

## Effect of reaction parameters on the quality of captured sulfur in Claus process



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### HIGHLIGHTS

- ▶ Examined quality of collected sulfur deposits under different reaction conditions.
- ▶ All sulfur deposits were analyzed and proved to be of cyclo-S<sub>8</sub> (α-sulfur) allotrope.
- ▶ Equivalence ratio did not show significant effect on the quality of sulfur deposits.
- ▶ Carbon dioxide did not show considerable effect on sulfur deposits quality as well.
- ▶ Methane and propane caused sulfur deposits to contain considerable amounts of carbon.

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### ABSTRACT

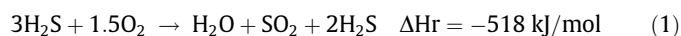
Quality of sulfur deposits collected from hydrogen sulfide combustion has been examined. Experimental conditions representing selected practical systems have been investigated. Combustion of hydrogen sulfide was allowed to occur under the different conditions with sulfur deposits collected for analysis. Experimental conditions represented effect of equivalence ratio of rich (Claus) conditions and stoichiometric conditions; effect of contaminants, other than H<sub>2</sub>S, in the acid gas stream; combustion of H<sub>2</sub>S with hydrocarbon fuels (methane and propane). Sulfur deposits from H<sub>2</sub>S combustion under various conditions were captured and analyzed using X-ray powder diffraction and laser induced breakdown spectroscopy (LIBS) diagnostics. X-ray powder diffraction was used to determine the type of deposited sulfur allotrope, while LIBS was used to identify the elemental analysis of deposited sulfur.

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## 1. Introduction

Hydrogen sulfide is known to be present in different quantities in crude natural gas extracted from the gas/oil wells. The use of crude natural gas in any chemical to thermal energy transformation process, e.g. combustion, furnaces or power system results in the formation of acid gases, such as, SO<sub>2</sub> and SO<sub>3</sub> which are then transformed to sulfurous and sulfuric acid, if released to the atmosphere. In addition, the presence of these gases lowers the dew point of the combustion gases so that exhaust gases must be released at higher temperatures. Therefore, hydrogen sulfide must be removed from natural gas prior to its utilization. Amine extraction process [1–3] is used for the removal of acidic gases, mainly H<sub>2</sub>S and CO<sub>2</sub>, from crude natural gas wherein alkaline-based organic compounds are used to absorb H<sub>2</sub>S and CO<sub>2</sub> from the fuel stream. Although the concentration of the absorbed H<sub>2</sub>S is fairly low, it is crucial that hydrogen sulfide undergoes treatment process to hin-

der its harmful effects on both the human health and environment from the industrial process. Claus process [4–8] is commonly used for the treatment of hydrogen sulfide wherein reaction between H<sub>2</sub>S and O<sub>2</sub> occurs under rich conditions ( $\Phi = 3$ ) to form elemental sulfur. During this reaction one third of H<sub>2</sub>S is burned to form SO<sub>2</sub> (reaction (1)). Afterwards, the reaction continues between the so formed SO<sub>2</sub> and unburned H<sub>2</sub>S to form sulfur (reaction (2)) which is then captured in liquid (in hot region) or solid form (in cold region). Practically, the process is divided into two main stages consisting of thermal stage and some catalytic stages. Both stages have same chemical reaction, but catalysts are used for the later stage wherein H<sub>2</sub>S concentrations are considerably low.



Sulfur collected from Claus process is considered a value-added product since it has many usage in several industrial and other applications. Selim et al. [9] analyzed the sulfur deposits collected from the reactor walls maintained at relatively low-temperatures.

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These results revealed that sulfur deposits primarily consist of cyclo-S<sub>8</sub> (α-sulfur) with orthorhombic crystal structure. However, the quality of collected sulfur was not examined. In this paper we investigate the quality of sulfur collected with respect to reactor conditions (gas stream composition and equivalence ratio).

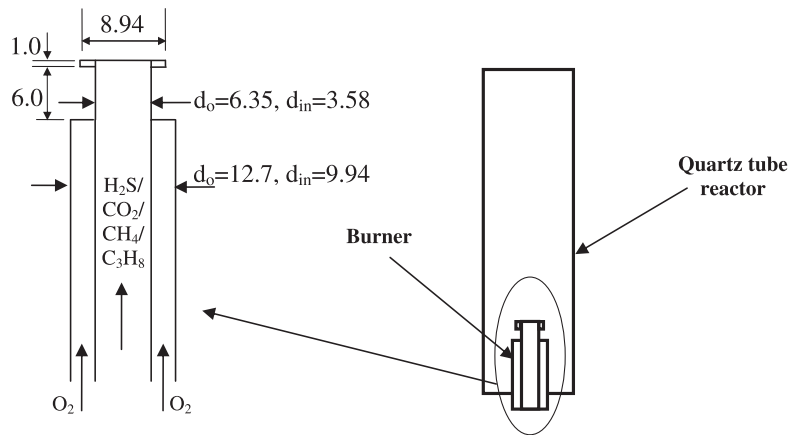
**2. Experimental setup and diagnostics**

A schematic diagram of the combustor used in this study is shown in Fig. 1. The facility consists of a quartz tube reactor of 19 cm length and 4 cm inner diameter. A double concentric tubular burner was designed and used for all experiments reported here. In addition, a bluff body was used to anchor the flame. In all the experimental results reported here, oxygen was used as an oxidizer and it was injected into the outer annulus of the burner. The hydrogen sulfide was introduced into the central tube of the burner wherein it was premixed with carbon dioxide, methane, or propane prior to their injection into the burner. Dimensions of the burner are given on Fig. 1. All flow rates were adjusted using thermal flow controllers. Quartz reactor was installed in a steel housing base which was used to collect the condensed sulfur. Fig. 2 shows a photograph of the sulfur formed with deposited onto the reactor housing. Average time of each experiment was about an hour in order to allow accumulation of sizeable amounts of sulfur deposit

form the tests. Laser induced breakdown spectroscopy (LIBS) was used for most of this study to analyze the chemical structure of deposited sulfur. The LIBS setup consisted of seven-channel spectrometer equipped with seven CCD cameras. The spectrometer covered a band of wavelengths extending from 200 nm to 970 nm, equally distributed on the seven CCD cameras. A 532 nm Nd:YAG was used to excite the samples inside the LIBS chamber. The sampling chamber is connected to the seven-channel spectrometer via a fiber optic cable. Fig. 3 shows a schematic diagram of the LIBS setup. Since LIBS gives only the elemental analysis of the sample, X-ray powder diffraction technique has been used primarily to determine the allotrope of collected sulfur.

**3. Experimental conditions**

Selected experimental conditions have been reported in this study. Firstly, we investigated the effect of reactants equivalence ratio on the quality of collected sulfur deposits. Two equivalence ratios examined here (stoichiometric and Claus conditions). Secondly, effect of other contaminant (carbon dioxide) likely to accompany hydrogen sulfide in the acid gas stream is examined. Finally, effect of hydrogen sulfide combustion in presence of hydrocarbon fuels (methane and propane) on the quality of



All dimensions are in millimeters

Fig. 1. A schematic diagram of the experimental reactor.

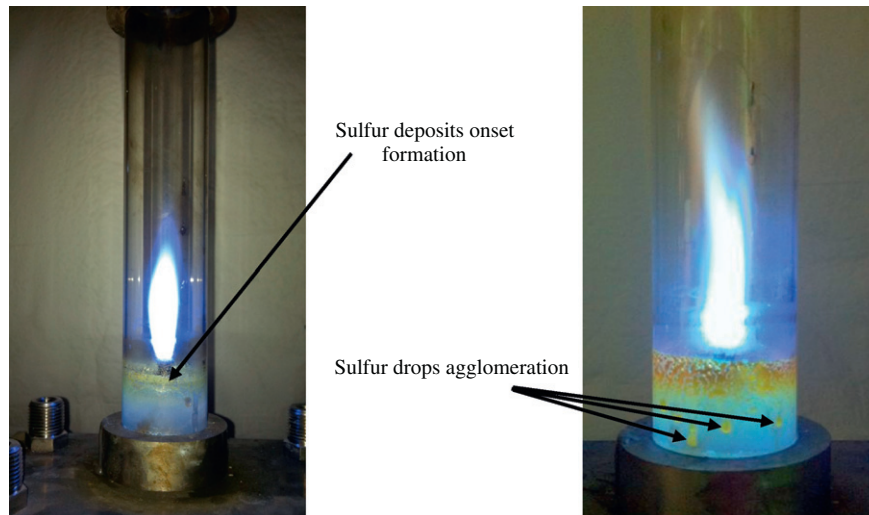


Fig. 2. The onset of sulfur formation, agglomeration and precipitation in reactor housing.

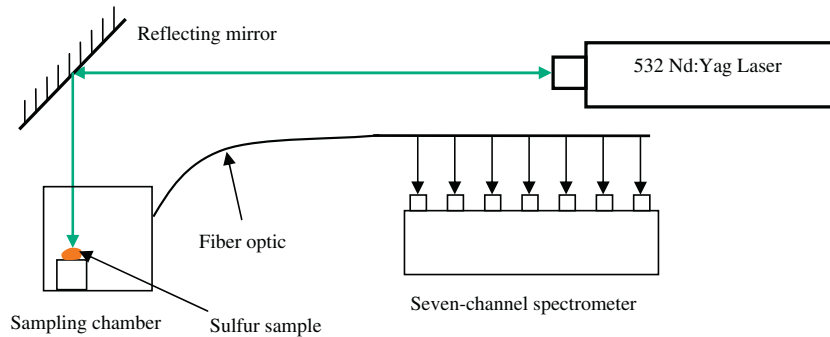


Fig. 3. A schematic diagram of the LIBS setup.

Table 1  
Test matrix.

Investigation	Case #	Reactants	Reactants flow rates, respectively, (l/min)
Effect of equivalence ratio	1	H <sub>2</sub> S/O <sub>2</sub> (stoichiometric)	0.7/1.05
	2	H <sub>2</sub> S/O <sub>2</sub> (Claus)	0.7/0.35
Effect of acid gas contaminants	3	H <sub>2</sub> S/O <sub>2</sub> /CO <sub>2</sub>	0.7/0.35/0.3
Effect of hydrocarbon fuels	4	H <sub>2</sub> S/O <sub>2</sub> /CH <sub>4</sub>	0.7/1.35/0.5
	5	H <sub>2</sub> S/O <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	0.7/2.85/0.5

captured sulfur is examined. Table 1 shows the test matrix used for this investigation.

#### 4. Results and discussion

Experiments initially focused on determination of the type of allotrope of the collected sulfur; meanwhile, effect of equivalence ratio was investigated (cases 1 and 2). Secondly, effect of other contaminants in the acid gas (carbon dioxide) on the collected sulfur deposits was studied (case 3). Finally, examination of the effect hydrogen sulfide combustion in hydrocarbon fuels was conducted (cases 4 and 5).

##### 4.1. Effect of equivalence ratio

Sulfur deposits were collected inside the reactor housing under both stoichiometric and Claus conditions. X-ray diffractogram of the captures samples revealed that sulfur deposits were all cyclo-

S<sub>8</sub> ( $\alpha$ -sulfur) allotrope with orthorhombic crystal structure. This supports the previous findings of Selim et al. [9] which also reported the presence of cyclo-S<sub>8</sub> allotrope. Change in reactants equivalence ratio showed insignificant effect on the crystal structure of captured sulfur. Fig. 4 depicts the diffractogram of collected sulfur deposits under Claus and stoichiometric conditions. These results are also compared with the typical diffractogram of cyclo-S<sub>8</sub> ( $\alpha$ -sulfur) from the literature [10]. The collected sulfur sample showed good agreement with diffractogram of cyclo-S<sub>8</sub>. It is important to note that the crystal structure was determined from the obtained spectrum peaks. Note that the change in peak intensity does not infer any change in the crystal structure. Change in peaks intensity could be attributed to several reasons, such as, difference in size of the sample analyzed, difference in received signal magnification, or difference in light source intensity and its variation.

After the determination of sulfur allotrope, LIBS experiments were conducted to investigate the quality of sulfur samples. The objective was to identify elemental analysis of sulfur deposits as affected by the experimental conditions imposed on these samples. Figs. 5 and 6 show the spectra of sulfur samples collected from cases 1 and 2. Emission spectra depict the presence of sulfur peaks within 547–564 nm. These results agree with the findings of Fowler and Vaidya [11] that showed that excited sulfur emits in this range of wavelengths. Difference in equivalence ratio did not pose any significant effect on the spectral emission characteristics.

##### 4.2. Effect of acid gas contaminants

Carbon dioxide is a common contaminant that accompanies hydrogen sulfide in the acid gas stream. Case 3 represents the

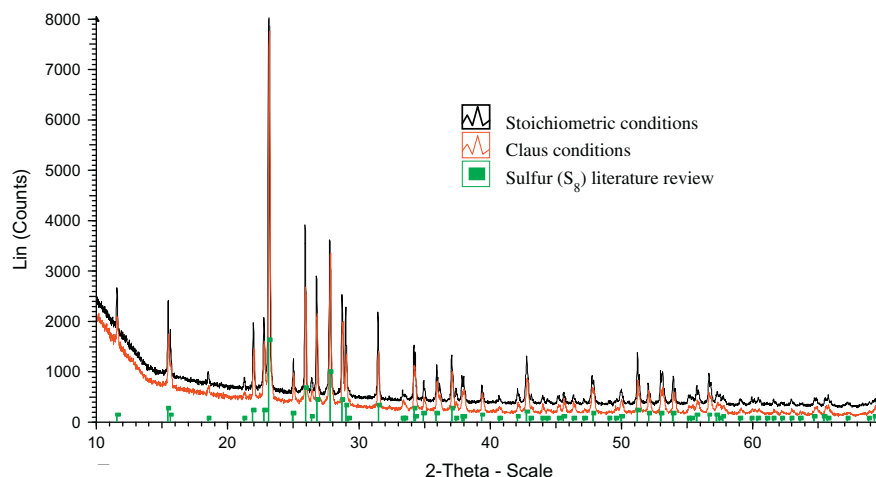
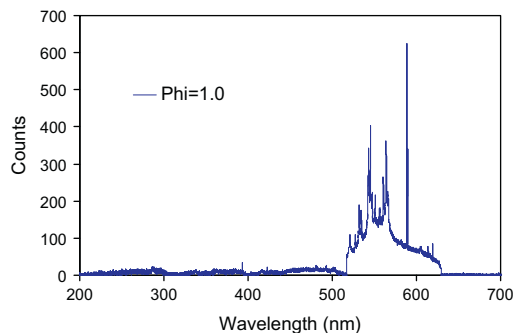
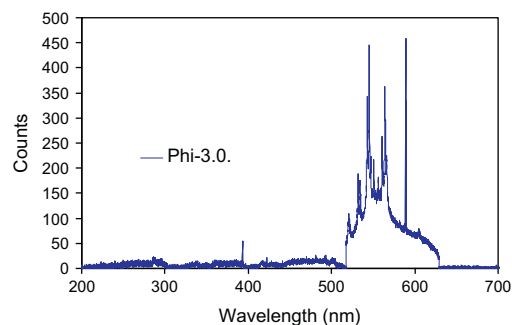


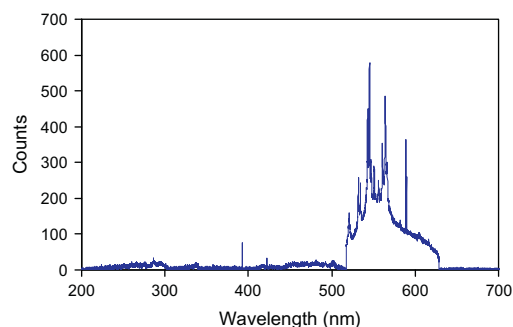
Fig. 4. Diffractograms of different sulfur samples.



**Fig. 5.** Emission spectrum of sulfur deposits collected from the combustion of  $\text{H}_2\text{S}/\text{O}_2$  (stoichiometric).



**Fig. 6.** Emission spectrum of sulfur deposits collected from the combustion of  $\text{H}_2\text{S}/\text{O}_2$  (Claus conditions).

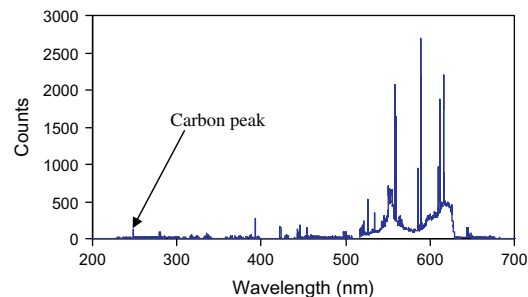


**Fig. 7.** Emission spectrum of sulfur deposits collected from the combustion of  $\text{H}_2\text{S}/\text{O}_2/\text{CO}_2$ .

investigation of sulfur deposits collected from (70%  $\text{H}_2\text{S}$  and 30%  $\text{CO}_2$ ) acid gas stream. Fig. 7 shows the spectrum of sulfur deposits collected under the experimental conditions representing case 3. Results show that sulfur peaks are obtained within the same bands as in cases 1 and 2. Presence of carbon dioxide in the acid gas stream did not show a prominent effect on the quality of deposited sulfur.

#### 4.3. Effect of hydrocarbon fuels

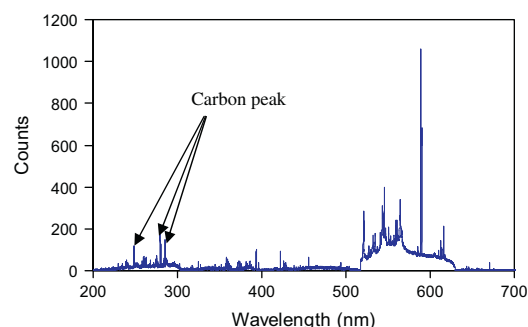
Hydrocarbon fuels could exist in the acid gas stream due to imperfect natural gas separation and amine extraction processes. This results in the presence of hydrocarbon fuels such as, methane and propane. Furthermore hydrocarbon fuels are used for the combustion of  $\text{H}_2\text{S}$  in Claus reactors in order to promote and sustain combustion. Cases 4 and 5 depict the collection of sulfur deposits in presence of methane (case 4) and propane (case 5). Fig. 8 shows



**Fig. 8.** Emission spectrum of sulfur deposits collected from the combustion of  $\text{H}_2\text{S}/\text{O}_2/\text{CH}_4$ .

the emissions spectrum of sulfur deposits collected from case 4. Results show carbon peak at  $\sim 250$  nm in addition to sulfur peaks in the range of 547–564 nm. This suggests that sulfur deposits collected under these conditions contain trace amounts of carbon to result in low quality of sulfur. On the other hand, Fig. 9 depicts the emissions spectrum of sulfur deposits collected under conditions of case 5. Results show the presence of several carbon peaks (within 250–280 nm) due to the formation of soot layer. This indicates that carbon concentration in captured sulfur is higher than case 4. Fig. 10 shows a magnified photograph of sulfur deposit collected from case 5 wherein one can clearly see soot layer covers the sulfur deposits.

Chemkin simulations were carried out to justify the presence of carbon (soot) in cases 4 and 5 and absence of carbon in case 3, using CHEMKIN PRO software by Reaction Design. The simulations were performed for both cases 3 and 4 in a plug flow reactor. Reactor dimensions were similar to the actual reactor, flow velocity was set to be 1 cm/s, and the chemical kinetics of the reactions were obtained via the GRI mechanism as defined in the operational procedures of the code. Figs. 11 and 12 depict carbon net reaction rate in a plug flow reactor under experimental conditions of case 3 and



**Fig. 9.** Emission spectrum of sulfur deposits collected from the combustion of  $\text{H}_2\text{S}/\text{O}_2/\text{C}_3\text{H}_8$ .



**Fig. 10.** Sulfur/soot deposits collected from the combustion of  $\text{H}_2\text{S}/\text{O}_2/\text{C}_3\text{H}_8$ .

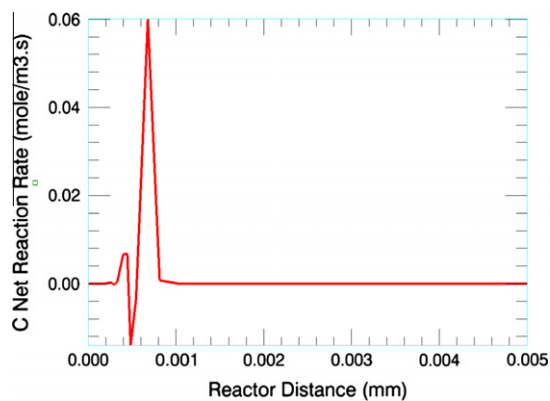


Fig. 11. Carbon net reaction rate from  $\text{H}_2\text{S}/\text{O}_2/\text{CO}_2$  flame, for case 3 (Chemkin simulations).

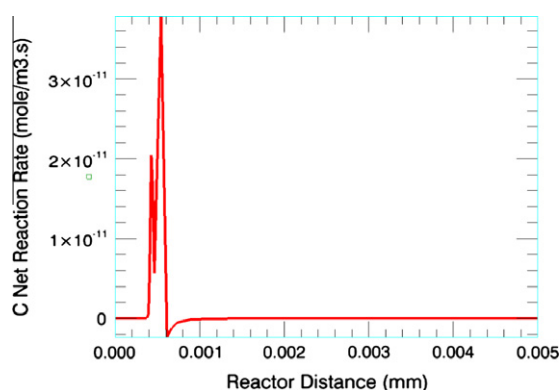
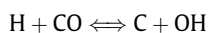
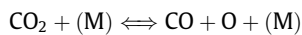


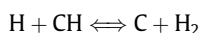
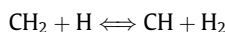
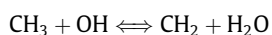
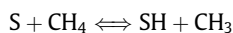
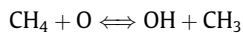
Fig. 12. Carbon net reaction rate  $\text{H}_2\text{S}/\text{O}_2/\text{CH}_4$  flame, for case 4 (Chemkin simulations).

4. The results show that carbon net reaction rate is nine orders of magnitude higher in cases 4 as compared to case 3. This is attributed to the fact that carbon dioxide is unlikely to release the carbon atom thorough chemical reactions. In addition, reaction temperature is relatively low to trigger  $\text{CO}_2$  dissociation to carbon and oxygen. However, hydrocarbon reactions are likely to form carbon through the reactions of the alkyl group ( $\text{CH}_3$ ). Possible chemical channels for the formation of carbon in each case are as follows:

#### Case 3



#### Case 4



## 5. Conclusions

Examination of sulfur deposits collected from the combustion of hydrogen sulfide has been conducted. Hydrogen sulfide combustion was carried out under different experimental conditions representing practical systems. First and second cases represented the variation of  $\text{H}_2\text{S}/\text{O}_2$  equivalence ratio between rich (Claus) condition and stoichiometric condition. Third case represented the presence of  $\text{CO}_2$  contaminant in the  $\text{H}_2\text{S}$  acid gas stream. Fourth and fifth case showed the combustion of  $\text{H}_2\text{S}$  with hydrocarbon fuels (methane and propane). Sulfur deposits were collected and analyzed in all cases using X-ray powder diffraction and laser induced breakdown spectroscopy (LIBS) diagnostics. X-ray powder diffraction showed that the allotrope of sulfur deposits is of cyclo- $\text{S}_8$  ( $\alpha$ -sulfur) with orthorhombic crystal structure. The LIBS experiments revealed that equivalence ratio of  $\text{H}_2\text{S}/\text{O}_2$  flame did not have any prominent effect on the quality of captured sulfur. Similarly, presence of carbon dioxide in the acid gas stream showed insignificant effect on the deposited sulfur. However, combustion of hydrogen sulfide in methane and propane showed sulfur deposits to contain carbon (soot). Concentration of carbon was higher in case of using propane instead of methane revealing that carbon content in the fuel has a significant effect on the amounts of carbon present in the deposited sulfur.

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