the experiments, which were performed over a period of 14 days. When the set-up was not in operation, it was sealed off to minimize degassing from the electrolyte.

2.4 Scanning Electron Microscopy (SEM) Analysis

The SEM used for analyzing the sulfur content was a Hitachi tabletop SEM TM3000 equipped with energy dispersive x-ray spectroscopy (EDS). The imaging was performed using backscattered electrons at 15 kV. The image was acquired at a working distance of 9500 μm and with a magnification of 1000. The EDS analysis was performed at 15 kV with a mapping time of 500 s.
3. Results and discussion

3.1 Effect of Current

In theory, the current required for the oxidation of sulfide to sulfur ($i_{\text{theory}}$) can be calculated applying Faraday's law [21]:

$$i_{\text{theory}} = \frac{n_{\text{sulfur}}}{t} zF = \frac{y_{\text{sulfur}} PV}{tRT} zF$$  \hspace{1cm} \text{Eq. 10}

Where $n_{\text{sulfur}}$ is the amount of sulfur, $t$ is time, $y_{\text{sulfur}}$ is the concentration of sulfur in the gas, $p$ is the pressure, $V$ the volume, $R$ the gas constant, $T$ the temperature, $F$ is the Faraday’s constant and $z$ is the number of electrons required for the reaction and is equal to 2, according to Eq. 1. It is assumed that H$_2$S may be considered an ideal gas at room temperature and atmospheric pressure. A 100% Faraday efficiency is assumed in combination with 100% scrubber efficiency in order to calculate the theoretical current. In reality, lower efficiencies may be expected. Typically, chloralkali plants are known to have efficiencies in the range of 50-75% [18] (3400-2100 kWh/ton Cl$_2$).

Lower current efficiency may be caused by undesired side reactions. This could include anodic O$_2$ generation [22]:

$$2H_2O = O_2(g) + 4H^+ + 4e^-$$  \hspace{1cm} \text{Eq. 11}

Or the oxidation of sulfur:

$$S + 4 H_2O = H_2SO_4 + 6 H^+ + 6e^-$$  \hspace{1cm} \text{Eq. 12}

Or cathodic chlorine reduction:

$$Cl_2 + 2e^- = 2Cl^-$$  \hspace{1cm} \text{Eq. 13}

$$ClO^- + 2e^- + 2H^+ = Cl^- + H_2O$$  \hspace{1cm} \text{Eq. 14}
All of which will decrease the current efficiency.

In Figure 2, the removal efficiency is presented for different applied currents relative to the theoretical minimum current ($i/i_{theory}$) for a constant gas flow of 200 l/h. In Figure 2a), the CO$_2$ content of the model biogas in and out of the system is shown for the different applied currents. It is observed that there is no correlation between the applied current and removal of CO$_2$. This result is very much in line with the proposed explanation for the lower CO$_2$ concentration at the exit of the cleaning unit, i.e. that the CO$_2$ is dissolved in the liquid. If the CO$_2$ removal was the result of dissolution into the liquid, the removal rate of CO$_2$ should only be dependent on the gas/liquid flow and not on the applied current. From Figure 2a it is evident that this seems to be the case.

For H$_2$S, it is expected that a higher applied current would increase the removal, and this is indeed observed. From Figure 2b), it is found that $i/i_{theory} = 3.46$ (an applied current of 4.5 A) resulted in a complete removal of sulfur as the H$_2$S level at the exit of the scrubber was below the detection limit. At lower applied currents, the system is not capable to remove all H$_2$S. However, significant removal of H$_2$S is observed for all applied currents.
Figure 2: Impact of changing the applied current. A constant gas flow of 200 l/h and liquid flow of 1.26 l/min. a) shows the CO$_2$ content in and out of the scrubber system, where it is observed that while some CO$_2$ is absorbed, it does not depend on the applied current. b) shows the H$_2$S removal efficiency, where it is seen that the current is directly linked to the amount of H$_2$S left in the exit gas. A current of 3.46 times the theoretical minimum is sufficient to completely remove the H$_2$S from the model biogas composition containing 1320 ± 59 ppm H$_2$S.
3.2 Current Efficiency

The removal efficiency is observed to increase with current and in order to analyze the correlation between current and removal efficiency, the data is compared across different gas flow rates, gas concentration and applied currents. For this comparison, the mass of the removed sulfur (S) is calculated as:

\[
S = \left( \frac{y_{\text{sulfur}} \text{(in)} - y_{\text{sulfur}} \text{(out)}}{RT} \right) M_{\text{sulfur}}
\]

where \(M_{\text{sulfur}}\) is the molar mass of sulfur (32.1 g/mole) and H2S is assumed to be an ideal gas. For comparison across parameters, S is used to determine the efficiency of the system.

In Figure 3, S is showed as a function of the applied current. A linear dependency is observed between the absolute sulfur removal (S) and the applied current (i). This linear dependency indicates that other parameters such as concentration of H2S and flow rate of H2S do not affect the overall efficiency of the system. The corresponding linear fit has a \(R^2\)-value of 0.993 and a slope of 0.169 ± 2 \(\times\) 10\(^{-3}\) g/(hA), and an interception at 6 \(\times\) 10\(^{-4}\). This indicates, that no matter the other parameters of the experiments performed, 0.17 g/h sulfur were removed per ampere applied. This value is 3.54 times lower than the theoretical value, which results in an overall current efficiency of 28.3% of the cleaning process. This efficiency is the combined efficiency of the electrochemical cell and the scrubber and may be improved upon optimizing the system. For the scrubber, better suited random packing material may increase the surface area for gas/liquid interaction, and it may also be possible to choose a more optimal packing material. The electrochemical cell may be further optimized by changing the electrode materials and surface area of the electrodes.

The linear dependency between the applied current and the measured efficiency indicates that the unwanted reactions consuming energy also increase with applied current. The reaction efficiency inside
the scrubbing tower is not expected to depend on the current in the electrochemical cell, and it may therefore be assumed that the unwanted side reactions at the electrodes are the main reason for the loss of efficiency.

Figure 3: The sulfur removed as a function of the applied current for all experiments. The absolute sulfur removal (g/hA) is observed to have a linear dependent as a function of the applied current across all performed experiments.
3.3 Sulfur

Throughout the experiments, elemental sulfur was formed as described in Eq. 8. Due to the low flow rates and concentrations, however, less than 5 g of sulfur were formed throughout the experiments. As expected, the sulfur was observed to float on top of the electrolyte [23]. While operating the system, the liquid was not filtered, allowing for the sulfur to be collected on the electrolyte surface. Upon finishing the experiments, sulfur was collected from the electrolyte and analyzed EDS and SEM, as seen in Figure 4. In Table 1, the elemental configuration is presented, as NaCl is part of the dried sulfur. The oxygen content could indicate that some of the sulfur has been oxidized to sulfate. This reaction could both take place inside the reactor as an unwanted side reaction or when the sulfur was exposed to air upon dissembling the scrubbing unit. However, no rapid reaction between elemental sulfur and atmospheric oxygen was observed. Another explanation for the oxygen content could be that hypochlorite (NaClO) is present in the sulfur instead of NaCl.

For continuous operation with batch recirculation, a filtration system for removal of elemental sulfur is required. A system operating with a mixture of NaCl and water can have periodical change of liquid without large expenses and thus, the filtration system should not increase the operational cost (OPEX) significantly. The elemental sulfur may be used as fertilizer either by mixing it with the degassed manure returning to the farms or by a separate sulfur handling system. If the quality of the sulfur is high enough, other applications within the chemical industry may even create a revenue from the scrubbing system.

*Table 1: The composition of the sulfur extracted from the system. The analysis is performed by EDS. Some of the sulfur appears to be oxidized, while most of it remains as elemental sulfur. Trace elements of NaCl from the electrolyte is detected as well.*

<table>
<thead>
<tr>
<th>Element</th>
<th>S</th>
<th>O</th>
<th>Na</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic%</td>
<td>72 ± 3</td>
<td>11 ± 1</td>
<td>8.9 ± 0.3</td>
<td>8.1 ± 0.4</td>
</tr>
</tbody>
</table>
Figure 4: a) SEM picture of sulfur extracted from the electro-scrubbing system. The sulfur was observed to be insoluble in the electrolyte and was therefore collected from the top of the liquid in the bottom of the scrubber. The EDS-analysis showed that the sample consisted mainly of sulfur (b), with oxygen present on the surface as well (c) and a few areas where sodium (d) and chloride (e) were present.
4. Conclusions

The electro-scrubbing desulfurization process based on a low pH electrolyte proved capable of removing H₂S from a synthetic biogas containing CO₂ and N₂ as replacement for CH₄. For a 200 l/h gas flow with 1320 ppm H₂S, a complete removal to below detection limit was achieved using a current of 4.5 A, corresponding to 3.5 times the theoretic needed current value.

A linear correlation was found between applied current and removal efficiency, as a constant value of 0.17 g sulfur was removed per ampere per hour independent on other parameters, i.e. the gas flow rate, H₂S concentration, and applied current. This value corresponds to an overall current efficiency of 28.3%. It is expected that the efficiency can be further improved by optimizing the electrode materials and surface area of the electrodes.

The sulfur removed from the gas was found floating on the electrolyte and confirmed by EDS analysis to be elemental with smaller amount of oxygen and NaCl present as well.

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Appendix IV

Pilot Plant Testing of Novel Electro-scrubbing Process for Biogas Desulfurization
Pilot Plant Testing of Novel Electro-scrubbing Process for Biogas Desulfurization

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Abstract

In the present paper the dynamic results from a pilot plant test of a new desulfurization technology is presented. The new technology is based on an electrochemical re-generation of an oxidative liquid, combined with a gas scrubbing system. It is designed to selectively oxidize hydrogen sulfide (H₂S) to elemental sulfur (S⁰) while not interacting with the methane and carbon dioxide constituents in the biogas. Operating with 5 Nm³/h of raw biogas, H₂S is removed using an applied potential of 9-13 V and a current of 12-42 A. The performance of the system proved to be flexible and could easily be adjusted to changes in the biogas composition. Analysis revealed that sulfur was removed down to a level below the detection limit (ppm). Furthermore, siloxanes were also shown to be effectively removed. Energy dispersive x-ray analysis of the elemental sulfur sample supports these observation.
1. Introduction

Biogas is a renewable energy source with a large potential as a carbon neutral green energy source [1]. The main compounds in biogas are methane (CH\textsubscript{4}) and carbon dioxide (CO\textsubscript{2}), together with a wide range of impurities [2]. The main impurity in biogas is hydrogen sulfide (H\textsubscript{2}S), which is both flammable, corrosive and toxic [3]. Desulfurization is also important for conversion of the biogas to other more high-value chemicals, since sulfur tends to de-activate any downstream catalytic conversion. The H\textsubscript{2}S concentration is often in the range of 2000 parts per million (ppm). This level depends critically on the feedstock [4]. A desulfurization process is usually situated just downstream the biogas reactor.

Presently, power-to-gas projects are receiving a huge scientific and politically interest. Thermocatalytic methanation of biogas is among the processes being extensively investigated [5]. Combining hydrogen and carbon from biogas is referred to as second generation upgrading. These applications include: methanation, synthesis of methanol, biomethanation, etc. [1].

Methanation of biogas requires deep desulfurization. The typical nickel-catalyst applied in the methanation process is highly sensitive to even trace amount of H\textsubscript{2}S. A concentration in the parts per billion (ppb) range are reported to deactivate the catalyst [6,7]. Other future applications of biogas may include synthesis of liquid fuels and utilization in solid oxide fuel cells [1,8]. All these applications of biogas requires a higher quality purification of biogas, i.e. deep desulfurization as well as removal of other catalyst poisoning agents such as e.g. siloxanes.

Current desulfurization technologies utilized in biogas plants include iron chloride salts, activated carbon and biological desulfurization. Of these technologies, both iron chloride salts and activated carbon are costly from an operating point of view (OPEX). The biological desulfurization process is affordable, although it requires supervision. Biological desulfurization also needs a steady biogas composition. This is often not the case. The biogas plants can have a fluctuating H\textsubscript{2}S production due to the variation in the feedstock. The biological desulfurization is therefore not capable of deep-cleaning and must rely on an expensive backup filters. This is a drawback to the biological desulfurization.

Furthermore, the biological desulfurization method requires the addition of oxygen for regeneration of the bacteria. It results in presence of oxygen in the produced purified biogas. This is highly unwanted for both first and second generation upgrading of biogas:

First generation upgrading of biogas produces biomethane by removing the CO\textsubscript{2} from the biogas. The biomethane is often used for injection into the natural gas grid. The injection has strict requirements for the O\textsubscript{2} content in the biomethane, as O\textsubscript{2} is highly unwanted [9,10].
For second generation upgrading the oxygen problem is present, but to some extend less severe. The O₂ added will react with hydrogen (H₂) and form water, which is unwanted both due to increase in reactor temperature and lowering of the energy efficiency.

In our previous work, we proposed a new process for removal of H₂S by combining electrochemistry and scrubbing in an electroscrubber [11]. It is a selective oxidative scrubber that removes H₂S by oxidation to pure sulfur. The scrubber is combined with an electrochemical cell where the oxidation agent is regenerated.

The electroscrubbing process has several advantages over the existing desulfurization technologies. An electroscrubbing process is highly flexible. The applied potential and resulting current can be changed to adjust the process to the H₂S concentration. Furthermore, the electroscrubbing process do not generate O₂.

The proposed reaction mechanism for the chemistry in the electroscrubber for removal of H₂S, are [11]

**Anode [12]:**
\[ 2Cl^- = Cl_2(aq) + 2e^- \]  
Eq. 1

**Cathode:**
\[ 2H^+ + 2e^- = H_2 \]  
Eq. 2

It is beneficial to operate at medium or low pH-values. Here, Cl₂ will spontaneously react with water [13]:
\[ Cl_2(aq) + H_2O = HCl + HClO \]  
Eq. 3

The CH₄ may be considered inert, while the CO₂ will saturate the liquid by dissolution. The low pH range will not give rise to carbonate formation. Only bicarbonate is expected to form in low amounts:
\[ CO_2(g) = CO_2(aq) \]  
Eq. 4
\[ CO_2(aq) = HCO_3^- + H^+ \]  
Eq. 5

Within the scrubber, the electrolyte and H₂S will interact as the H₂S is expected to dissolve and dissociate [14] and subsequently it is oxidized either by hypochlorite or dissolved Cl₂:
\[ H_2S(g) = H_2S(aq) \]  
Eq. 6
\[ H_2S(aq) = HS^- + H^+ \]  
Eq. 7
\[ HS^- + HClO = S + H_2O + Cl^- \]  
Eq. 8
HS^- + Cl_2(aq) = S + HCl + Cl^-  \hspace{1cm} \text{Eq. 9}

The elemental sulfur formed is insoluble in the electrolyte [15]. It floats on the surface of the electrolyte due to surface tension, from where it can be skimmed off. If the sulfur is not removed, it may be further oxidized to sulfate. The sulfur to sulfate oxidation are considered slow when compared to the sulfide to sulfur oxidation [16]. If the sulfur is further oxidized it may happen either by the consumption of excess HClO or Cl_2:

\[
S + 3\text{HClO} + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 3\text{HCl} \hspace{1cm} \text{Eq. 10}
\]

\[
S + 3\text{Cl}_2 + 4\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 6\text{HCl} \hspace{1cm} \text{Eq. 11}
\]

These reactions consume addition 3 active oxidation compounds per sulfur atom, and thus, these reactions are highly unwanted due to the lowering of the overall process energy efficiency. Furthermore, the formation of H_2SO_4 will decrease the pH value and dilute the electrolyte, both of which are expected to lower the efficiency of the process.

Following the promising results from recent laboratory work [11] a pilot plant has been constructed for validation of the process. In this paper, the main results from the pilot plant are presented and discussed.
2. Materials and Methods

A pilot-system was constructed with the main parameters summarized in Table 1. The overall pilot design is shown in Figure 1. A 50 cm scrubber with a diameter of 31.5 cm was used, as 5 Nm³/h of raw biogas was cleaned using 0.78 m³/h of electrolyte. The system was created for gas flows up to 26 Nm³/h, however, due to limitations elsewhere in the set-up, the gas flow was limited to 5 Nm³/h throughout the experiments.

Table 1: The main design parameters of the pilot setup.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Rate</td>
<td>5 Nm³/h</td>
</tr>
<tr>
<td>Space velocity</td>
<td>128 h⁻¹</td>
</tr>
<tr>
<td>Liquid flow rate</td>
<td>780 L/h</td>
</tr>
<tr>
<td>Bed height</td>
<td>50 cm</td>
</tr>
<tr>
<td>Bed volume</td>
<td>39 L</td>
</tr>
<tr>
<td>Chemical consumption</td>
<td>0</td>
</tr>
<tr>
<td>Electrical consumption</td>
<td>200 W - 700 W</td>
</tr>
<tr>
<td>Temperature</td>
<td>10 °C – 25 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>pH</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Loading rate gH₂S pr. m³ reactor pr. hour</td>
<td>90-580</td>
</tr>
<tr>
<td>Reaction time</td>
<td>28 s</td>
</tr>
<tr>
<td>Amount of electrolyte</td>
<td>20 L</td>
</tr>
</tbody>
</table>

2.1. The scrubbing system

A scrubbing tower was constructed using a PVC 315 mm diameter corrugated shaft from Wavin with an active height of 50 cm (39 L packing material). Polypropylene Koch-Glitch FLEXIRING® Random Packing, nominal size: 38 mm, void fraction 91 % and bulk weight 70 kg/m³ (according to the supplier) was used as packing material. The liquid was distributed using a shower/spray type of liquid distribution. The gas flow was monitored using a variable area flowmeter.
2.2. The liquid system

The electrodes used for regeneration of the oxidation medium were Titanium (ASTM B265) coated with a stable mix metal oxide (MMO) of Platinum Group Metals (PGM) and non-PGM supplied by MAGNETO special anodes B.V. The electrode dimensions being 300 mm × 350 mm and a thickness of 1.0 mm. The electrochemical reactor was operated with 3 cells with a distance of 4.0 cm between the plates. Initially, the electrolyte initially consisted of 20 L of demineralized water with $4.00 \times 10^3$ g NaCl. The current was applied by a standard power supply model RSP-3000-48 from MEAN WELL.

A seal-less mag drive pump, model DB5, from Finish Thompson with 2900 RPM made from corrosion protected elements (PVDF and PTFE) gave a liquid flow of 13 L/min throughout the system.

The redox potential and pH-value was measured continuously using sensors from OxyGuard International A/S. The sensors were calibrated before use by reference samples.

Figure 1: Overview of the electro-scrubber set-up.

2.2.1. CO₂ dissolution in the electrolyte

The aqueous electrolyte and the biogas interact. Besides the desulfurization process, CO₂ from the biogas will dissolve in the electrolyte resulting in a lowering of the pH-value (Eq. 4 and 5, respectively). An
important requirement of the desulfurization processes, for second generation biogas upgrading, is to let the CO$_2$ remain in the desulfurized biogas. The purpose of the biogas upgrading it to reduce CO$_2$ into a valuable end-product. Therefore, the desulfurization process has been designed in order to ensure that CO$_2$ do not interact with the aqueous phase. This is obtained through the application of low pH. This prevents the CO$_2$ from leaving the system through absorption into the liquid or from carbonate precipitation. Thus, the electrolyte will be saturated with a small amount of CO$_2$, reaching an equilibrium with the CO$_2$ content in the biogas. Once this equilibrium has been reached within a short while of operation, no more CO$_2$ will be absorbed. The saturation by CO$_2$ is expected to have little impact on the results.

2.2.2. Filtration

Initially, the pilot was equipped with a filtration unit. However, during initial experimentation, the severe corrosion caused by H$_2$S damaged the filtration unit beyond functionality. Following the removal of the initial filtration system, no other system was installed. Without a functioning filtration unit, the sulfur generated (Eq. 8 and 9) is slowly accumulating on the system. The amount of sulfur formed during the testing was not significant. The sulfur production was in the order of a few grams per hour, and the electrolyte was changed periodically.

2.2.3. Electrolyte development

The pH-value was observed to decrease and stabilize around 1 during the testing. No filtration was applied, therefore reduced sulfur may have oxidized to sulfate by reaction Eq. 10 and 11. These reactions are expected to result in a further acidification of the electrolyte. This may explain the decreasing in pH-value during operation.

Unplanned maintenance of the scrubbing system resulted in interaction between the electrolyte and atmospheric air a few times during the experimental period. This resulted in an increase in pH-value as CO$_2$ was removed from the liquid. These increases in the pH-value were quickly neutralized once the desulfurization experiments were resumed. The analysis shows clearly if the results may have been prone to bias from oxygen contamination. There were no bias.

2.3. Biogas compositional measurements

The gas compositions entering and exiting the desulfurization system were measured with an MRU SWG 100 stationary biogas analyzer, where the CO$_2$ is measured between 0-100 % ± 0.3 % using NDIR. H$_2$S is measured electrochemically between 0-10.000 ppm ± 50 ppm and O$_2$ is also measured electrochemically, although between 0-21 % ± 0.2 %. For each desulfurization experiments, at least 4 measurements were
made after reaching steady-state. Typically, steady state was attained after 10 minutes. This timeframe is also found in the literature [17,18]. The standard deviation of the steady state period was used as uncertainty of the measurements, in case it was larger than the uncertainty of the analysis equipment.

Additional gas analysis was performed by an external gas laboratory, Danish Gas Technical Centre. Gas samples were taken before and after the desulfurization pilot-unit using Tedlar® sampling bags. The external gas analysis was performed using a combination of a gas chromatograph with thermal conductivity detection (GC/TCD) and a thermal desorption gas chromatograph with a mass spectrometer (TD/GC/MS).

2.4. Scanning Electron Microscopy Analysis

Scanning Electron Microscope (SEM) Hitachi tabletop TM3000 equipped with an Energy Dispersive X-ray (EDX) detector was used for imaging and analyzing the chemical composition of the produced sulfur. The elemental analysis was made by 15 kV energetic electrons.
3. Results and discussion

3.1 Basic definitions

The dynamic data from a total of three days of the campaign is presented in the following sections. In order to have an in-depth understanding of the process, three graphs are shown for each experiment, see Figures 2, 3 and 4. The graphs are:

The first graph, Figures 2a, 3a and 4a, shows the continuous biogas composition measurements entering and exiting the desulfurization system. Abrupt changes in the biogas composition was expected, and high priority was given for documentation of potential H₂S removal and compositional changes at the inlet. CH₄ and CO₂ content of the biogas entering and exiting the desulfurization unit remained the same throughout the experiments, only the incoming concentrations are shown, which are identical to the exit composition.

The second graph, Figures 2b, 3b and 4b, shows the measured electrolyte condition, in terms of applied potential (U), resulting current (i), and pH-value. The applied potential is the only value that is actively controlled. Due to the constant interaction between biogas and electrolyte, the conductivity and pH-value changes both between and within experiments.

The third graph, Figures 2c, 3c and 4c, shows how the system is being operated. Here, the redox potential of the liquid is presented. The redox potential gives a clear indication of the condition of the electrolyte, i.e. the potential to oxidize H₂S. A value which is directly measured using the redox sensors. The removal efficiency (ΔS) is also presented. This value is calculated using simple mass balance principles, based on gas side H₂S concentrations, entering and exiting the system:

$$\Delta S = \frac{y_{\text{sulfur}}(\text{in}) - y_{\text{sulfur}}(\text{out})}{y_{\text{sulfur}}(\text{in})}$$

Eq. 12

where, $y_{\text{sulfur}}$ is the H₂S mole fraction in the biogas.

The amount of electrical energy used relative to the theoretically needed energy, is calculated as a measure of system efficiency. The applied current ($i$) is compared to the theoretic minimum current ($i_{\text{theory}}$), given by $i/i_{\text{theory}}$. $i_{\text{theory}}$ is calculated using Faraday’s law [19]:

$$i_{\text{theory}} = \frac{n_{\text{sulfur}} z F}{e} = y_{\text{sulfur}} \frac{p G_v}{RT} z F,$$

Eq. 13

where $n_{\text{sulfur}}$ is the mole amount of H₂S, $z$ is the amount of electrons required to oxidize H₂S ($z=2$, see Eqs. 1, 2 and 8), $F$ is Faraday’s constant, $p$ is the pressure, $G_v$ the volume gas flow, $R$ the gas constant and $T$ is the temperature. The gas is assumed ideal since the pressure is approximately 1 atmosphere.
The current efficiency \((S/i)\) is calculated as the absolute amount of sulfur removed \((S)\) compared to the applied current \((i)\), where \(S\) is calculated based on mass balance from sulfur on the gas side, as:

\[
S = (y_{\text{sulfur (in)}} - y_{\text{sulfur (out)})} \frac{PV}{RT} M_{\text{sulfur}},
\]

Eq. 14

Where \(M_{\text{sulfur}}\) is the molar mass of \(\text{H}_2\text{S}\). This value indicates the efficiency of the system and can be compared across experiments with different biogas compositions.

These three graphs are used to give an overview of the performance of the electroscrubbing process during the campaign.

### 3.2. Desulfurization of Biogas

Figure 2a shows the biogas entering and exiting the system over the course of 5.5 hours of experiments. The biogas entering the system is observed to have a composition of \(\sim 70\% \text{ CH}_4, \sim 30\% \text{ CO}_2\) and \(\sim 1750\) ppm \(\text{H}_2\text{S}\). After less than 2 hours of experimentation, the \(\text{H}_2\text{S}\) content is removed to below the detection level in the cleaned biogas.

In Figure 2b, the electrolyte condition during the experiment is presented. Following 1.5 hours of adjusting the applied potential, it is kept constant at 13 V throughout the experiment. This potential is observed to be sufficient to remove the \(\text{H}_2\text{S}\) in the biogas. The current follows the applied potential and fluctuates slightly once the constant voltage is applied. The current stabilizes around 42 A following 2.5 hours of constant applied voltage. Throughout the experiment, the pH-value is constant between 0.9-1.

A constant redox potential is obtained at a value of 1100 mV. This is maintained shortly after the applied potential is adjusted to 13 V. Thus, it is observed that a stable redox potential is obtained before stabilization of other parameters, e.g. current and \(\text{H}_2\text{S}\) content in the cleaned gas.

The dependency of \(S\) on \(i\) is investigated further in Figure 2c. Here, the amount of sulfur removed relative to the concentration \((\Delta S)\) and the amount of sulfur removed per ampere hour \((S/i)\) is plotted throughout the experiment. Following a steady increase during the first 2 hours of experimentation, 100 % of the sulfur is removed. However, the \(S/i\) value reaches a steady value following after only 0.5 h into the campaign, as \(0.277 \pm 0.006 \text{ g A}^{-1} \text{ h}^{-1}\) sulfur is removed. A small decrease in \(S/i\) is observed once 100 % removal rate is achieved. The explanation is related to the non-optimized power consumption. In this campaign the objective was to prove the feasibility of sulfur removal. Energy consumption for 100 % sulfur removal is expected to be lower than the applied current in future experiment campaigns, as the electrochemical cell will be optimized.
Figure 2: Dynamic data from an experiment with removing sulfur down to below the detection limit. 

a) The biogas composition. b) The electrolyte condition. c) The operation parameters of the electroscrubber.
3.3. Constant applied potential and varying H₂S concentrations

As discussed in section 2.3, the biogas composition may fluctuate. Figure 3a shows the results from a pilot campaign performed which included large fluctuations in the biogas composition. During the first 3 hours, the CH₄ and CO₂ content remains constant. The H₂S content increases from 650 to 900 within the first 1.5 hour and then from 900 to 1000 within the following 1.5 hour. Nevertheless these changes are small compared to the sudden shift in concentrations after 3 hours where the CH₄ content decreases from 70% to 63%, while the CO₂ content increases from 28% to 34%. The largest change in concentration, is the H₂S content that increases from 1000 ppm to 2600 ppm within a time span of 20 minutes (which is the interval between measurements). The concentration continues to increase to 3000 ppm within 1 hour, after a total of approximately 4 hours into the campaign. In parallel, the H₂S content in the cleaned biogas increases from 100 ppm to 1500 ppm and later to 1700 ppm. This clearly indicates that a deep-desulfurization system need to be able to handle abrupt changes in the biogas composition. The current system will be able to handle this variability with an expense of higher use of current to produce more oxidation agent.

The applied potential was kept constant to investigate the effect on the system. In Figure 3b, the applied potential is shown to be constant at 8.9 V throughout the campaign. The resulting current is not constant. The explanation is as follows: During the first three hours of experimentation, the current increases from 20.5 A to 24.5 A. Following the change in biogas composition, the current increases even faster, from 24.5 A to 29.9 A within 1.5 hour. The pH-value follows the same trend. The pH-value decreases from 1.2 to 1.0 before the change and decreases faster from 1.0 to 0.8 after the change. The increase in current is linked to a decrease of the liquid resistance of the entire system, and the change in pH-value clearly indicates that the electrolyte is not in a stable condition during the experiment.

In Figure 3c, the parameters are presented which characterize the H₂S cleaning efficiency. At the first 2 hours of desulfurization the redox potential, the removal rate, the removal efficiency, and the current compared to the theoretical expected current are observed to have obtained stable steady-state values. The stability is not expected based on the electrolyte condition, where the pH-value and current is not stable. However, the H₂S content increases at the same rate as the current. This makes the $\frac{i}{i_{\text{theory}}}$-value become constant. With the $\frac{i}{i_{\text{theory}}}$-value constant, the $\Delta S$, $S/i$ and the redox potential of the liquid also obtains stable values following the first 2 hours of experimentation.

Based on these results, it may be expected that the system requires 2 hours of operation before stable conditions are met. Once the run-in time is over, the system responds to changes within 10 min. Prior to
this experiment, the system had been idle for 10 days. This could be part of the explanation behind the run-in time.

Following the sudden change in biogas composition, see Figure 2, $\Delta S$, the redox potential and $i/i_{\text{theory}}$ decreases significantly to approximately half of the value before the change in composition. However, $S/i$ is observed to increase. In the previous work, it was found that the $S/i$ value kept constant across different parameters evaluated. This do not seem to be the case here, as the $S/i$ value is increased with almost 50%. Although it was not found with the parameters previously tested, it is expected that large concentrations of $\text{H}_2\text{S}$ benefits the desulfurization due to the larger partial pressure, hence activity of $\text{H}_2\text{S}$. 

Figure 3: The experimental data from an experiment with constant applied potential. a) The biogas composition. b) The electrolyte condition. c) The operation parameters of the electroscrubber.
3.4. Adjusting potential to the H$_2$S concentration

An important issue for desulfurization of biogas is the ability for the process to follow changes in biogas inlet composition. In Figure 2, it is observed that rapid changes in biogas composition may occur. Besides being able to follow increases in H$_2$S concentration, the process should also be able to follow decreases. This is important in order to achieve a high energy efficiency and avoid unwanted side reactions within the system.

In Figure 4a, the biogas composition is presented together with the amount of H$_2$S in the cleaned biogas. It is observed that the H$_2$S content changes from 1000 ppm up to 1600 ppm and down to 1200 ppm throughout the day and that the CH$_4$ and CO$_2$ content also fluctuates. Following the initial hour of experimentation, the H$_2$S content in the cleaned biogas reaches a non-detectable level when the cleaning process is put into effect. It remains low for more than 5 hours.

Figure 4b explains what happens in the process. It shows process variables similar to Figure 2b and 3b. The applied potential is deliberately varied throughout the experiment. Initially it is set to increase until a complete removal of H$_2$S is achieved. This initial adjustment of the applied potential is a clear indication that the cleaning system can be adjusted to match the current H$_2$S content. The same initialization of the system was performed in Figure 3b where 13 V was found to be required for complete removal, where in Figure 4b 11.5 V is found to be enough for removal down to below the detectable limits. Once this is achieved, the applied voltage is decreased in order to find the amount of energy required for complete removal without excess energy consumption. However, the estimation of the optimum process parameters are continuously disturbed as the experiment is performed during 5 hours of fluctuating H$_2$S content.

In Figure 4c the cleaning parameters from the experiment are presented. The changes in applied potential clearly result in changes in the current, following the increase to an $i/i_{\text{theory}}$ value of 6, the current is decreased and $i/i_{\text{theory}}$ ends at a value of 2.9. Following the initial increase in the current, the cleaning rate ($\Delta S$) reaches 100% and remains there until the experiments was terminated. The measured redox potential of the electrolyte is again indicating a stable process since the cleaning rate since it reach a stable and high potential after 1.5 hours after which the potential steadily decreases following the decrease in the current. For the final data point, the redox potential has decreased down to 1070 mV which apparently is not enough to ensure complete removal of H$_2$S to below the detection limit. From previous experiments, the removal rate $S/i$ is known to be the parameter which requires the most time with constant values for stable results. As both the H$_2$S content and applied potential varies throughout this experiment, these criteria are not met. It can, however, be observed that $S/i$ increases as the current decreases while $\Delta S$ remains at 100% and a maximum value of 0.18 g h$^{-1}$ A$^{-1}$ is achieved.
Figure 4: Dynamic data from experiment with adjusting the applied potential. a) The biogas composition. b) The electrolyte condition. c) The operation parameters of the electroscrubber.
3.5. Static conditions

In the results presented above only dynamic data are analyzed, however, comparing desulfurization across experiments, stable conditions are required. During the three experiments presented in the previous sections, only three stable points were achieved:

- Figure 2 from 2 hours to 5.5 hours
- Figure 3 from 2.2 hours to 3.4 hours
- Figure 3 from 3.6 hours to 5 hours

These static conditions have been treated as single data points and are compared with data from other experiments as static data in Figure 5.

In Figure 5a, the amount of removed sulfur ($S$) is compared with the applied current. In our previous work [11], $S$ was found to be directly linearly linked to the applied current across experimental conditions. This is not the case here. $S$ increases with current, however, not linearly. There may be several reasons for this, with the perhaps best explanation being that upon applying more than 25 A, the system leaves the area where $S$ is linearly dependent on $i$.

In Figure 5b the removal rate ($\Delta S$), it is observed that it increases initially, reaching complete removal at $i/i_{\text{theory}} = 6$. For higher values, $\Delta S$ remains constant. This could indicate that mass transfer or reaction kinetics limits the pollutant removal process.

**Figure 5**: Results from experiments with stable steady-state conditions. a) The absolute amount of sulfur removed ($S$) compared with the applied current ($i$)  b) The removal efficiency ($\Delta S$) compared with the current compared with the theoretical current ($i/i_{\text{theory}}$).
3.5.1. Sulfur content in desulfurized biogas

As the detection limit during normal operation was rather high, i.e. 50 ppm, an external gas analysis was performed in order to estimate the actual H₂S content in the purified biogas. Unfortunately, the analysis was performed at a period in time when the biogas plant had added iron chloride to the reactor and the H₂S content therefore was not high, i.e. 221 mg/m³ = 160 ppm.

In Figure 6, the results of the external analysis are presented. The first sample was taken directly before the system, while the second sample was taken directly after the system, both samples were collected in Tedlar® sampling bags. The sulfur content is observed to be 221 mg/m³ = 160 ppm before the pilot-unit and below the detectable level after the pilot-unit. Of other contaminants, only siloxanes are detected, as both octamethylcyclotetrasiloxane (D₄) and decamethylcyclopentasiloxane (D₅) are present with 17 mg/m³ and 8 mg/m³, respectively. Siloxanes, especially D₄ and D₅, are known to be present in biogas [20]. These contaminants could not be measured with the gas analysis equipment used during normal operation and was therefore not known to be present in the raw biogas prior to the external analysis. However, both D₄ and D₅ were removed with 76% and 75%, respectively.

The main gas components are showed to remain the same following the desulfurization. The nitrogen/argon (N₂/Ar) and O₂ content is seen to increase in a total amount of 1.40 mol-% which could be explained by a small dilution by atmospheric air. This claim is supported by the distribution of the increased mol-%, as the N₂ content is increased by 79.3 % (1.11 mol-%) of the added gas and O₂ is increased by 20.7 % (0.29 mol-%) of the added gas. Meanwhile, the CH₄ and CO₂ contents are decreased by 1.42 mol-%. Here, the CH₄ content is responsible for 56.3 % (0.80 mol-%) of the decrease and the CO₂ content is responsible for 43.7% (0.62 mol-%) of the decrease. This is not distributed equally according to the initial concentrations, however, it is expected that CO₂ is constantly interacting with the electrolyte which could explain why more CO₂ is removed as compared to CH₄. Either way, the changes of the main gas components are not that large.

The deviation due to dilution of air is used as uncertainty for the external analysis. Besides the elements quantified, significant amounts of chemical residues were detected in the purified biogas. These elements were not further quantified and consisted mainly of HCl and Cl₂. These compounds are highly unwanted and must be removed or avoided. It is expected that better process control will result in a significant decrease in the concentration of the unwanted chemical residues in the desulfurized biogas.
a) Results from the external gas analysis. a) The main gas components entering and exiting the system. b) The impurities of the biogas entering and exiting the system.

3.5.2. Solid compounds

As mentioned, the initial pilot-unit was equipped with a filtration unit in order to remove the solid compounds formed during the desulfurization process. However, following only a few hours of operation, the filtration unit was corroded beyond functionality and no replacement filtration unit was implemented. Thus, for the experiments presented in this paper the electrolyte was not continuously filtrated.

Solid samples were collected during decommissioning of the system. A brown/yellowish solid that proved to be sulfur was present in the system. The greatest amount was present in the water lock where the filtration unit was initially installed, although samples were also collected from other places in the system. In Figure 7 shows a SEM picture of the collected sulfur together with an elemental map of the different elements detected. Sulfur was the main component, with traces of the electrolyte (NaCl) present. Silicon was also detected to a lesser extent. These results strengthen the hypothesis that the siloxanes in the raw biogas also were removed by oxidation as a solid silicon compound was formed. From the literature, it may be expected that siloxanes are oxidized to SiO₂ [21].
Figure 7: a) SEM picture of the solid sulfur extracted from the system. The EDS-analysis showed that the solid consisted mostly of sulfur. b) Sulfur distribution. c) Electrolyte (NaCl) distribution. d) Silicon distribution.
4. Conclusion

The desulfurization process was found to be remove H$_2$S from a real on site biogas stream of 5 Nm$^3$/h. No additional oxygen was measured throughout the experiments and the main gas components CH$_4$ and CO$_2$ were not affected by the cleaning system during steady-state operation. The H$_2$S was removed down to level below the detection limits using only an applied potential.

The desulfurization system was found to be agile and could easily be adjusted to the incoming H$_2$S content by adjusting the applied potential. While the H$_2$S content is immediately decreased upon adjusting the potential, it was observed that could take up to 2 hours for stable conditions to be met throughout the system on measured parameters.

Analyzing the steady-state conditions, it was found that a $i/i_{\text{theory}}$-value close to 6 provides the best process parameters, as 0.1 g sulfur per ampere per hour is removed, resulting in a complete removal of H$_2$S.

Elemental sulfur was found within the system, supporting the suggested sulfide oxidation reactions. EDS-analysis of the reduced sulfur revealed trace amounts of the electrolyte and silicon. The silicon may be the result of removal of siloxanes.

An external gas-analysis showed that the H$_2$S content was below 0.5 ppm in the purified biogas. The analysis furthermore revealed that 76% and 75% of siloxanes D4 and D5 were removed, respectively. The external gas analysis also showed that there were significant unwanted chemical residues present in the purified biogas from the electrolyzer. These unwanted chemical residues will have to be addressed in the future work with the process but are expected to be minimized by properly adjustment of the electrochemical parameters.

Acknowledgements

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Appendix V

Holistic Biogas Desulfurization within the MeGa-StoRE Project
Holistic Biogas Desulfurization within the MeGa-StoRE Project

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Abstract

A holistic biogas desulfurization system was tested at pilot scale as part of the MeGa-StoRE project. In this project, biogas is converted to natural gas through thermochemical methanation over a catalyst, and the main goal of the desulfurization system was to protect the catalyst from hydrogen sulfide (H\textsubscript{2}S). Part of the overall project goal was to develop a new desulfurization technology that would completely remove H\textsubscript{2}S while not generating waste or using toxic chemicals. In this work, the results from this development are presented. The system was designed to minimize human interaction as automatic processes ensured continuous operation. The desulfurization technology removed H\textsubscript{2}S down to non-detectable concentrations in a single step, as a scrubbing tower height of 0.8 m was used to remove H\textsubscript{2}S concentrations of 1000 ppm – 1600 ppm in biogas flows of 48 L/min to 105 L/min. The system used only electricity and had no waste production as sulfur was the only bi-product. The system was found to have the highest current efficiency of 0.108 ± 0.006 g sulfur per. ampere hour. At this value, a 100\% removal of the detectable H\textsubscript{2}S was also obtained. The sulfur extracted from the system was found to consist mostly of sulfur with trace amounts of salts from the electrolyte. The overall power consumption of the process was found to be 22.7 kWh per kg of sulfur removed, before optimization.
1. Introduction

The biogas market is growing in Europe [1]. As the European gas network is trying to limit their dependency on fossil fuels, biogas is growing in importance and may be the largest contributor of gas to the grid in both the UK the Netherlands by 2040 [2]. However, as the natural gas consumption in EU in 2015 was 416 billion Nm$^3$ and the potential biogas production estimated to only be able to cover 18.7% of this, there is an energy gap to be closed if biogas should replace natural gas in Europe [3,4].

Biogas consists of 48% to 65% methane (CH$_4$) and 36% to 41% carbon dioxide (CO$_2$) with different trace elements [5]. As CO$_2$ reduces the burning value by diluting the CH$_4$, biogas is considered a low quality gas, and the many impurities must be removed before injection into the natural gas grid [6,7]. The process of purifying the CH$_4$ from the biogas is referred to as first generation biogas upgrading [8]. The amount of first generation upgrading plants throughout Europe is growing with 540 plants in 2017 [1].

In first generation biogas upgrading, CO$_2$ is the main impurity and is removed by conventional carbon capture technologies, such as membrane, pressure swing adsorption, amine/water scrubbing or cryogenic technologies [9,10]. The CO$_2$ is then vented into the atmosphere, leaving the purified methane, called biomethane, to be injected into the natural gas grid [11]. However, second generation of biogas upgrading with more advanced applications of biogas is under development [8].

In the second generation biogas upgrading, the biogas is considered a carbon source and the CO$_2$ content of the biogas is therefore used [8]. The main advantage of using biogas a feed gas for Carbon Capture and Utilization (CCU) processes, is the fact that the energy consuming carbon capture process is not necessary as biogas already consists almost entirely of carbon based gases. Generally, the utilization of CO$_2$ from biogas may be directly compared to other CCU technologies, as the biogas plant may be considered the carbon capture plant.

The main difference between biogas and the CO$_2$ from carbon capture plants is the large amount of CH$_4$ present in biogas. Directly conversion of the CO$_2$ over a copper catalyst to form either methanol or other organic compounds may therefore not a valid option, as the CH$_4$ has to be converted to syngas before the synthesis [12]. However, if the biogas is converted into a syngas, the CH$_4$ will add valuable H$_2$ to the system during the reforming process. Conversion of biogas to syngas allows for production of liquid organic compounds, such as methanol [13].

The high selectivity and efficiency of the methanation catalyst allows for another option [14]. Conversion of CO$_2$ to CH$_4$ is possible through the Sabatier process [15].

$$\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta G_{300^\circ C} = -61.1 \text{ kJ/mol.} \quad \text{Eq. 1}$$
This process requires large amounts of hydrogen (H\textsubscript{2}) and has therefore been proposed as a method for storage of renewable energy through electrolysis [16]. A nickel catalyst is used for the Sabatier process and it is known to have a high selectivity and conversion [17]. Due to these properties, conversion of a CH\textsubscript{4}/CO\textsubscript{2} gas mixture to pure CH\textsubscript{4} is possible [18].

For biogas utilization, the Sabatier process has several advantages. Firstly, the usual operating conditions of a Sabatier-reactor are close to ambient (350-400°C and down to atmospheric pressure [17]) and secondly, only a single process is required for the upgrading. For comparison, methanol production from biogas requires two processes (reforming and synthesis) with usual operating conditions of up to 830-910°C and 50-100 bar [19]. However, there are also disadvantages: the Sabatier reactor requires large amount of H\textsubscript{2} and the nickel catalyst is highly sensitive to H\textsubscript{2}S [20,21].

H\textsubscript{2}S is the main impurity in biogas, with concentrations up to 10,000 parts per million (ppm) [22]. Independently of the downstream application, H\textsubscript{2}S has to be removed from the biogas [23]. The biogas applications of today, i.e. heat and power generation or first generation upgrading, requires the H\textsubscript{2}S content of the desulfurized biogas to be <500 ppm and <4 ppm respectively [24]. However, for second generation utilization of biogas with a nickel catalyst, the H\textsubscript{2}S content of the biogas is required to be down to 10-100 parts per billion (ppb) [25]. If the H\textsubscript{2}S is not removed from the biogas, it will deactivate the nickel catalyst by the deactivation reaction [26]:

\[
\text{H}_2\text{S} + \text{NiO} = \text{NiS} + \text{H}_2\text{O} \quad \Delta G_{300^\circ C} = -48.5 \text{ kJ/mol},
\]

Eq. 2

Thus, for second generation utilization of biogas, further reduction of the H\textsubscript{2}S content is required when compared with the technologies of today.

1.1 Desulfurization within the MeGa-StoRE Project

In this paper, the desulfurization results from the Methane Gas for Storage of Renewable Energy (MeGa-StoRE) demonstration project is presented. In Figure 1, the project processes are presented, as the thermochemical catalytic methanation upgrading of biogas is performed downstream the desulfurization. The overall project goal was to demonstrate second generation biogas upgrading through the Sabatier process. Part of the project goal was to develop a new desulfurization process to meet the requirements of the nickel catalyst used in the thermochemical upgrading process.

One of the main goals of the new desulfurization process was to avoid waste products. In order to achieve deep removal of H\textsubscript{2}S from biogas, absorbers are often used [27]. Generally, the spent absorbers must be
disposed as waste due to their absorption of H$_2$S. This is not sustainable for large scale implementation of second generation biogas upgrading.

The process developed is based on an oxidative scrubber for oxidation of H$_2$S to elemental sulfur. The elemental sulfur is then removed from the oxidative liquid by a filter, and the oxidative compound of the liquid is regenerated in an electrochemical cell. In this way, the electrolyte can be reused in a closed loop where the only added chemical is electrical energy. The sulfur is extracted as elemental sulfur which, depending on the quality, may be used as a fertilizer. Early results from this process have been presented elsewhere. The suggested chemical reactions within the reaction are:

**Anode** [28]:

$$2\text{Cl}^- = \text{Cl}_2(\text{aq}) + 2e^-.$$  
Eq. 3

**Cathode:**

$$2\text{H}^+ + 2e^- = \text{H}_2,$$  
Eq. 4

where the dissolved chlorine (Cl$_2$) may spontaneously react with the water, depending on the pH-value [29]:

$$\text{Cl}_2(\text{aq}) + \text{H}_2\text{O} = \text{HCl} + \text{HClO},$$  
Eq. 5

Inside the scrubber, the hydrogen sulfide is expected to dissolve and dissociate [30]:

$$\text{H}_2\text{S}(\text{g}) = \text{H}_2\text{S}(\text{aq}),$$  
Eq. 6

$$\text{H}_2\text{S}(\text{aq}) = \text{HS}^- + \text{H}^+,$$  
Eq. 7

and subsequently being oxidized, either by hypochlorite or dissolve chlorine:

$$\text{HS}^- + \text{HClO} = \text{S} + \text{H}_2\text{O} + \text{Cl}^-,$$  
Eq. 8

$$\text{HS}^- + \text{Cl}_2(\text{aq}) = \text{S} + \text{HCl} + \text{Cl}^-.$$  
Eq. 9

The elemental sulfur is then removed from the liquid in a filtration unit and the electrolyte regenerated.

In this paper, desulfurization results from the final demonstration of the MeGa-StoRE project is presented. The desulfurization process has previously been tested in the laboratory and on real biogas [31,32]. However, for the final demonstration in the MeGa-StoRE project, a complete redesign of the cleaning unit was performed in order to optimize the process.
Figure 1: The MeGa-StoRE project. Top: the MeGa-StoRE container situated at the Midtfyn biogas plant. Within the container, a pilot plant desulfurization system and methanation system are present. Gas tubes are observed to connect the container with the biogas digestion tank and another set of tubes connect the container with the electrolysis container not pictured. Bottom: The MeGa-StoRE project goal, to convert raw biogas to natural gas through thermochemical upgrading by the utilization of renewable H₂.
2. Materials and Methods

A pilot scale scrubbing set-up was developed and constructed for the experiments on real biogas. The set-up was based on a previous tested set-up [32]. The main parameters of the demonstration unit are presented in Table 1, where they are compared with the previous set-up.

Table 1: Parameters of the pilot demonstration plant developed and tested in this paper. The demonstration plant is compared with previous work [32]. The new set-up was designed for higher flows, however, experimental conditions limited the gas flow rate of the system.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This work</th>
<th>Previous work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Rate</td>
<td>50-120 L/min</td>
<td>83.3 L/min</td>
</tr>
<tr>
<td>Space velocity</td>
<td>48-116 h⁻¹</td>
<td>128 h⁻¹</td>
</tr>
<tr>
<td>Liquid flow rate</td>
<td>12.5 L/min</td>
<td>13 L/min</td>
</tr>
<tr>
<td>Scrubber diameter</td>
<td>31.5 cm</td>
<td>31.5 cm</td>
</tr>
<tr>
<td>Bed height</td>
<td>80 cm</td>
<td>50 cm</td>
</tr>
<tr>
<td>Bed volume</td>
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<td>39 L</td>
</tr>
<tr>
<td>Chemical consumption</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Electrical consumption</td>
<td>100 W - 660 W</td>
<td>200 W - 700 W</td>
</tr>
<tr>
<td>Temperature</td>
<td>20 °C - 35 °C</td>
<td>10 °C – 25 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>Atmospheric</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>pH</td>
<td>0.8-1.2</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>Loading rate gH₂S pr. m³ reactor pr. hour</td>
<td>50-151</td>
<td>90-580</td>
</tr>
<tr>
<td>Reaction time</td>
<td>31-75 s</td>
<td>28 s</td>
</tr>
<tr>
<td>Amount of electrolyte</td>
<td>27 L</td>
<td>20 L</td>
</tr>
</tbody>
</table>

The aim of the new demonstration unit was to develop a pilot set-up that could run continuously with minimal human interaction for a prolonged period of time. Emphasis was therefore put into designing the pilot plant to be completely automatic. This was achieved through implementation of multiple capacitance sensors, programmed valves throughout the system and several fail-safe conditions, e.g. increased resistance and insufficient liquid for the pump.

Besides the redesign to make the system automatic, several other components were improved or changed, including:
• Implementation of a filtration unit
• See-through window for visual inspection of the scrubbing tower
• Power supply with more suitable specifications in order to control the process better
• Fewer electrochemical cells which minimizes cross current uncertainties
• Better dimensioning of liquid and gas tubes

These improvements let to better control of the system and fewer uncertainties. Another main change between the two systems is the gas analysis equipment described below.

As the desulfurized biogas was used downstream, a polishing unit was implemented as well. Here, activated carbon was used to remove H₂S if any was left following the scrubbing system. The analysis of the desulfurized biogas was performed upstream the polishing filter, see Figure 2.

2.1 Scrubbing System

A corrugated polyvinyl chloride (PVC) shaft with an internal diameter of 315 mm was used as scrubbing tower, see Figure 3. The tower had a total height of 1.0 m with 0.80 m of active height. Two see-through polycarbonate (PC) windows were added to the PVC shaft in order to allow for visual inspection during operation. The packing material was 15 mm x 15 mm polypropylene (PP) Koch-Glitch Raschig Pall Rings. A spiral nozzle was used to ensure the liquid distribution within the scrubber. The gas flow through the system was measured through a variable area flowmeter. Following the scrubbing tower, the biogas was cooled in order to remove excess water and electrolyte from the desulfurized biogas.

2.2 Liquid System

A continuous flow through electrochemical cell was constructed using mixed metal oxide coated titanium electrodes supplied by MAGNETO special anodes B.V. The submerged dimensions of the electrodes were 300 mm x 350 mm x 1.0 mm, with a solid connection outside the electrolyte. The electrochemical system was operated with 2 cells, consisting in total of three plates, with a distance of 4.5 cm between them. The potential was applied using a model RSP-3000-12 power supply from MEAN WELL.

The liquid system was constructed to be completely automatic. A system of capacitive sensors and automatic valves ensured that a constant amount of active electrolyte was kept in the system. The liquid removed from the desulfurized biogas was collected in a container with two automatic valves. One of these valves would open if the liquid system required additional liquid. The other valve would open if the collection container were completely full, draining the container only until a certain point. Liquid were always kept in the collection container if the electrolyte system should require it.
A bag filter was implemented in order to collect the elemental sulfur from the electrolyte. Bag filtration is a batch operation, which is not the ideal solution for a continuous flow system. However, it was not possible to find a suitable continuous filtration process for the size of the pilot plant. The liquid was pumped through the system using a single seal less mag drive pump (2900 RPM) from Finish Thompson, resulting in a flow of 12.5 L/min. The initial electrolyte consisted of 27 L demineralized water with 8.100 kg NaCl dissolved.

2.3 Gas Analysis

The apparatus employed for analyzing raw- and pre-cleaned biogas was a portable high-resolution multi-component FTIR analyzer (atmosFIR, Protea Ltd.). The gas analyzer consists of a 4.2 m path length aluminum cell coated with nickel, and pre-aligned coated mirrors. The optic consists of a zinc selenide beam splitter. The frequency range was from 750 cm\(^{-1}\) to 5000 cm\(^{-1}\) with an average of 10 scans at a resolution of 4 cm\(^{-1}\). The analyzer was calibrated at 60°C for biogas containing CH\(_4\), CO\(_2\), and H\(_2\)S up to 70%, 50%, and 5000 ppm respectively. The analyzer was also calibrated for siloxane content.

Dry N\(_2\) (99.99%) gas was purged into the cell at 1 bar gauge with a gas flow rate of 3 l/min. The cell was heated to 60°C to avoid water condensation on the cell-walls. Before carrying out sampling, a background spectrum was collected using dry N\(_2\). A manifold was connected to the FTIR in order to choose between raw- or pre-cleaned biogas. The sample flow was 2.5 L/min. The outlet exhaust gas was removed by the vacuum pump. The FTIR was designed to run with the Protea Analyzer Software (PAS). The software allows for continuous data logging of e.g. concentration, pressure, and temperature.

H\(_2\)S has a very weak infrared response [33]. Unfortunately, this results in rather large detection limits. For a freshly calibrated analyzer, the detection limit of H\(_2\)S was estimated to be between 30 ppm and 50 ppm by the supplier. For the experiments, an uncertainty of 50 ppm have been used for detection of H\(_2\)S at low concentrations.

2.4 SEM and EDS analysis

A tabletop TM3000 scanning electron microscope (SEM) from Hitachi equipped with an energy dispersive X-rays (EDS) is used for high-resolution imaging of the samples and EDS analyses. The SEM uses a focused electron beam to produce an image of the surface. Electrons are send in a focused electron beam at 15 kV towards the surface of the sample. The electrons interacts with the atoms at the surface, and send out signals that is detected by an electron detector. In this case, the detector detect the backscattered electrons.
For EDS, electrons at 15 kV are used. When the electrons from the beam are interacting with the surface it also send out X-rays that can be detected by a X-ray detector and the X-rays energy level is characteristic for the element from which it was emitted. By analyzing the energy levels of the X-rays, the elements in the samples can be determined.
Figure 2: The pilot set-up, as operated on the Midtfyn Biogas Plant. The corrugated orange shaft acts as the scrubbing tower (A) with see-through windows implemented. The gas enters at the bottom and leaves the scrubber to enter a condenser (B) where excess electrolyte is collected. A set of valves allows for adding from the collection tank to the liquid cycle in the bottom. The electrolyte enters a filter (C) after leaving the scrubber. Following filtration, the electrolyte enters the continuous current electrochemical cell (D) where the active oxidizing species is regenerated. The liquid is then pumped back into the scrubber. Points (1) and (2) indicate where the gas analysis points.
3. Results and Discussion

Two parameters were varied, i.e. the total biogas flow and the applied potential. Besides these parameters, also the raw biogas composition and conductivity of the electrolyte changed over time. The conductivity of the electrolyte was closely monitored, as the applied potential and resulting current were noted throughout the experiments. The raw biogas composition was measured periodically. Both values are presented in Figure 3, where the background color indicates the different experimental periods. The H$_2$S concentration in the raw biogas is observed to change a few % over the course of an hour, and the periodic measurements will capture this change in concentration. The main drop in H$_2$S concentration happens between two different days of experimentation.

The resistance of the system is observed to change more rapidly. During the first periods of experimentation, a gradual decrease in resistance of the system is observed, and during the third period the resistance is observed to change drastically over the course of minutes. The decrease in resistance of the system may be explained by a gradual increase in conductivity of the electrolyte. The electrolyte is expected to consist of a combination of several ions, e.g. Na$^+$, Cl$^-$, ClO$^-$, CO$_3^{2-}$, where the CO$_2$(aq)/CO$_3^{2-}$ is in an active equilibrium with the biogas. Due to this complex nature of the electrolyte, changes in conductivity are expected over time and constant measurements were used to ensure this gradual change was taken into account during data analysis. The rapid changes during the third period are suggested to be the result of the changes in current. Larger currents result in larger bubble generation, which limits the conductivity of the system. This suggestion is supported by the fact that the average resistance of the system seems to be constant.
Figure 3: The H$_2$S content of the biogas and the resistance within the system throughout different periods of experimentation. The green, orange and blue background indicate, respectively, period 1, 2, and 3 of experimentation. The H$_2$S content is observed to change only slightly within the time frame of the experiments, and these changes are caught by the periodic measurements. The resistance of the system is observed to change gradually during the first two periods, while

From previous work, it is known that static data are obtained once all measured quantities are constant. Throughout the experiments, the static data were obtained by measuring the inlet gas composition until the measured quantities of the liquid were stabilized, and the switching to measuring on the outlet gas composition. The stabilization time depended greatly on the relative change performed, with usual times of 10 min - 20 min before the measurements started, corresponding to changing the liquid in the system 5 – 10 times, followed by >10 min of analysis of the gas.
3.1 Static data

There are two parameters which are of the greatest interest, i.e. the current efficiency and the removal efficiency. The current efficiency \( (S/i) \) is calculated as the absolute amount of sulfur removed \( (S) \) compared with the applied current \( (i) \), where \( S \) is calculated as:

\[
S = \left( y_{\text{sulfur (in)}} - y_{\text{sulfur (out)}} \right) \frac{pV}{RT} M_{\text{sulfur}}, \tag{10}
\]

Where \( y_{\text{sulfur}} \) is the concentration of \( \text{H}_2\text{S} \) in and out of the cleaning system, \( p \) is the pressure, \( V \) is the volume, \( R \) the gas constant, \( T \) the temperature and \( M_{\text{sulfur}} \) is the molar mass of sulfur.

The removal efficiency is calculated as

\[
\Delta S = \frac{y_{\text{sulfur (in)}} - y_{\text{sulfur (out)}}}{y_{\text{sulfur (in)}}} \tag{11}
\]

Both these parameters are plotted against the applied current compared with the theoretical current. This is done to allow for comparison across experimental settings, e.g. gas flow and \( \text{H}_2\text{S} \) concentration. The theoretical current is calculated as:

\[
i_{\text{theory}} = \frac{n_{\text{sulfur}} z F}{t} = y_{\text{sulfur}} \frac{pV}{RT} z F, \tag{12}
\]

where \( n_{\text{sulfur}} \) is the amount of moles of sulfur, \( z \) is the amount of electrons involved in the oxidation process and \( F \) is Faraday’s constant.

The two parameters, \( S/i \) and \( \Delta S \), are important as \( S/i \) indicates the overall energy efficiency of the system and \( \Delta S \) shows how much of the sulfur is removed. For a successful process, both of these parameters must be optimized.

The current efficiency, \( S/i \), is expected to be highly dependent on the electrochemical cell design. An efficient electrochemical cell will decrease the amount of current required to generate the active components for the oxidation of the \( \text{H}_2\text{S} \). To more directly measure the efficiency of the electrochemical cell, an alternative parameter could be introduced as the amount of oxidizing agents generated per ampere. Such a parameter, however, would depend heavily on precise and continuous measurements of the concentration of the oxidizing agents before and after the electrochemical cell, which was not of
interest in this work. S/i gives an overview of the energy efficiency of the whole system, which is of great interest for a potential future applications.

For a biogas utilization pilot plant with a methanation reactor downstream, $\Delta S$ may be considered the most important parameter. As $\text{H}_2\text{S}$ is poison to the methanation catalyst, deep removal of $\text{H}_2\text{S}$ is required [20,21]. Therefore, operation of the desulfurization pilot have been focused on achieving a high removal efficiency, preferably 100%, during operation.
Table 2: Static data points obtained during stead-state operation of the desulfurization system. Limitations due to pressure drop in the piping meant that the gas flows investigated were lower than the designed flow of up to 700 l/min.

<table>
<thead>
<tr>
<th>$G$ [L/min]</th>
<th>$y_{H_2S\text{in}}$ [ppm]</th>
<th>$y_{H_2S\text{out}}$ [ppm]</th>
<th>$U$ [V]</th>
<th>$i$ [A]</th>
<th>$J$ [A/cm²]</th>
<th>$\Delta S$ [%]</th>
<th>$S$ [g/h]</th>
<th>$S/i$ [g A⁻¹ h⁻¹]</th>
<th>$\dot{i}/i_{\text{theory}}$</th>
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<td>6.0</td>
<td>55.5</td>
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<td>6.22</td>
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<td>100</td>
<td>5.72</td>
<td>0.054</td>
<td>11.09</td>
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</tbody>
</table>
3.1.1 Removal Efficiency

In Figure 4, the removal efficiency ($\Delta S$) is plotted against $i/i_{\text{theory}}$. Data from previous work [32], is plotted with the new data for comparison. It is observed that until the applied current is approximately 6 times the theoretical current, the removal efficiency is below 100 %. Once $i/i_{\text{theory}} \leq 5.6 \pm 0.2$, complete removal of sulfur may be obtained. Most of the steady-state data points in this work achieved a 100% removal efficiency when $i/i_{\text{theory}} \leq 5.6 \pm 0.2$, whereas the same was not the case during the previous work. For both cases, a significant increase in removal efficiency is observed with increasing $i/i_{\text{theory}}$ as it approaches 5.6 ± 0.2.

The change in behavior is observed for $i/i_{\text{theory}} > 5.6 \pm 0.2$, where 10/11 of the new steady-state data points has a removal efficiency of 100 %. In the previous work, stagnation of the removal efficiency is observed, with some of the steady-state data points achieving a complete removal efficiency, however, this is far from all data points. This may be explained by a better liquid distribution within the new scrubbing system. In the previous scrubber, a home-made system was developed to ensure the liquid distribution, whereas in the new scrubber an industrial spiral nozzle combined with visual inspection was used to ensure the liquid distribution. In order to achieve complete removal efficiency, the liquid distribution is key, and this may be the reason why the previous experiments did not achieve complete removal efficiency.

It may be assumed, that for $i/i_{\text{theory}} \leq 5.6 \pm 0.2$, the reaction is limited by the amount of active compound present in the electrolyte. For $i/i_{\text{theory}} > 5.6 \pm 0.2$ the reaction inside the scrubbing tower is limited by kinetics or mass transfer. This would especially seem to be the case for the previous work, where only 1/5 data points achieve complete removal of $\text{H}_2\text{S}$. 
Figure 4: Removal efficiency, $\Delta S$, as a function of the applied current compared with the theoretical current. For $i/i_{\text{theory}} < 5.6$, the removal efficiency is observed to be consistently below 100%, while for $i/i_{\text{theory}} > 5.6$, 100% removal efficiency may be achieved. The 100% removal efficiency is mostly achieved during this work, while in the previous work the removal efficiency stagnated at approximately 90% for $i/i_{\text{theory}} > 5.6$. 
3.1.2 Current Efficiency

The current efficiency \((S/i)\) for the steady-state data points are plotted in Figure 4, where they are compared with data from previous experiments. The current efficiency is compared plotted as a function of the removal efficiency, however, no correlation between the two are observed.

It is observed that the electroscrubber in this work reaches a maximum value of \(0.108 \pm 0.006 \text{ g h}^{-1} \text{A}^{-1}\) at a removal efficiency of 100%. Based on the data from the previous work, the current efficiency is observed to decrease when the removal rate is increased. However, this may have been due to limitation in reaction kinetics or mass transfer in the previous work. In this work, the highest current efficiencies are achieved at the highest removal efficiencies.

The current efficiency presented here is not directly comparable with the Faraday current efficiency. \(S/i\) is an indirect current efficiency, as it measures the efficiency of the current in removing the solvent. During operation with real biogas, it is expected that other pollutants will be removed as well. These reactions consumes active compounds, and lowers the \(S/i\) value of the process. The Faraday current efficiency does not take these reactions into account, as it directly measures the efficiency of the electrochemical reaction.

![Figure 5: The current efficiency (S/i) compared with the removal efficiency (∆S). The highest current efficiency is achieved at a removal efficiency of 100%.](image-url)
3.2 Liquid and Elemental Sulfur Analysis

3.2.1. Electrical analysis:

The total cell voltage, also referred to as the terminal voltage \( U_T \) in an electrochemical cell is described as \[34\]

\[ U_T = E_d + \eta_a + (-\eta_c) + \Sigma IR \]  \hspace{1cm} \text{Eq. 13} 

Where \( E_d \) is the decomposition voltage, \( \eta_a \) and \( \eta_c \) are the overvoltage at the anode and cathode and \( \Sigma IR \) is the sum of the ohmic voltage drops in the system. In practice, a linear dependency between the applied voltage and resulting current is often observed, with the form \[35\]

\[ U_T = U_0 + R_s i \]  \hspace{1cm} \text{Eq. 14} 

Where \( U_0 \) is the apparent decomposition voltage and \( R_s \) is the resistance of the overall system. In Figure 6 the applied potential is plotted as a function of the resulting current, and an expected linear dependency is found corresponding to Eq. 14. The interception voltage is found to be 2.41 V and the ohmic resistance of the system, i.e. the slope, is found to be 0.064 \( \Omega \).

For chlorine production from electrolysis of hydrochloric acid, a decomposition potential of down to 1.16 V have been reported for high concentrations of electrolyte and elevated temperatures (> 15% HCl and 70°C) \[36\]. The apparent decomposition voltage estimated in Figure 6, is the decomposition voltage for two electrochemical cells, resulting in a single cell decomposition voltage of 1.21 V. The agreement with the reported value (≥ 1.16 V) is excellent \[36\].

From the resistance of the system the resistivity (\( \rho \)) and conductivity (\( \kappa \)) can be calculated:

\[ \rho = R \frac{A}{l} = 0.064 \Omega \frac{300 \text{ mm} \cdot 350 \text{ mm}}{9.0 \text{ cm}} = 0.075 \Omega \text{m} \]  \hspace{1cm} \text{Eq. 15} 

\[ \kappa = \frac{1}{\rho} = 13 \Omega^{-1} \text{m}^{-1} = 0.13 \Omega^{-1} \text{cm}^{-1} = 130 \text{ mS/cm} \]  \hspace{1cm} \text{Eq. 16} 

as the surface area, \( A \), is 300 mm x 350 mm, and the distance between the two outermost electrodes, \( l \), is 9.0 cm. Here, it is assumed that the difference in conductivity between the middle electrode and the electrolyte is negligible and thus that it is 9.0 cm of electrolyte between the two outermost electrodes. The conductivity of the electrochemical cell is not only dependent on the electrolyte composition but also on the amount and size of the bubbles generated at the electrodes \[37\]. With the expected decrease in conductivity form the bobbles the calculated conductivity of 130 mS/cm is within the framework of the value of 222 mS/cm for a 25% NaCl solution \[38\].
Figure 6: The applied potential and resulting current of the system. A clear linear dependency is observed with an interception value of 2.41 V and a slope of 0.064 $\Omega$. The data presented is for two electrochemical cells, resulting in a terminal cell voltage of 1.21 V for each cell. The measured resistance of 0.064 $\Omega$ corresponds to a conductivity of 130 mS/cm of the electrolyte during operation.
3.2.2. Sulfur Analysis

Sulfur was extracted from the system as a yellowish-brown substance was caught in the bag filter. Samples were collected and dried for closer analysis. In Figure 7, a SEM picture of one of these samples is presented and analyzed. Cubic crystals are observed to be present throughout the sample, and may be estimated to have sizes in the order of 10 µm. In Figure 7b) and c) an EDS-analysis of the sample is performed. From 7b), the cubic crystals are observed to have high concentrations of Na (yellow) and Cl (red), and it may therefore be assumed that the cubic crystals are NaCl. Figure 7c) shows that the greater part of the sample consists of sulfur.

It is expected that the trace elements of NaCl will not interfere with the plans to use the extracted sulfur as fertilizer. Commercial sulfur fertilizer can be found with a 99.5% purity [39]. An optimized drying of the extracted sulfur will minimize the liquid and thus NaCl content of the sulfur. This is preferred both in order to minimize the loss of NaCl from the system and to minimize the amount of trace elements of NaCl in the fertilizer.

![Figure 7: SEM picture of the extracted sulfur.](image)

*a) The sulfur sample extracted from the electrolyte by the bag filter was yellowish and contained significant amounts of moisture. After drying, the sample was analyzed in a SEM using EDS. b) The sample was observed to have cubic crystals that the EDS-analysis confirmed to be NaCl (yellow and red). c) The rest of the sample consisted of mainly sulfur (green).*
4. Conclusion

A pilot plant for demonstration of a new electroscrubbing desulfurization process was designed and constructed. The design proved capable of operating without manual interaction throughout the experiments. The newly developed set-up successfully removed the H₂S content to non-detectable limits in a single step.

An applied current of $i/i_{\text{theory}} = 5.6 \pm 0.2$ was the point where 100 % removal rate was achieved, i.e. the H₂S content was removed down to non-detectable concentrations. This was one of the main targets as the methanation unit downstream is highly sensitive to the H₂S content.

It was found that the highest current efficiency was $0.108 \pm 0.006$ g h⁻¹ A⁻¹ and it was achieved at $\Delta S = 100\%$. This is highly advantageous as a complete removal of H₂S is preferred.

The system designed only used electricity and the only output is elemental sulfur that was analyzed by EDS. Here, it was found that trace amounts of NaCl was present as cubic crystals while the bulk material consisted of elemental sulfur.

The power consumption of 22.7 kWh/(kg S) makes the process comparable OPEX with several of the existing biogas desulfurization technologies of today, and optimization may decrease the power consumption further.

Acknowledgements

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Bibliography


Appendix VI

Supplementary Material

Spiral Nozzle

A picture of a spiral nozzle is presented in Figure VI.1. In Figure VI.2, the spiral nozzle implemented in the second campaign electroscrubber is observed during initial testing. The liquid distribution inside the scrubber was found to be optimized when the spiral nozzle was a vertical distance of 10 cm from the top of the packing material. This calculation was based on the angle of liquid distribution and the diameter of the scrubber.
Figure VI.1: A spiral nozzle.
Figure VI.2: The spiral nozzle used in the second campaign electroscrubber.
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