

Experimental and modeling study of CH₄/H₂S oxidation at high pressures

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INTRODUCTION

Hydrogen sulfide can be found in raw natural gas and as a by-product during different fuel industrial processes like coal or biomass gasification, gas sweetening and other desulfuration processes. However, the nature of the combustion of sulfur compounds remains unknown in relation to many aspects, and the different fuel compositions, together with the presence of different combustion atmospheres, may affect the conversion of H₂S. Nowadays, the increasing importance of fuel sources such as sour gas and shale gas brings interest to the direct use of these fuels without the use of expensive cleaning treatments. In this context, the main goal of this work is to study the influence of operating pressure on the conversion of sour gas, mainly CH₄ and H₂S mixtures, and the main reactions involved in their oxidation.

EXPERIMENTAL METHOD

The experiments were carried out in a high-pressure tubular flow reactor set-up, which is described in detail elsewhere [1]. The oxidation of CH₄/H₂S mixtures was studied, testing different manometric pressures (10, 20 and 40 bar) and different reaction systems (CH₄/O₂, H₂S/O₂ and CH₄/H₂S/O₂), in the temperature range of 500-1100 K. Briefly, the set-up includes gas cylinders that supply the gases to the system, while mass flow controllers assure a total flow rate of 1 L (STP)/min. Gases used in this work (CH₄, H₂S and O₂) were highly diluted in nitrogen and the experimental conditions are detailed in Table 1. The reaction system included a quartz tubular reactor (inner diameter of 6 mm and 1500 mm in length) enclosed in a stainless-steel tube that acts as a pressure shell. The steel tube is placed horizontally in a tubular oven, with three individually controlled electrical heating elements that ensure an isothermal reaction zone of approximately 50 cm, with a uniform temperature profile (± 5 K). The reactor temperature is monitored by type K thermocouples positioned between the quartz reactor and the steel shell. Gas residence time in the set-up depends on pressure and temperature and it can be expressed as: $t_r[s] = 261.1 P[\text{bar}]/T[\text{K}]$. Previously to the gas analysis systems, gases pass through a filter and a condenser to ensure gas cleaning and water-free content. Products are analyzed by a gas chromatograph equipped with thermal conductivity detector (TCD) to measure H₂S, CH₄ and O₂, and a continuous analyzer with an UV detector to quantify the SO₂ concentration. The uncertainty of the measurements is estimated within 5%.

Table 1: Experimental conditions

Set	Pressure [bar]	λ_{total}	λ_{CH_4}	$\lambda_{\text{H}_2\text{S}}$	CH ₄ [ppm]	H ₂ S [ppm]	O ₂ [ppm]	$t_r[s]$
1	20	1.59	1.59	-	1348	-	4286	5222/T(K)
2	20	2.04	-	2.04	-	497	1520	5222/T(K)
3	10	1.03	1.77	2.44	1282	1243	4550	2611/T(K)
4	20	1.01	1.73	2.45	1303	1224	4503	5222/T(K)
5	40	1.03	1.74	2.49	1320	1230	4600	10444/T(K)

KINETIC MODEL

The experimental results were interpreted in terms of kinetic modeling using Chemkin-PRO. The kinetic model used in this work is a revised version of that from Colom-Díaz et al. [2] for describing H₂S conversion at atmospheric pressure, which counts with an updated subset of H₂S reactions and where the kinetic parameters of reaction $\text{HSOO} \rightleftharpoons \text{HSO}_2$, a key step in H₂S oxidation, were proposed, what was supported by recent theoretical works. This model also counts with reactions related to the interaction of carbon and sulfur species, from the work by Alzueta et al. [3] about the inhibition and sensitization of fuel oxidation by SO₂. The kinetic model also considers another study about CS₂ and COS conversion under different combustion conditions [4], and the work from Abián et al. [5] where the impact of SO₂ on the formation of soot from ethylene pyrolysis was evaluated. On the other hand, kinetic models from recent works have also been considered, like the one from Gersen et al. [6] about CH₄ oxidation at high pressures and its interaction with H₂S, where the authors claimed the need for a better characterization on the reactions of H₂S and SH with peroxides (HO₂ and CH₃OO) and those on the formation and consumption of organosulfuric compounds. Another recent work, by Zeng et al. [7], studied the system CH₄/CS₂/O₂ in a jet stirred reactor, and mentioned the complexity of the C-H-O-S combustion chemistry.

RESULTS AND CONCLUSIONS

In this work, the CH₄/H₂S/O₂ system has been studied at different pressures, in the temperature range of 500-1100 K and nearly stoichiometric conditions. A comparison of the conversion of CH₄, H₂S and CH₄/H₂S at 20 bar is shown in Figure 1 (sets 1, 2 and 4 in Table 1). In this figure, H₂S and CH₄ concentrations are normalized, dividing the outlet concentration by its respective inlet concentration. As can be seen, the oxidation of CH₄ is promoted to lower temperatures with the addition of H₂S, as well as the oxidation of H₂S is promoted when CH₄ is present in the gas. In the latter case, the presence of O₂ (represented by $\lambda_{\text{H}_2\text{S}}$) is slightly higher in comparison to the one in the oxidation of neat H₂S. The kinetic model fits well the experimental trends, mainly when CH₄ and H₂S are oxidized separately. When H₂S and CH₄ are mixed, the model underpredicts the oxidation of both. In the case of CH₄, its conversion is due to the presence of OH radicals that come from the oxidation of H₂S, through reaction: $\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$. Another important reaction in the present conditions is the interaction between CH₃ radicals and H₂S: $\text{CH}_3 + \text{H}_2\text{S} = \text{SH} + \text{CH}_4$. However, some other important interactions between sulfur and carbon species are expected to happen, because the concentrations are not well matched by the model. In particular, the reactions involving peroxides (H₂O₂, HO₂, CH₃OO) may be important, as was pointed by Gersen et al. [6] in their work about H₂S oxidation at high pressures. Finally, the important role that peroxides play in H₂S oxidation [2] indicates that new reactions should be proposed. In this sense, Zeng et al. [7], in their work about co-oxidation of CH₄ and CS₂ in a jet stirred reactor, found that methane conversion was also promoted by the CS₂ presence to lower temperatures, presumably due to the interaction of CH₄ with radicals from CS₂ oxidation, and performed quantum calculations for interactions CH₄+O, CH₄+S, CH₄+S₂, CH₄+SO and CH₄+O₂. On the other hand, CS₂ experimental oxidation was shifted to higher temperatures by the CH₄ presence, which has also been seen for H₂S in another experiment performed nearly absolute atmospheric pressure (1.65 bar) (results not shown). The kinetic model proposed by Gersen et al. [6] was tested under the present experimental conditions, and no real improvement in the results was appreciated with it.

The influence of pressure was also evaluated for the oxidation of CH₄/H₂S. In Figure 2, H₂S and CH₄ concentrations obtained at different pressures are plotted vs. temperature (sets 3, 4 and 5 in Table 1). The same gas mixture was used in all the tests, and different manometric pressures were tested (10, 20 and 40 bar). As it is observed, higher pressures shift the conversion of both CH₄ and

H₂S to lower temperatures. These trends are captured by the model, although differences of 50-100 K with respect to experimental concentrations are found.

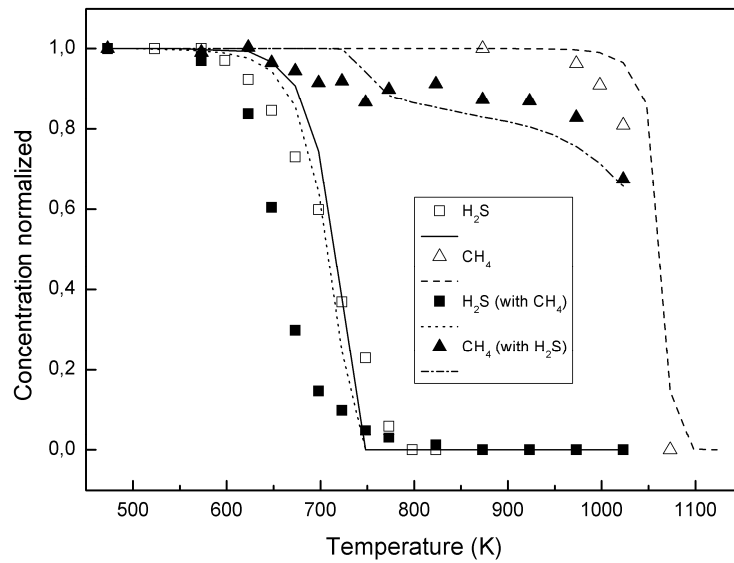


Figure 1: Results obtained under 20 bar of pressure for the conversion of H₂S and CH₄ individually (open symbols), and conversion of CH₄/H₂S mixtures (full symbols) vs. temperature. Lines denote model predictions. Conditions of sets 1, 2 and 4 in Table 1.

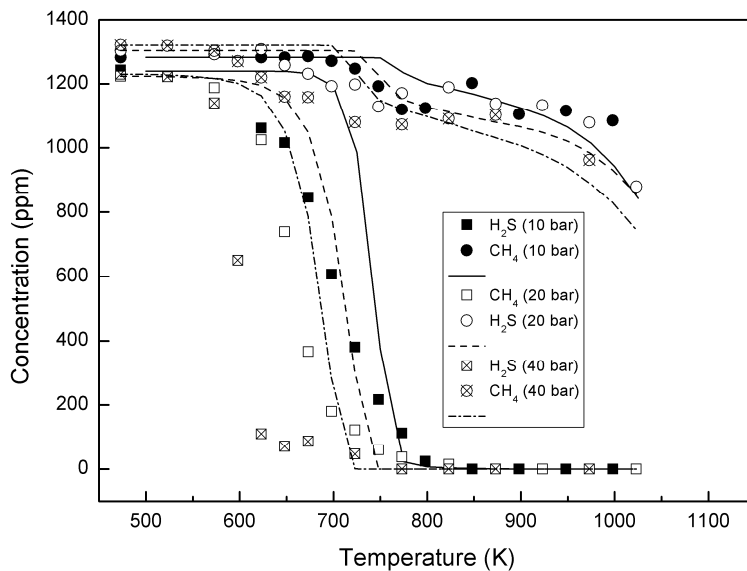


Figure 2: Results obtained for the same gas mixture of CH₄/H₂S at different manometric pressures. Symbols represent experimental concentrations and lines model predictions. Conditions of sets 3, 4 and 5 in Table 1.

In conclusion, at high pressures, the oxidation of CH₄ and H₂S is promoted to lower temperatures. Additionally, while the oxidation of CH₄ is still promoted at atmospheric pressure, the conversion of H₂S is inhibited. Furthermore, the influence of pressure promotes the oxidation of both species

to lower temperatures. The kinetic model can predict the experimental trends. However, in order to reproduce the experimental results accurately and be able to explain CH₄/H₂S oxidation, some reactions involving peroxides between carbon and sulfur species should be revised and proposed.

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