Chemie Ingenieur Technik

# **Experimental Splitting of Hydrogen Sulfide by Halogens for Application in Reaction Cycles**

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Hydrogen sulfide is a toxic gas that is almost always present in the processing of crude oil or natural gas and must be removed. In addition, hydrogen can be used as an energy carrier if it can be separated from  $H_2S$ . In this work, as the first step of a reaction cycle that could achieve just that, the bromination and chlorination of hydrogen sulfide are experimentally studied. It can be shown that both halogens are capable of completely converting hydrogen sulfide in a gas phase reaction. While the chlorination can produce byproducts, the bromination is free of such.

Keywords: Bromine, Chlorine, Hydrogen sulfide, Sulfur

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#### 1 Introduction

Today, the world's population has greater energy demands than ever before, and it continues to grow. As more and more people now have access to energy, especially in developing countries, global energy consumption increased from 482.8 to 583.9 Exajoule between 2009 and 2019, an increase of close to 21 % [1]. The three largest primary energy sources to meet this global demand are oil (33 % in 2019), natural gas and coal, with natural gas rising consistently from 21 % in 1994 to 24 % in 2019 and coal, especially outside Asia, falling sharply, from 30 % in 2014 to 27 % in 2019 [1,2].

The first two sources have one thing in common: their production is accompanied by the release of large amounts of hydrogen sulfide (H<sub>2</sub>S). While H<sub>2</sub>S is a component of natural gas, with fractions ranging from a few parts per million to several percent [3], it occurs in petroleum in the form of sulfur rich hydrocarbons and is formed during hydrodesulfurization [4]. Hydrogen sulfide is a colorless, smelly gas, which, in addition to being highly toxic to humans, also causes damage to the environment [5, 6] and must therefore be neutralized at all costs. However, direct oxidation of H<sub>2</sub>S is not advisable, since the resulting sulfur dioxide (SO<sub>2</sub>) is also highly damaging to the environment, for example being a cause of acid rain [7].

In today's industry, hydrogen sulfide is removed in majority by the Claus process, which also produces most of the world's sulfur [8, 9]. In this process,  $H_2S$  is reacted with oxygen via an intermediate step to form sulfur (S) and water ( $H_2O$ ) by Eq. (1).  $H_2S$  is thus only partially oxidized and full oxidation to SO<sub>2</sub> can be avoided.

$$2 H_2 S + O_2 \longrightarrow 2 S + 2 H_2 O \tag{1}$$

The Claus process does a good job of rendering the problematic H<sub>2</sub>S ecologically harmless, but it does not take advantage of the hydrogen (H<sub>2</sub>) contained in the molecule, which in this case forms water with oxygen  $(O_2)$ . If a chemical reaction cycle was able to simultaneously oxidize hydrogen sulfide to sulfur and form hydrogen, in the case of petroleum, the H<sub>2</sub> needed for hydrodesulfurization would be recovered. In the case of natural gas, H<sub>2</sub> would be available for use as a secondary energy carrier, sometimes referred to as the energy form of the future [10]. Due to the fact that more natural gas sources with low H<sub>2</sub>S content become exhausted and more sources with higher H<sub>2</sub>S content are extracted [11], this possibility becomes even more important. The high effort for the complete conversion of H<sub>2</sub>S, the separation of gases as well as the catalyst maintenance suggest considering alternatives to the Claus process for the purification of hydrogen sulfide from gas streams [12, 13].

In this work, the possibility of partially oxidizing  $H_2S$  with the help of the halogens chlorine ( $Cl_2$ ) and bromine ( $Br_2$ ) in the gas phase is investigated, forming hydrogen halide (HX) and sulfur. Importantly, the utilized halogen is not lost and can be recovered, which results in the following cycle (Fig. 1), where  $X_2$  represents  $Cl_2$  or  $Br_2$ .

The second step of the cycle, the production of hydrogen from HCl and HBr with simultaneous halogen regeneration

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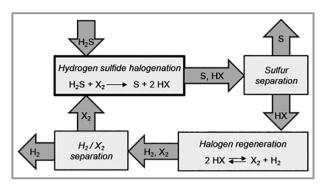


Figure 1. Scheme for a cyclic halogen based  $H_2S$  oxidation and halogen (X) regeneration.

is well studied, amongst other methods, electrolysis can be used to achieve that [14, 15]. Halogen regeneration by oxidation with  $O_2$  is also thinkable [16], but this reaction for HCl, the Deacon reaction [17], is rather problematic and the net reaction equation would be the same as in the Claus process, since water would also be formed as a by-product here.

Various studies have already been carried out on the halogenation of hydrogen sulfide. This publication itself is a follow up to preliminary tests and first measurements published in 2019 [18]. Since then, the experimental setup has been extensively improved, allowing for more numerous and more precise measurements. Parker [19] investigated the bromination in liquid phase, where H<sub>2</sub>S-containing gas is passed through an absorption reactor with aqueous bromine solution and exits as sweetened gas. The work-up of HBr is carried out by means of liquid-phase electrolysis. Challenges of this concept are certainly the large amount of water needed to dissolve bromine and the separation of the azeotropic HBr/H<sub>2</sub>O mixture [20]. The possibility of splitting hydrogen sulfide with a thermochemical iodine cycle was investigated by Green et al. in a mostly simulative work [21]. The authors also refer to previous work from the 1980s and 1990s. Sims et al. published a detailed paper on gas phase chlorination of H<sub>2</sub>S [22], on which the chlorine chapter of this work is based and is intended to extend the said work in terms of more experimental parameters studied.

## 2 Thermodynamics of H<sub>2</sub>S Halogenation

The halogenation of hydrogen sulfide with elemental halogens can be expressed by Eq. (2), where  $X_2$  represents  $Cl_2$  and  $Br_2$ .

$$H_2S + X_2 \longrightarrow \frac{1}{x}S_x + 2 HX$$
 (2)

A thermodynamic calculation was performed for bromination and chlorination to look more accurately at previous observations about the 1089

exothermicity of the reactions [18,22]. At atmospheric pressure and above 445 °C, sulfur is present in gaseous molecular form from  $S_2$  to  $S_8$  with varying proportions depending on the temperature, which must be considered when calculating enthalpy and entropy. Accordingly, Eqs. (3–5) [23] are obtained and the results of the calculations are presented in Fig. 2.

$$\Delta H_{\rm R,T} = \nu^{\rm H_2S} \Delta H_{\rm f,T}^{\rm H_2S} + \nu^{\rm X_2} \Delta H_{\rm f,T}^{\rm X_2} + \nu^{\rm HX} \Delta H_{\rm f,T}^{\rm HX} + \sum_{i=2}^{8} \gamma_i \frac{\nu_i}{i} \Delta H_{\rm f,T}^{\rm S_i}$$
(3)

1

Z

$$\Delta S_{\mathrm{R,T}} = \nu^{\mathrm{H}_{2}\mathrm{S}} \Delta S_{\mathrm{T}}^{\mathrm{H}_{2}\mathrm{S}} + \nu^{\mathrm{X}_{2}} \Delta S_{\mathrm{T}}^{\mathrm{X}_{2}} + \nu^{\mathrm{H}\mathrm{X}} \Delta S_{\mathrm{T}}^{\mathrm{H}\mathrm{X}} + \sum_{i=2}^{8} \gamma_{i} \frac{\nu_{i}}{i} \Delta S_{\mathrm{T}}^{\mathrm{S}_{i}}$$

$$(4)$$

$$\Delta G_{\rm T}^{\rm j} = \Delta H_{\rm f,T}^{\rm j} - T \Delta S_{\rm f,T}^{\rm j} \tag{5}$$

In the investigated temperature range from 100 °C to 650 °C both reactions are exothermic and exergonic. Chlorination is more exothermic and exergonic than bromination, which is due to the higher stability of the HCl molecule compared to HBr. This is an advantage for the halogenation reaction, but with the whole cycle in mind it could become a disadvantage, as the necessary splitting of the HCl molecule requires more energy. At 445 °C, both enthalpy curves feature a sharp bend, which is caused by the evaporation of the sulfur. The Gibbs energy increases only slightly in this process since the evaporation is accompanied by an increase in entropy. Above 550 °C the enthalpy values change only slightly, because the S<sub>2</sub> molecule has the largest proportion here and thus the proportions of the Sx molecules stay almost the same. Below that temperature S<sub>8</sub> and S<sub>6</sub> rings are dominating and only at temperatures above 2000 °C atomic sulfur  $(S_1)$  is formed [24]. The calculations showed that for the bromination no by-products are formed in relevant amounts. The chlorination of hydrogen sulfide, however, involves the formation of partly undesirable by-products such as disulfur dichloride (S<sub>2</sub>Cl<sub>2</sub>) [22], sulfur dichloride (SCl<sub>2</sub>) and other chlorinated sulfur compounds [25], which are monitored during the reaction.

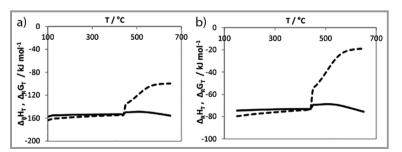


Figure 2. Reaction enthalpy (-) and Gibbs energy (-) of hydrogen sulfide (a) chlorination and (b) bromination at 1 bar.

## 3 Experimental

#### 3.1 Plant Setup

The layout of the plant for hydrogen sulfide chlorination is displayed in Fig. 3, the flowsheet for the bromination plant was previously published [18]. Chlorine (99.8 %, Linde) and hydrogen sulfide (99.5 %, Linde) are supplied by gas cylinders and diluted by the inert gases argon (Ar, 99.996%, Messer) and nitrogen (N2, 99.5%, Messer), with which the reactant bottle attachments can also be flushed before and after the experiments to avoid corrosion. All gases are dosed via mass flow controllers (MFCs) and the mixture is fed into a tubular electrically heated quartz glass reactor, which includes a short preheating section. Afterwards the produced sulfur is split from the product gas by a spiral shaped separator, which is heated in an oil bath to 130 °C to keep the sulfur in liquid state. This step is accompanied by a filter that separates any solid sulfur particles from the gas stream. Following the separation are two analysis bottles for HCl and Cl<sub>2</sub> analysis, which can be bridged if necessary and the neutralization solutions containing sodium hydroxide (NaOH, 99.5%, Merck) and sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 98%, Merck) to make sure that the exhaust gas is free from all dangerous substances, following Eqs. (6) and (7). Downstream the plant is open to atmosphere, which is why there is almost ambient pressure in the whole system.

The reaction temperatures  $(T_R)$  investigated are  $T_R = 450-600$  °C, where all reactants and products are in gaseous state. Below these temperatures, sulfur is present in liquid state, for which the plant is not designed, as the reactor outlet would clog, whereas the upper limit is based on the maximum temperature of the heating jacket. The

selected mean residence times ( $\tau$ ) are  $\tau = 1.5-9$  s, smaller reaction times, while interesting, are not investigated due to limitations in gas dosing.

### 3.2 Safety

Because of the hazardous properties of H<sub>2</sub>S, Cl<sub>2</sub>, HCl, and the corresponding bromine compounds, the plant is designed with safety for users and equipment in mind. Since all the educt and product gases are highly corrosive, all pipes are made of fluorinated ethylene propylene (FEP). Regarding the plant equipment quartz glass was used for high temperature areas and borosilicate glass for lower temperatures. The mass flow controllers are made of stainless steel, which can withstand dry H<sub>2</sub>S and Cl<sub>2</sub>. In this case silica gel was used to prevent moisture from coming into contact with the gases, thus avoiding corrosion. For detection of potential gas leaks during the experiment, gas detectors for H<sub>2</sub>S, Cl<sub>2</sub>, HCl and their bromine counterparts are set up near the plant. In case of any leaking gases, spray bottles with the mentioned solution were used for neutralization.

To be able to control the system remotely and thus avoid unnecessary contact of personnel during the experiment, the LabVIEW software was utilized, through which most valves, all heaters and all gas dosing can be controlled from a computer. An emergency program, which can be activated manually, ensures that the heating is switched off, the supply of reactants is interrupted, thus stopping any reaction, and the system is purged with inert gas.

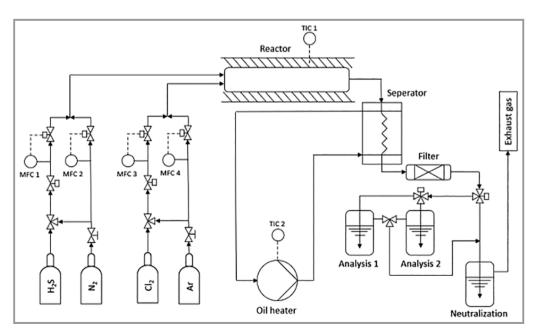


Figure 3. Flowsheet of the hydrogen sulfide chlorination plant.

#### 3.3 Analysis

To determine the conversions and yields from the tests, both the remaining halogen and the produced hydrogen halide are analyzed. An analysis of the generated sulfur is possible but impractical, since the sulfur particles are widely distributed in the plant. Due to their good solubility in water, all halogen compounds can be easily collected by passing the product gas through aqueous solutions and quantified by different titration methods.

For hydrogen halides an acid base titration with sodium hydroxide is carried out following Eq. (6) [26] in which the required volume of KOH is measured. The halogens are collected in aqueous potassium iodide (KI, 99%, Carl Roth) solution and react as in Eq. (7) [27]. The analyte in the sample, here  $Cl_2$ , is first converted into an iodine solution in a redox reaction. The iodine also serves as an indicator due to its brown coloration and is subsequently reduced to iodide ions by a reducing agent such as sodium thiosulfate until it is colorless, following Eq. (8) [27].

$$HCl + KOH \longrightarrow KCl + H_2O$$
 (6)

$$Cl_2 + 2 \text{ KI} \longrightarrow 2 \text{ KCl} + I_2$$
 (7)

$$I_2 + 2 S_2 O_3^{-2} \longrightarrow 2 I^- + S_4 O_6^{2-}$$
 (8)

Because both analytes, halogen and hydrogen halide, can be found together in a sample, their cross-sensitivity, the effect of one analyte on the quantification method of the other one is investigated in preliminary studies. These experiments show, that the iodometric method is not cross sensitive, which means that hydrogen chloride does not falsify the results of Cl-analysis. However, chlorine dissociates in water forming acidic products as in Eq. (9) [28] and will thus interfere with the pH based HCl analysis.

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$
 (9)

To prevent this from happening, KI is also added to the distilled water, which is used for HCl analysis to react with chlorine forming the much slower dissociating iodine displayed in Eq. (7) [28]. In the end, the product gas stream can be analyzed without prior separation of the gases. For both analysis methods, a medium error deviation of 0.8% could be determined, they are thus considered to be sufficiently precise.

#### 4 Results and Discussion

#### 4.1 Bromination of Hydrogen Sulfide

For the  $H_2S$  bromination a parameter study was carried out to find ideal experimental variables to maximize  $H_2S$  yield. To convert as much hydrogen sulfide as possible, a lot of experiments are carried out with a stoichiometric excess of halogen  $(u_{\text{Hal}})$ . In this series of experiments, the yield was investigated instead of the conversion, since the reactant Br<sub>2</sub> cannot be analyzed; it dissolves in the liquid sulfur inside the separator and does not reach the analysis vial. This series of experiments is based on the previously published results [18] and, since the plant was generally fine-tuned a lot, partially repeats them in order to compare both generations.

One property that was investigated extensively prior to the study is the time required for the bromination plant to reach stationary state, which means that for the same conditions it also produces the same results. It was found that, depending on the residence time investigated, the system is only stationary after t = 20-60 min (Fig. 4). This is considered for all bromination experiments.

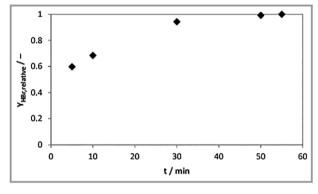
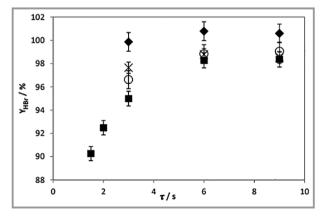


Figure 4. Relative Yield of H<sub>2</sub>S bromination in stationary state experiments;  $\tau = 9 \text{ s}$ ,  $T_R = 450 \text{ °C}$ .

The determined test parameters to find optimum yields are mean residence time, reaction temperature and excess bromine. In a first series of experiments all tests were done with  $u_{\rm Br2} = 10$  Mol %, with a residence time of  $\tau = 3-9$  s and temperatures of  $T_{\rm R} = 450-650$  °C. Because the resulting HBr yields are very high, an attempt was made to fully utilize the plants potential with very short residence times of  $\tau = 1.5-3$  s and the lowest temperature of  $T_{\rm R} = 450$  °C, the results are displayed in Fig. 5.



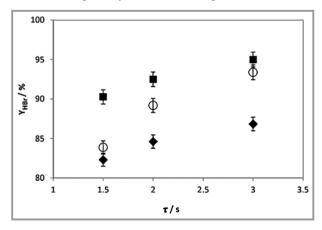
**Figure 5.** HBr yields of the H<sub>2</sub>S bromination parameter study;  $\tau = 1.5-9 \text{ s}$ ,  $u_{\text{Br2}} = 10 \text{ Mol } \%$ ,  $T_{\text{R}} = 450 \,^{\circ}\text{C} (\blacksquare)$ ,  $500 \,^{\circ}\text{C} (\bigcirc)$ ,  $550 \,^{\circ}\text{C} (x)$ , and  $600 \,^{\circ}\text{C} (\diamondsuit)$ .

The main conclusion from this series of experiments is that with appropriately high temperatures and/or long residence times, a nearly complete reaction of H<sub>2</sub>S can be achieved. The maximum yield for each temperature seems to be reached already at  $\tau = 6 s$ , a significantly increased yield for  $\tau = 9$  s, compared to  $\tau = 6$  s, cant be observed. An increase in reaction temperature, however, always leads to improved yields in the range investigated. The highest value obtained at  $T_{\rm R} = 600$  °C and  $\tau = 6$  s is 100.7 %, which means complete or almost complete yield, considering measurement inaccuracy and system fluctuations. Furthermore, the experiments with  $\tau < 3 s$  are accompanied by lower yields, which shows that there is a temperature-specific optimum value in the investigated residence time range at which very good yields are still obtained but below which the yields drop rapidly.

Next, the influence of excess bromine on the yields was investigated, which was previously set relatively high at  $u_{Br2} = 10 \text{ Mol }\%$ . This was reduced to 5 Mol % and 0 Mol % in the following series of experiments; the short residence times of  $\tau < 3$  s were kept to observe potential yield differences more conveniently. The results of the series of experiments are shown in Fig. 6. The temperature was kept constant at  $T_R = 450 \,^{\circ}\text{C}$  and for better comparison, the results from Fig. 5 with  $u_{Br2} = 10 \text{ Mol }\%$  are included.

Generally, the results are in line with expectations. In the range of  $\tau = 1.5-3$  s the residence time has more impact on the yield than at  $\tau = 3-9$  s examined previously. The difference in yield ( $\Delta Y_{\rm HBr}$ ) between 1.5 s and 3 s is between 4 % and 9 % for the individual series of measurements, for  $\tau = 3-9$  s it is  $\Delta Y_{\rm HBr} = 1-4$  %. With a higher amount of excess bromine, the yields also increase by 8 %, which shows that the bromine excess is very helpful for higher conversions. However, at  $\tau = 3$  s, yields similar to those obtained with 10 Mol % excess bromine were obtained with  $u_{\rm Br2} = 5$  Mol %, which suggests that a 10 % Br<sub>2</sub>-excess may not be necessary to completely convert H<sub>2</sub>S.

Another argument in favor of lower bromine excess is that bromine partially dissolves in the procured sulfur and



**Figure 6.** HBr yields of the H<sub>2</sub>S bromination parameter study;  $\tau = 1.5-3$  s,  $T_R = 450$  °C;  $u_{Br2} = 10$  Mol % ( $\blacksquare$ ), 5 Mol % ( $\bigcirc$ ), and 0 Mol % ( $\blacklozenge$ ).

the higher the surplus, the more bromine dissolves. A test for  $Br_2$  with KI, analogous to the chlorine detection displayed in Eq. (7), proves the substance is elemental bromine and not a Br-S-compound. Due to the high bromine price [29], it is essential for the entire cycle that the bromine loss remains minimal and as much as possible can be recycled for the reaction with H<sub>2</sub>S. The two elements can be separated by purging with inert gas for 12 h, during which the dissolved bromine re-evaporates, but this is a step that is not unsignificant in the design of the cycle. Overall, there seems to be an ideal bromine excess, which also depends on the plant used and which puts the advantage of higher yields and the disadvantage of separation from sulfur in an ideal relationship to each other.

#### 4.2 Chlorination of Hydrogen Sulfide

The objectives for the H<sub>2</sub>S chlorination experiments were similar to those for the bromine series. Here, too, the experimental parameters for the best possible yields should be found. Since chlorine also partially dissolves in sulfur, the conversions were not investigated further. However, it is important that unlike its bromine counterparts, sulfur chlorides such as the bright yellow disulfur dichloride (S<sub>2</sub>Cl<sub>2</sub>), darker orange-red sulfur dichloride (SCl<sub>2</sub>) and polysulfanes (S<sub>n</sub>Cl<sub>2</sub>) can be formed here following Eqs. (10) and (11) [31] and are thermodynamically favored [30].

$$H_2S + \frac{3}{2}Cl_2 \rightleftharpoons \frac{1}{2}S_2Cl_2 + 2 HCl$$
 (10)

 $H_2S + 2 Cl_2 \rightleftharpoons SCl_2 + 2 HCl$ (11)

Within the scope of this work, no evidence for by-products can be provided, since the plant cannot be opened during the experiments. However, it was observed in the sulfur condenser that light liquid droplets form when the  $Cl_2/H_2S$ ratio is stoichiometric and darker liquid forms when there is excess chlorine which are matching the colors and brightnesses described in literature and can therefore be taken as indication (Fig. 7). Since these are equilibrium reactions, they run backwards when the system is flushed and fully

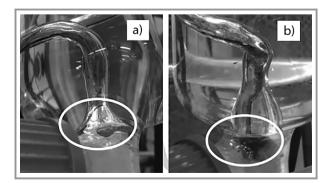


Figure 7. Sulfur deposits at the separator outlet, a)  $u_{Cl2} = 0 \text{ Mol } \%$ , b)  $u_{Cl2} = 10 \text{ Mol } \%$ .

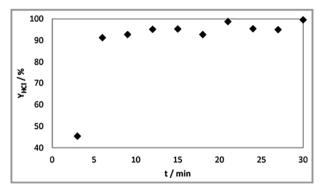
disappear after two hours of flushing, therefore the potential by-products cannot be analyzed further.

What at first glance looks like a disadvantage to the desired reaction, the formation of by-products, may be an advantage, as a closer look at the side reactions of H2S and sulfur chlorides shows. It turns out that  $SCl_2$  and  $S_2Cl_2$ , when contacted with  $H_2S$ , are capable of removing the toxic gas to form the major products as displayed in Eqs. (12) and (13) [22]. Properly used, the sulfur chlorides thus form a buffer for the reaction system. Excess chlorine reacts to form sulfur chlorides, which dissolve well in sulfur and can release the products sulfur and chlorine upon contact with  $H_2S$ , further increasing the conversion of hydrogen sulfide. On the other hand, excess  $H_2S$  would react with the chlorine bound in sulfur chlorides, which prevents the impact of fluctuations in the reactant feed on the reaction yield.

$$H_2S + SCl_2 \longrightarrow \frac{2}{x} S_x + 2 HCl$$
 (12)

$$H_2S + S_2Cl_2 \longrightarrow \frac{3}{x} S_x + 2 HCl$$
(13)

Examination of the inlet behavior shows that a nearly steady-state condition is reached during chlorination after only about 5 min (Fig. 8). However, the measured yield varies by up to 8 % for the analysis time used, which cannot be attributed to measurement error.



**Figure 8.** HCl yields in stationary state H<sub>2</sub>S chlorination experiments;  $T_R = 450$  °C,  $\tau = 6$  s,  $u_{Cl2} = 10$  %.

Initially, the variation of the molar ratio of the two reactants chlorine and hydrogen sulfide at  $\tau = 5$  s and  $T_{\rm R} = 450$  °C is investigated. An experiment was also run with a chlorine undercut and molar ratio of Cl<sub>2</sub>/H<sub>2</sub>S = 0.9, which makes no practical sense but serves to better identify a trend (Fig. 9). Due to the more fluctuating yields, the time of sampling was greatly increased to obtain comparable mean values; in addition, the higher deviation is taken into account in the error column. An ascending progression with increasing excess chlorine can be observed, presumably approaching full yield.

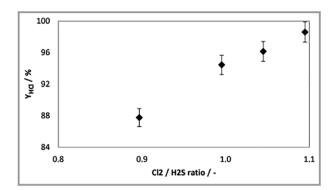
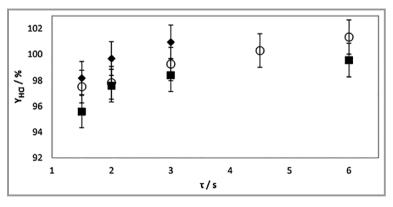


Figure 9. HCl yields of the experimental series with  $T_{\rm R}$  = 450 °C and  $\tau$  = 5 s.

Furthermore, the parameters residence time and reaction temperature were investigated for the chlorination of H<sub>2</sub>S, with ranges of  $T_{\rm R} = 450-550$  °C and  $\tau = 1,5-6$  s were studied, while the excess chlorine was kept constant at  $u_{\rm Cl2} = 10$  Mol%. In preliminary tests, it was observed that these values do not need to be increased further. The results are shown in Fig. 10.

In the chlorination of H<sub>2</sub>S, very high yields are achieved even at low residence times. At a temperature of 550 °C, complete yields are already recorded after  $\tau = 3$  s; for  $T_{\rm R}$  = 500 °C, 6 s are needed to achieve the same. A temperature increase of 100 °C leads, depending on the residence time, to a yield increase of 2-3%. For the residence times considered, a doubling from 1.5 s to 3 s also results in a yield increase of 2-3%, depending on the temperature. A further doubling to  $\tau = 6 \,\mathrm{s}$  means higher yields of only 1–2%. In general, it should be said that it is difficult to make reliable statements in these small ranges due to the imprecision of the analyses, but a temperature rise of 100 °C seems to have a similar effect on yields as doubling the residence time. In general, when examining the results, it can be said that, despite the higher measurement inaccuracy, complete or nearly complete yields can be achieved in the gas phase chlorination of hydrogen sulfide.



**Figure 10.** HCl yields of the H<sub>2</sub>S chlorination parameter study;  $\tau = 1.5-6$  s,  $u_{Cl2} = 10$  Mol %;  $T_R = 450$  °C ( $\blacksquare$ ), 500 °C ( $\bigcirc$ ), and 550 °C ( $\blacklozenge$ ).

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#### 4.3 Comparison of Bromination and Chlorination

The thermodynamically calculated reaction enthalpies and Gibbs energies for H<sub>2</sub>S chlorination and bromination differ from each other only in their magnitude. Both are exothermic and exergonic, but the chlorine enthalpies are lower by about 80 kJ mol<sup>-1</sup>. This facilitates the reaction with H<sub>2</sub>S, but the subsequent splitting of HCl is much more energy consuming than for HBr.

Regarding the laboratory tests, it can be positively emphasized for chlorination, that usable measurement results are already produced after a start-up time of 5 min, whereas start-up times of 20-60 min are necessary for bromination. With regard to the experimental results for all cases considered, higher yields are measured for chlorination than for bromination for the same operating parameters. Maximum yields could be determined for the chlorination of H<sub>2</sub>S at slightly milder conditions than for bromination, although reaching Y = 100 % is achieved in both cases.

In both halogenation experiments, the resulting sulfur was analyzed. While no by-product evidence can be confirmed for bromination, SCl<sub>2</sub> and S<sub>2</sub>Cl<sub>2</sub> formation can be reasonably suspected as a side reaction in H<sub>2</sub>S chlorination. Therefore, chlorination is associated with a higher risk potential, since chlorine is not only more reactive than bromine, but also an irritant and health-hazardous byproduct is formed. However, despite the byproducts generated, the purification of sulfur from halogens and chlorinated sulfur takes less flushing time for chlorination than for bromination. It can be added that if halogen loss occurs and it must be replaced, this would be more significant for bromine, since it is much more expensive than chlorine [29].

#### Summary 5

In this work, hydrogen sulfide was split into sulfur and hydrogen halide by the halogens bromine and chlorine at high temperatures. The idea behind this is to regenerate the halogen in a second reaction, while producing hydrogen and thus extracting H<sub>2</sub> from hydrogen sulfide while the toxic gas itself is neutralized.

Laboratory experiments have shown that hydrogen sulfide can be completely reacted with both halogens in exothermic reactions, with slightly lower temperatures and residence times acceptable for chlorination. For bromination, complete yield was observed at  $\tau = 6 s$  and  $T_{\rm R}$  = 600 °C, while for chlorination the parameter values are 3 s and 550 °C, both reactions worked best with a 10 % excess of halogen.

No by-products were observed for bromination; the excess bromine just dissolves in the sulfur and can be separated, for example, by an inert gas stream. During chlorination, sulfur chlorides are most likely formed from the excess chlorine and sulfur produced, but the evidence for this is still lacking. Since these are equilibrium reactions, when

purged with inert gas they run in the direction of the reactants, resulting in the purification of the sulfur and recovery of the chlorine.

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## Symbols used

С	$[mol L^{-1}]$	concentration
$\Delta G$	$[kJ mol^{-1}]$	Gibbs energy
$\Delta H$	$[kJ mol^{-1}]$	enthalpy
$\Delta S$	$[J K^{-1} mol^{-1}]$	entropy
$T_{\mathbf{x}}$	[°C]	temperature of x
t	[s]	time
$u_{\rm Hal}$	[-]	excess of halogen
X	[-]	conversion
Y	[-]	yield
$y_{i}$	[-]	molar fraction of gases

## Greek symbols

$\overline{\Delta}$	[-]	difference
τ	[s]	mean residence time
$\nu_{\mathrm{i}}$	[-]	stoichiometric factor

### Sub- and superscripts

R	reactor, reaction
Hal	halogen
$Cl_2$	chlorine
Br <sub>2</sub>	bromine

### Abbreviations

- MFC mass flow controller
- TIC temperature indicating controller
- FEP fluorinated ethylene propylene
- Hal halogen

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