

# Parametric study of COS and CS<sub>2</sub> formation from H<sub>2</sub>S conversion in the presence of CO<sub>2</sub>, CO and CH<sub>4</sub>

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## Abstract

The aim of this work is to evaluate the impact of the presence of given gases (i.e. carbon dioxide, carbon monoxide and methane) on the formation of COS and CS<sub>2</sub> from the conversion of H<sub>2</sub>S in an oxygen lean environment. To this end, the present work shows a systematic experimental study, in a laboratory quartz tubular reactor, of the wet oxidation of H<sub>2</sub>S in the presence of variable amounts of CO<sub>2</sub> (0.1-10 %), CO (0.05-0.4 %) or CH<sub>4</sub> (0.025-0.3 %). Experiments are performed under well-controlled conditions in a diluted N<sub>2</sub> atmosphere, at atmospheric pressure, in the 300-1500 K temperature range and at fuel rich conditions.

## Introduction

Non-conventional natural gas may contain hydrogen sulphide in its composition. During combustion, the H<sub>2</sub>S is mainly converted to SO<sub>2</sub>, but also to COS and/or CS<sub>2</sub> due to side reactions between sulfur and carbon containing compounds.

Besides to the general interest of analyzing the formation of COS and CS<sub>2</sub> for the utilization of non-conventional natural gas (e.g. sour gas and shale gas) in energy applications, in the Claus process, the formation of CS<sub>2</sub> and COS arises as an operational problem derived from the post-flame region of the furnace [1].

Global reactions for the formation of COS and CS<sub>2</sub> in these processes include the interaction of H<sub>2</sub>S with CO<sub>2</sub> (reactions r.1 and r.2) and CH<sub>4</sub> (reaction r.3). Both CO<sub>2</sub> and CH<sub>4</sub> are main components of non-conventional natural gases and are present as impurities in the Claus process as well.



The extent of these interactions and, consequently, the final emission of COS and CS<sub>2</sub>, depends on the specific operating conditions considered and the atmosphere environment [2]. In this context, this work shows a parametric study of the experimental formation of COS and CS<sub>2</sub> from the conversion of H<sub>2</sub>S in the presence of CO<sub>2</sub>, CO and CH<sub>4</sub> over a wide range of operating conditions.

## Methodology

The experiments are performed in an experimental installation constituted by a gas feeding system, a reaction system, and a gas analysis system. The gas feeding system consists of gas cylinders, a water vapor injection system and mass flow controllers; the reaction system consists of a premix quartz tubular reactor inside an electrically heated oven; and the gas analysis system consists of a Fourier Transform Infrared (FTIR) spectrometer and a gas chromatograph. A similar experimental installation was previously used by Giménez-

López et al. [3], albeit with a premix alumina tubular reactor, to study the HCN oxidation process with success. Table 1 shows the conditions of the test cases.

Table 1. Matrix of experimental conditions. All experiments are performed at atmospheric pressure, with a total flow rate of 1000 mL(STP)/min and using N<sub>2</sub> as bath gas.

Set	H <sub>2</sub> S (ppm)	Partner Gas (ppm)	H <sub>2</sub> O (%)	λ*	Temperature (K)
1	500	CO <sub>2</sub>	1000	1	300-1500
2	500		1000	1	300-1500
3	1500		100000	0.5	0.3
4	1000	CO	2000	0.5	300-1500
5	1000		500-4000	0.5	1275
6	1000		500-4000	0.5	0.7
7	1000	CH <sub>4</sub>	2000	0.5	300-1500
8	1000		250-3000	0.5	0.3

\*λ: air excess ratio referred to the oxidation of H<sub>2</sub>S.

## Main results

Three systems have considered in this work: H<sub>2</sub>S-CO<sub>2</sub>, H<sub>2</sub>S-CO and H<sub>2</sub>S-CH<sub>4</sub> system.

### H<sub>2</sub>S-CO<sub>2</sub> system

This system include the interaction of H<sub>2</sub>S with both 0.1 % and 10 % CO<sub>2</sub>, under fuel-rich conditions, over the 300-1500 K temperature interval. The concentration results of COS and CS<sub>2</sub> are shown in Figure 1.

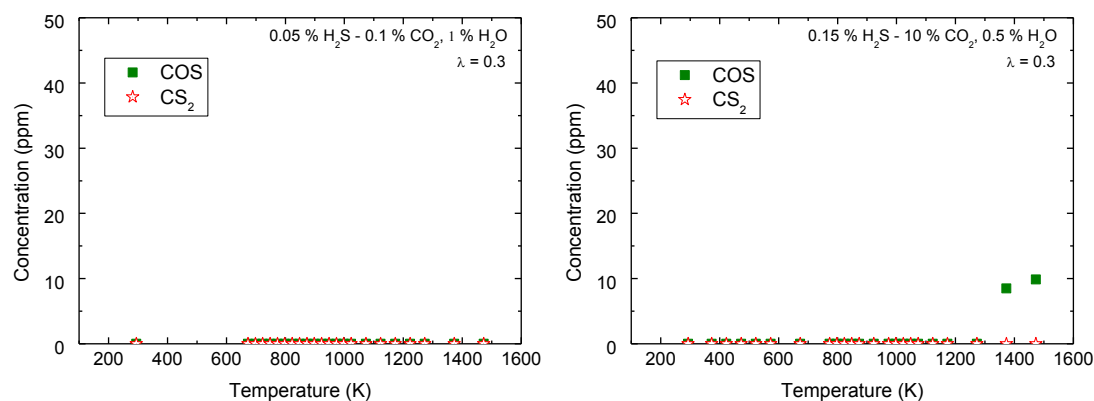


Figure 1. Concentration results of COS and CS<sub>2</sub> from the conversion of H<sub>2</sub>S in the presence of 0.1 % CO<sub>2</sub> (left side) and 10 % CO<sub>2</sub> (right side) as function of the reaction temperature, and for λ = 0.3. Sets 2 and 3 in Table 1.

In this system, CS<sub>2</sub> was not detected at any of the operating conditions considered, neither for a high inlet CO<sub>2</sub> concentration. Low COS concentrations were detected in the presence of high CO<sub>2</sub> concentrations at high temperatures (≥ 1375 K).

### H<sub>2</sub>S-CO system

This system includes the interaction of H<sub>2</sub>S with 2000 ppm CO over the 300-1500 K temperature interval, and with different concentrations of CO (500-4000 ppm) at 1275 K, under fuel-rich conditions. The concentration results of COS and CS<sub>2</sub> are shown in Figures 2 and 3.

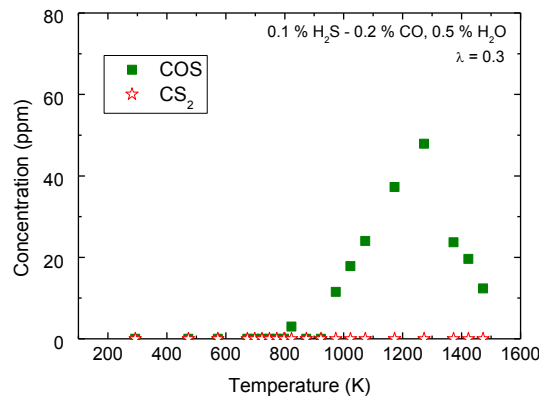


Figure 2. Concentration results of COS and CS<sub>2</sub> from the conversion of H<sub>2</sub>S in the presence of 0.2 % CO as function of the reaction temperature, and for  $\lambda = 0.3$ . Set 4 in Table 1.

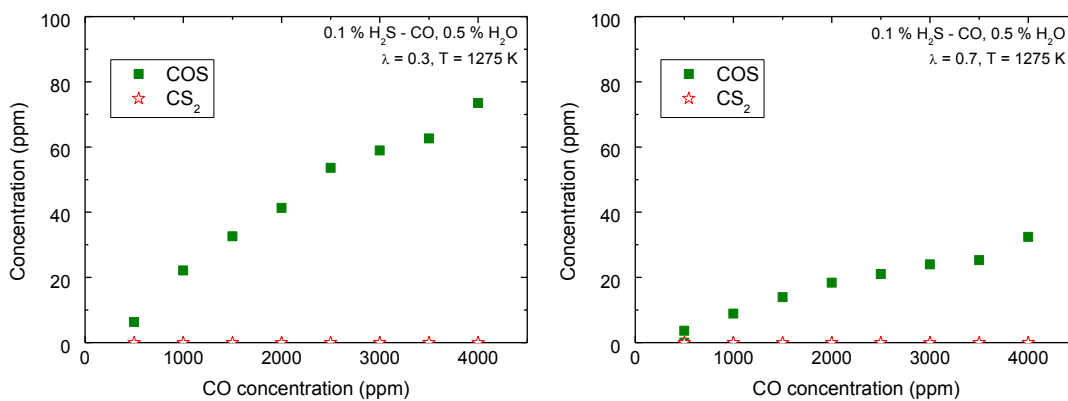


Figure 3. Concentration results of COS and CS<sub>2</sub> from the conversion of H<sub>2</sub>S in the presence of different CO concentrations at 1275 K for  $\lambda = 0.3$  (left side) and  $\lambda = 0.7$  (right side). Sets 5 and 6 in Table 1.

In this system, CS<sub>2</sub> was not detected at any of the operating conditions considered. For a given CO concentration (Figure 2), COS starts to be quantified at 825 K and shows its maximum concentration value at 1275 K. At this reaction temperature, either increasing the CO concentration or decreasing the oxygen concentration in the reaction environment, leads to an increased COS concentration at the reactor outlet (Figure 3).

#### H<sub>2</sub>S-CH<sub>4</sub> system

This system includes the interaction of H<sub>2</sub>S with 2000 ppm CH<sub>4</sub> over the 300-1500 K temperature interval, and with different concentrations of CH<sub>4</sub> (250-3000 ppm) at 1475 K, under fuel-rich conditions. The concentration results of COS and CS<sub>2</sub> are shown in Figures 4 and 5.

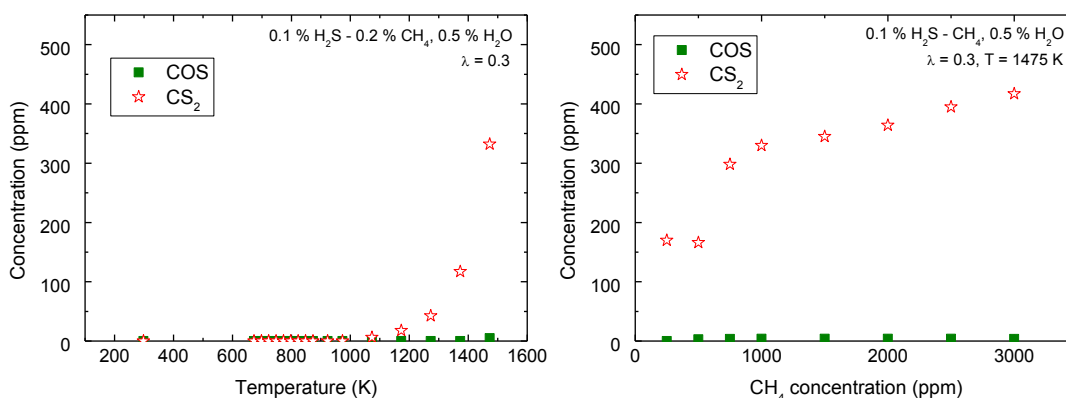


Figure 4. Concentration results of COS and CS<sub>2</sub> from the conversion of H<sub>2</sub>S in the presence of 0.2 % CH<sub>4</sub> as function of the reaction temperature (left side) and in the presence of different CH<sub>4</sub> concentrations at 1475 K (right side), for  $\lambda = 0.3$ . Sets 7 and 8 in Table 1.

In this system, COS was not detected at any of the conditions analyzed. For a given CH<sub>4</sub> concentration, CS<sub>2</sub> starts to be quantified at 1075 K and shows an increasing concentration tendency with temperature. At 1475 K, the higher the inlet CH<sub>4</sub> concentration, the higher the outlet CS<sub>2</sub> concentration.

## Conclusions

- The COS production is favored by both increased CO concentration and low O<sub>2</sub> level in the reaction environment, at relative high temperatures (~ 1275 K).
- The CS<sub>2</sub> production is favored by the increase of both CH<sub>4</sub> concentration in the reaction environment and reaction temperature.

## Acknowledgements

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## References

- [1] K. Karan, L.A. Behie, *Ind. Eng. Chem. Res.* 43 (2004) 3304-3313.
- [2] M. Abián, M. Cebrián, A. Millera, R. Bilbao, M.U. Alzueta, *Combust. Flame* 162 (2015) 2119-2127.
- [3] J. Giménez-López, M. Martínez, A. Millera, R. Bilbao, M.U. Alzueta, *Combust. Flame* 158 (2011) 48–56.