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Efficient new process for the desulfurization of mixtures of air and hydrogen sulfide via a dielectric barrier discharge plasma

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The efficient removal of hydrogen sulfide, H₂S, from streams of H₂S in air via a dielectric barrier discharge (DBD) plasma has been investigated using a quadrupole mass spectrometer. A suitable plasma device with a reservoir for storing sorbent powder of various kinds within the plasma region was constructed. Plasma treatments of gas streams with high concentrations of hydrogen sulfide in air yielded a removal of more than 98% of the initial hydrogen sulfide and a deposition of sulfur at the surface of the dielectric, while small amounts of sulfur dioxide were generated. The presence of calcium carbonate within the plasma region of the DBD device resulted in the removal of over 99% of the initial hydrogen sulfide content and the removal of 98% of the initial sulfur dioxide impurities from the gas mixture.

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I. INTRODUCTION

The presence of hydrogen sulfide usually causes significant problems due to its toxicity and its corrosive behavior. Hydrogen sulfide is present in high concentrations within most natural gases, but also in biogas and landfill gas.

Currently, the most commonly used solutions for the removal of hydrogen sulfide are activated carbon and the Claus process. Activated carbon is employed as a passive sorbent for H₂S due to its large surface area. However, its production is very expensive and the used up activated carbon can hardly be regenerated, thus most activated carbon has to be treated as hazardous waste after being used for H₂S filtering purposes. The Claus process operates above 900°C, partly oxidizing the gas to produce water and atomic sulfur via the two steps given in equations (1) and (2).

H₂S + 3/2 O₂ → H₂S + SO₂
2 H₂S + SO₂ → 3 S + 2 H₂O

To ensure high rates of desulphurization, the Claus process usually has to be combined with post-treatment processes such as the SCOT process. Therefore, these devices are complex to handle and the oxidation step consumes all of the hydrogen that otherwise might be utilized for the production of energy. Furthermore, these techniques always require a lot of energy due to the high temperatures needed to start the reaction.

The production of the energy necessary to start gas phase reactions, however, can be done by plasma-based approaches, as already demonstrated by several groups. One of the first groups was Kolodkina et al., who demonstrated a direct endothermic dissociation of H₂S via a high frequency (HF) plasma. Higher dissociation rates were found for other types of non-thermal plasmas, like ultra-high frequency, radio frequency (RF), glow discharge or corona plasmas.
for example, found a complete H$_2$S dissociation via a RF plasma with an energy consumption of 2 kWh/m$^3$(n). Microwave (MW) plasmas can produce similar rates even at 0.8 kWh/m$^3$(n), which is mainly driven by a thermal decomposition of the H$_2$S. In gliding arc plasmas used for H$_2$S abatement, reactions of the following type have been found:

$$\text{H}_2\text{S} + \text{CO}_2 \rightarrow \text{H}_2\text{O} + \text{CO} + \text{S} \quad (3)$$

The gliding arc plasmas driving the reaction according to equation (3) required 1 kW/m$^3$(n) for 75% H$_2$S removal.

The addition of O$_2$ further enhances the H$_2$S removal rates via similar reaction pathways as for the Claus process. The presence of oxygen, however, might well have a negative impact like the production of SO$_2$ and SO$_3$ for thermal and non-thermal plasmas as well as for combinations of plasma and photolysis. Thus, some groups even use the ozone downstream of a plasma discharge. An oxidation of H$_2$S was also observed in the presence of CO$_2$ when using thermal plasmas.

A very simple and versatile implementation of a non-thermal plasma is the dielectric barrier discharge (DBD). It is able to dissociate H$_2$S and thereby producing H$_2$ but has mostly been investigated at low pressures such as 150 Torr. It was found to be more effective at high temperatures, but a sufficient efficiency was gained only in combination with other systems. DBD discharges have been shown to be able to oxidize H$_2$S towards H$_2$SO$_4$ and to induce reactions with surfaces like InP. The use of a packed-bed DBD reactor, however, only enhanced the dissociation via the gases’ residence time. Nevertheless, some catalysts have been employed to enhance the dissociation of H$_2$S towards the production of atomic sulfur. The biggest problem employing plasma-based dissociation or oxidation processes for hydrogen sulfide abatement, however, is the irreversible removal of the sulfur and its reaction products from the gas stream. Some attempts were made to combine plasma treatments with activated carbon or other complex filtering systems. So far, no approaches were made to use directly plasma-induced reactions of hydrogen sulfide with solid matter for desulfurization purposes.

This study explores the possibility to apply a sorbent powder material for DBD plasma-induced hydrogen sulfide removal from gas streams. As sorbent powder, calcium carbonate was chosen, due to its ability to bind sulfur via the formation of calcium sulfate that is commonly used in wet gas scrubbers.

II. EXPERIMENTAL

A planar DBD setup was chosen for the plasma device due to its simple construction, high electrical efficiency and homogeneous character of the resulting discharge. The most commonly used materials for dielectric barriers are alumina (Al$_2$O$_3$) and quartz glass (SiO$_2$). Even though alumina exhibits a dielectric constant (relative permittivity) of approximately $\varepsilon = 9$ and would thus be favorable over quartz with $\varepsilon = 4$, the chemical stability and commercial availability in a variety of geometries is far better for quartz.

Reductive gases affect quartz much less than alumina, even reactive plasma discharges are only able to induce modifications as deep as 100 nm at most. Furthermore, the electrical breakdown strength is one order of magnitude larger for quartz than for alumina (c.f. Yoshimura and Bowen. A Petri dish made from quartz glass was used as dielectric, where the high edges of the glass dish support the prevention of surface flashovers and the rounded shape simplifies the sealing of the assembly.

The plasma device, shown in Fig. 1, consists of two large parts; a top piece holding the HV electrode and quartz glass dielectric as well as the gas inlet and outlet connections. The base plate provides cutouts for the gas streams as well as a powder reservoir with the same diameter as the dielectric. Threaded holes within the base plate allow for the device to be assembled and disassembled quickly, e.g. for cleaning or powder exchange purposes. The top piece has an end-to-end bore hole with a ledge (c.f. Fig. 1(b)) for carrying the dielectric. The quartz dielectric is sealed via heat resistant silicone (Gasket Seal, Soudal N.V.), thus exhibiting a leakage rate below 0.01 hPa-l/s which allows operation under medium vacuum pressures. The gas inlet and outlet are created by drilling 15 bore holes each and can be fed via Swagelok fittings (c.f. Fig. 1(c) and Fig. 1(d)).
FIG. 1. The plasma device as a CAD cross section drawing (a) with a detailed view of the junction between the dielectric and the metal part (b), a photograph of the disassembled reactor (c) and the gas feed (d).

The setup of the measuring system is schematically depicted in fig. 2. Atmospheric air and pure hydrogen sulfide can be supplied using dosing valves (V1 and V2). A rotary vane pump (RVP) is connected via another dosing valve (V3), thus being able to control the absolute pressure within the DBD plasma reactor which is indicated by the attached Pirani vacuum gauge. A partial gas current is

FIG. 2. Flow chart of the setup combining the DBD plasma device with a gas analyzer (MGA), a dual gas supply system and a pumping stage.
redirected into a commercial mass spectrometer system (multi gas analyzer MGA, MFM analytical systems GmbH) directly after the DBD reaction chamber.

III. RESULTS AND DISCUSSION

The first experiments were conducted without the utilization of any sorbent material, thus reproducing the dissociation of hydrogen sulfide known from the literature.\textsuperscript{33,36} Fig. 3 shows mass spectra of a gas stream consisting of atmospheric air at 20 hPa and hydrogen sulfide at 5 hPa before (red lines) and after plasma treatment (black lines). The spectrum of the untreated gas stream closely resembles the known composition of atmospheric air. There are additional peaks from H\textsubscript{2}S and SO\textsubscript{2} as common contamination within H\textsubscript{2}S, as well as their fragments from the electron impact ionization in the mass spectrometer.

The plasma discharge led to a reduction of the H\textsubscript{2}S by 98.3\% (c.f. inlet in Fig. 3), while the SO\textsubscript{2} increased by 49.7\%. Most likely, the water content within the gas stream is due to desorbed water from the tubings and reactor walls. This got significantly reduced due to flushing during the ongoing experiment as well as from adsorption in the product layer within the reactor. The atomic nitrogen and the carbon monoxide were both slightly increased after plasma treatment as a result of dissociation processes within the plasma discharge, as indicated by a reduction of carbon dioxide and molecular nitrogen. The hydrogen content diminished by 83\%, probably due to oxidation by the plasma discharge. This reduced the oxygen content in concurrence to the formation of water. No significant amounts of ozone or nitrogen oxides were detectable. Also, none of the sulfur-containing byproducts that other groups found downstream of the plasma reactor like organic polysulfides\textsuperscript{52} could be observed in our case. Furthermore, the plasma treatment led to the formation of pure sulfur as debris in the form of yellow, needle-like crystals at the surface of the dielectric. According to literature, plasma discharges with gas temperatures below 400 K would initially lead to the formation of mainly S\textsubscript{8} clusters in the gas phase\textsuperscript{53} prior to condensing. This often occurred at the reactor walls\textsuperscript{54}.

While CaCO\textsubscript{3} powder was located within the device as a sorbent material, the plasma discharge led to the removal of 99.2\% of the initial H\textsubscript{2}S content as well as of 95.2\% of the initial SO\textsubscript{2} content within the gas stream. Again, the plasma treatment was found to lead to the formation of atomic nitrogen and carbon monoxide due to the dissociation of molecular nitrogen and carbon dioxide.

![Mass spectra of gas streams of atmospheric air with a high H\textsubscript{2}S content; with and without plasma treatment devoid of a powder sorbent within the plasma device.](image-url)
respectively. Furthermore, hydrogen and oxygen were concurrently removed, probably due to oxidation processes induced by the plasma discharge. No significant amounts of ozone or nitrogen oxides were detected.

No visible traces of sulfur or other products in the plasma-chemical reactions were recognizable at the sorbent material after one hour of plasma experiments. The sorbent powder was further investigated by means of X-ray photoelectron spectroscopy (XPS, not shown), yielding no sign at all for the influence of the plasma treatment in comparison to the untreated raw powder. The overall hydrogen sulfide gas would amount to about 2 g of sulfur, while approximately 200 g of calcium carbonate sorbent powder was used. Thus, the product of the plasma-chemical reactions would be below the detection limit of XPS, if homogeneously distributed. The exact chemical nature of this product will be addressed in prospective investigations.

The energy consumption of the presented device was not measured directly. However, it can be estimated via the flow rates and the high voltage supply’s electrical characteristics. During both of the presented experiments, a mixture of 20 hPa of atmospheric air as well as 5 hPa of pure H₂S was fed into the plasma device. The rotary vane pump generated a volume flow of approximately 2.2 hPa·l/s, corresponding to about 0.5 reactor charges per second, being treated at 1.6 kHz. Thus, a total number of 3142 pulses per reactor charge were needed to obtain the results presented above. Since the exact energy per pulse has not been recorded, the maximum energy possibly delivered by the high voltage generator of 40 mJ is taken into account, yielding an energy consumption equal to or less than 0.2 kWh/m³. On one hand, in comparison to Hong et al., who reported the most effective plasma-based approach for the removal of hydrogen sulfide from gas streams so far, the process and device presented within this paper consumes at least half an order of magnitude less energy. On the other hand, the commonly used Claus process would require at least 0.3 kWh/m³, considering the heat capacity air as well as working temperatures above 900°C.

IV. CONCLUSION

The problems raised by the presence of hydrogen sulfide justifies the use of desulfurization techniques that require high amounts of energy or expensive reagents. These problems can be overcome by means of a non-thermal plasma treatment. Therefore, a laboratory-scale dielectric barrier discharge reactor was constructed in order to examine the use of a cold plasma for desulfurization purposes. Furthermore, the use of calcium carbonate stored within the plasma zone as a sorbent powder was explored.

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FIG. 4. Schematic representation of the relations found during the plasma treatment of air gas streams with a high H₂S content using the plasma device without a powder sorbent (a) and using CaCO₃ as the sorbent (b).
The results are summarized in Fig. 4, indicating the plasma experiments for the removal of hydrogen sulfide from low-pressure air streams. No powder sorbent is present in (a). CaCO$_3$ is the sorbent within the plasma device in (b). Without a sorbent material, the plasma discharge was able to remove more than 98% of the H$_2$S, precipitating pure sulfur at the dielectric while some small amount of SO$_2$ was generated. Using CaCO$_3$ as the powder sorbent led to a removal of more than 99% of the H$_2$S as well as 98% of the SO$_2$. Considering the energy consumption of the DBD plasma device, these high degrees of H$_2$S removal are achieved while requiring at least half an order of magnitude less energy than all processes found within the literature.

Earlier plasma-based approaches for desulfurization technologies mostly neglect the segregation and removal of the sulfur from the gas stream. During the operation of a filter, this might lead to a clogging of the device or to a resurgence of the previously-removed sulfur back into the gas stream. This study clearly shows a possible solution that is able to thoroughly remove both hydrogen sulfide and sulfur dioxide from the gas streams. The next steps in this process will be the implementation for distinctive processes, i.e. the desulfurization of biogas or flue gas, which will be presented in future publications.

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33 U. Kogelschatz, E. Killer, and B. Eliasson, in 52nd Annual Gaseous Electronics Conference, Norfolk (Virginia), USA, October 1999.