

# EVALUATION OF KINETIC MODEL FOR THE OXIDATIVE DECOMPOSITION OF H<sub>2</sub>S

G. Pio<sup>1,2</sup>, D. Barba<sup>1</sup>, V. Palma<sup>1</sup>, E. Salzano<sup>2</sup>

gianmaria.pio@unibo.it

<sup>1</sup> Dipartimento di Ingegneria Industriale, Università degli studi di Salerno

<sup>2</sup> Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna

## Abstract

This paper is focused on the definition, validation and application of a kinetic model for the H<sub>2</sub>S decomposition reaction path in oxidative conditions. In order to achieve this goal, experimental and numerical simulations were carried out. Results show the good model predictions in almost all tested conditions, excepted for the conditions of lower temperature and oxygen content, where discrepancies between experimental results and model calculations may be due to the lack of kinetic data related to Sulfur chemistry under the investigated conditions.

## Introduction

Environmental and economic considerations on the presence of sulfuric compounds in crude oil, natural gas and biogas, suggest further development on sulfur removal, starting from the well-known hydrodesulphurization process, which produces H<sub>2</sub>S as the main byproduct, and by the following Claus process, which is required to oxidize H<sub>2</sub>S to elemental Sulphur through a two-step reaction [1]. Because of thermodynamic limitations, a complete Sulphur conversion cannot be achieved. For this reason, further treatments are required before the tail gas emission in atmosphere to comply with the environmental regulations.

In this framework, a particularly attractive process is the thermal decomposition of H<sub>2</sub>S, where H<sub>2</sub> production makes this route potentially profitable. This reaction being strongly endothermic is often coupled with exothermic reaction, by adding a sufficient amount of oxygen in order to obtain a quasi-auto-thermal process [2]. This paper is then focused on the model evaluation for H<sub>2</sub>S decomposition reaction path in oxidative conditions. In order to achieve this goal, experimental and numerical simulations were carried out. The experiments were carried out in a temperature controlled quartz tubular reactor. The model was based on a new kinetic reaction network obtained by unifying those developed by University of California at San Diego [3], Leeds University [4] and Zhou research group at University of Sidney [5]. The kinetic network was first validated by reproducing the experimental data for stationary flames of premixed H<sub>2</sub>S-Air mixtures as retrieved from literature. Once validated, the experimental data for the oxidative decomposition were simulated by considering a Perfectly Stirred Reactors at constant volume. Particularly attention was paid to the effects of different O<sub>2</sub>/H<sub>2</sub>S molar ratio in the feeding mixture and to the effect of reactor temperature on product composition and heat generation.

The model will be devoted to the definition of process conditions, laminar burning velocity and safety parameters for tail gases, including more complex mixtures as hydrogen-based syngas mixtures, biogas, and waste gases [6, 7]

## Methodology

Experiments were carried out by treating H<sub>2</sub>S/O<sub>2</sub>/N<sub>2</sub> containing gaseous streams in a tailor-made quartz tubular reactor, consisting in a 300 mm length and 12 mm diameter tube, at different composition and temperature and at atmospheric pressure. The O<sub>2</sub>/H<sub>2</sub>S molar ratio has been varied in the range 0.2 - 0.35. The temperature was tested between 970 - 1400 K feeding gas mixture composed by H<sub>2</sub>S 10 % v/v, Oxygen and Nitrogen. Further details on the experimental equipment can be found in previous work [8].

Treated streams were analyzed by a quadrupole filter mass spectrometer (Hiden HPR 20) assuming the presence of following gaseous species  $\text{H}_2\text{S}$ ,  $\text{O}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$  and  $\text{N}_2$ .

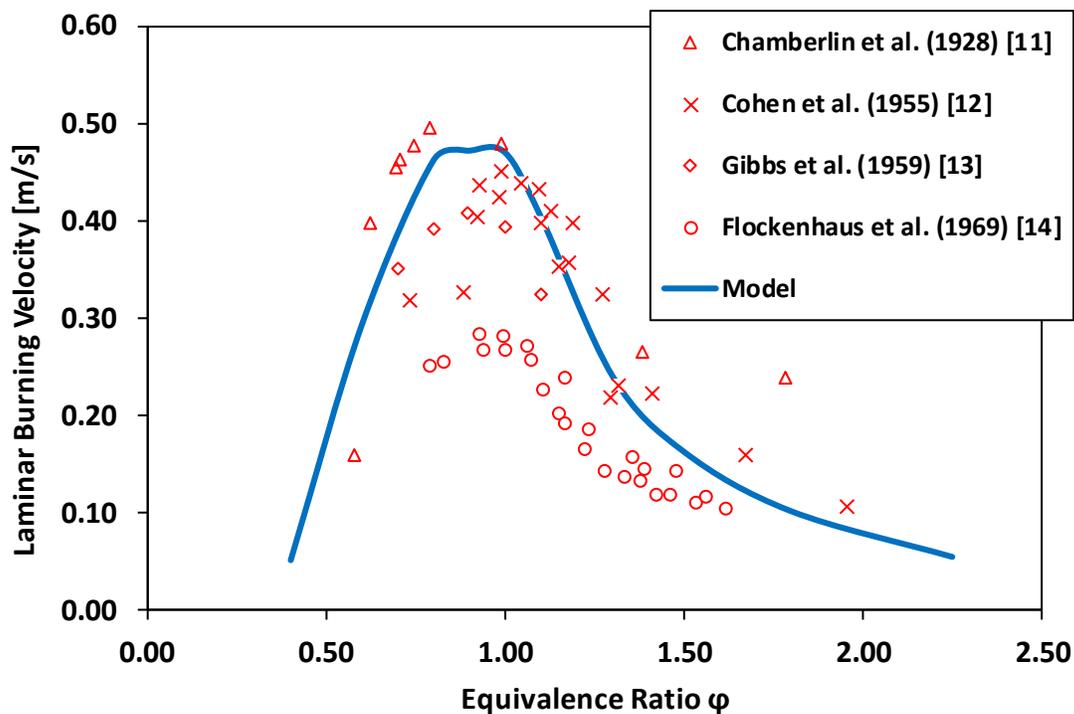
Experimental results were first compared with equilibrium data obtained by using the free access software GasEq [9] for thermochemical considerations. Hence, a modeling effort was carried out by considering a linear network of Perfectly Stirred Reactors (PSR) at constant volume, assuming perfect reactants mixing, by using the open source software Cantera [10].

### Model validation

In order to fully validate the new kinetic model, the Laminar Burning Velocity (LBV) was calculated and compared with data retrieved from literature at atmospheric pressure, room temperature (298 K) and different Equivalence Ratio  $\phi$  within the range 0.4 – 2.3, where  $\phi$  is defined as:

$$\phi = \frac{(n_f/n_{ox})}{(n_f/n_{ox})_{st}} \quad (1)$$

where  $n_f$  and  $n_{ox}$  represent the fuel and oxidizer mole at the actual and at the stoichiometric (st) conditions, respectively. Stoichiometric conditions were calculated considering the oxidation of  $\text{H}_2\text{S}$  to  $\text{SO}_2$  and  $\text{H}_2\text{O}$ . Results are shown in Figure 1.



**Figure 1.** Comparison of literature data (symbols) and model prediction (line) of Laminar Burning Velocity at 298 K and 1 bar as function of equivalence ratio.

Model predictions are within the experimental results for investigated composition. Nevertheless, large discrepancy among experimental data obtained by different authors may be observed. That can be attributed to differences in setup, procedure and correlation used to obtain un-stretched flames data. Indeed: Chamberlin et al. (1928) [11] in a pioneer study on  $\text{H}_2\text{S}$ -Air mixture measured the LBV by using horizontal glass tube 1 m long and

with internal diameter of 2.5 cm and photographic method, whereas data reported by Cohen et al. (1955) [12] and Gibbs et al. (1959) [13] were obtained by using a Bunsen burner and speed graphic camera. Besides, Flockenhaus et al. (1969) [14] have obtained the LBV by using counter-flow nozzle burning method.

The Quadratic Sum (QS) of the difference between model values ( $V_{Mod}$ ) and experimental data ( $V_{Exp}$ ) (Eq. 2); the  $R^2$  coefficient (Eq. 3); Fractional Bias (FB) (Eq. 4), the Normalized Mean Square Error (NMSE) (Eq. 5) and fraction of predictions within a factor of two observations (FAC-2, corresponding to the fraction of data that satisfies the condition in Eq. 6) were adopted to evaluate the model fitting quality.

**Errore. L'origine riferimento non è stata trovata.**

$$QS = \sum_i^N (V_{Mod,i} - V_{Exp,i})^2 \quad (2)$$

$$R^2 = \frac{\sum_i^N ((V_{Mod,i} - V_{Mod,av})(V_{Exp,i} - V_{Exp,av}))^2}{\sum_i^N (V_{Mod,i} - V_{Mod,av})^2 \sum_i^N (V_{Exp,i} - V_{Exp,av})^2} \quad (3)$$

$$FB = \frac{\sum_i (V_{Exp,i} - V_{Mod,i})}{0.5 * \sum_i (V_{Exp,i} + V_{Mod,i})} \quad (4)$$

$$NMSE = \frac{\left(\frac{QS}{N}\right)}{V_{Mod,av} * V_{Exp,av}} \quad (5)$$

$$0.5 \leq \frac{V_{Mod,i}}{V_{Exp,i}} \leq 2 \quad (6)$$

where the subscript “av” represents the average value and “i” the “i-th” observation. The FB and NMSE values can be combined in a single parameter for fitting quality (FQ):

$$FQ = \sqrt{(FB^2 + NMSE^2)} \quad (7)$$

Models are usually accepted if FAC-2 is greater than 0.8; the absolute value of FB is smaller than 0.5; and the random scatter of data, valued through NMSE, is smaller than 0.5 [15, 16]. FQ represents the distance from the perfect model, having FB and NMSE equal to zero, and the real model.

Results for the case analyzed in this paper are reported in Table 1. Computed parameters clearly show that model well predict LBV values, except for data reported by Flockenhaus et al. (1969) [14], which are strongly overestimated as indicated by corresponding FB value.

**Table 1.** Statistical parameter evaluating used model fitting quality for each experimental data retrieved in the literature.

	FB	NMSE	FQ
Chamberlin et al. (1928)	0.12	0.04	0.13
Cohen et al. (1955)	-0.03	0.03	0.04
Gibbs et al. (1959)	-0.16	0.03	0.17
Flockenhaus et al. (1969)	-0.47	0.31	0.57
<b>Overall</b>	<b>-0.14</b>	<b>0.10</b>	<b>0.22</b>

## Results

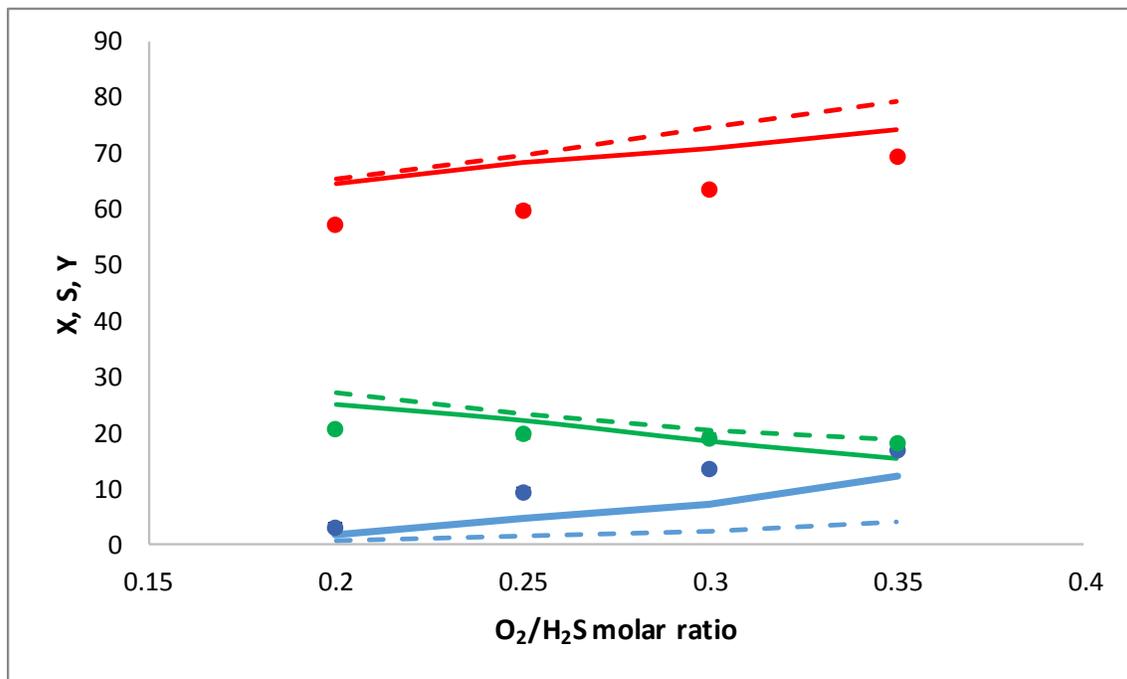
It is very important to note that the model is based on a kinetic reaction network that is already validated for the equivalence ratio values in the range 0.4-2.3, that are very different from that relevant to the H<sub>2</sub>S oxidative decomposition reaction and specifically studied in this work. So, in order to verify the model performances in our conditions, the experimental results, the model simulations and the equilibrium calculations are compared at different conditions. For the sake of brevity, we have reported only H<sub>2</sub>S conversion (X), SO<sub>2</sub> selectivity (S) and H<sub>2</sub> yield (Y) defined as:

$$X = \frac{H_2S^{IN} - H_2S^{OUT}}{H_2S^{IN}} * 100 \quad (8)$$

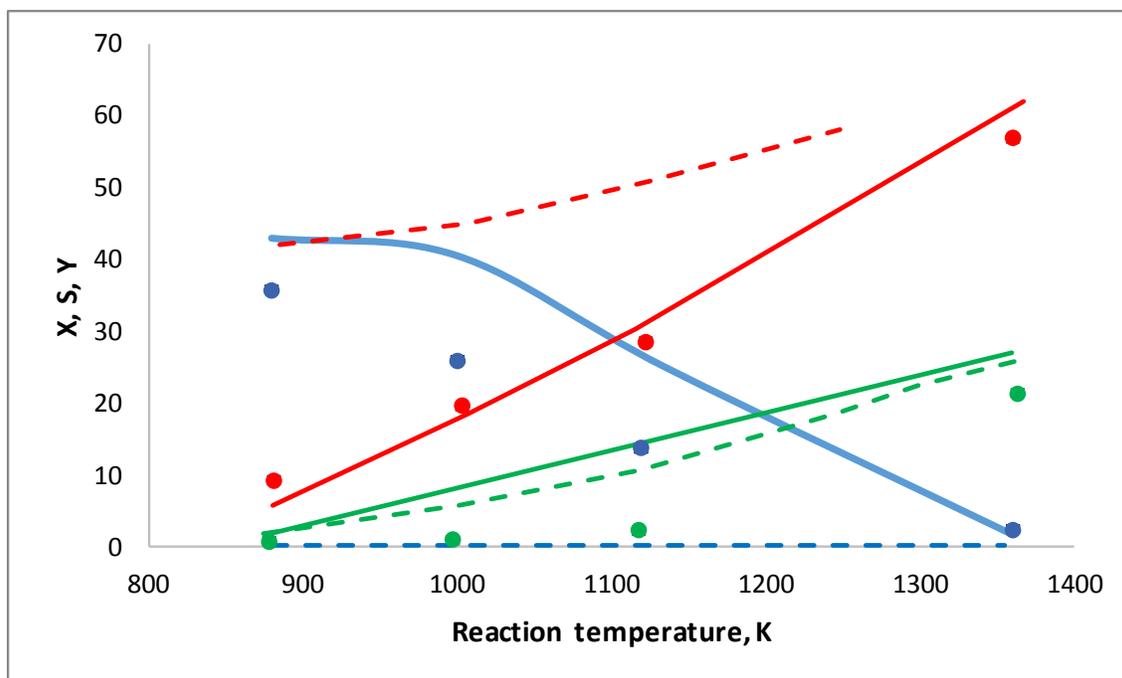
$$S = \frac{SO_2^{OUT}}{H_2S^{IN} - H_2S^{OUT}} * 100 \quad (9)$$

$$Y = \frac{H_2^{OUT}}{H_2S^{IN}} * 100 \quad (10)$$

These three parameters are plotted with respect to the molar ratio O<sub>2</sub>/H<sub>2</sub>S in the feeding gas mixture at constant reactor temperature of 1373 K (Figure 2) and with respect to the reactor temperature at constant O<sub>2</sub>/H<sub>2</sub>S of 0.2 (Figure 3).



**Figure 2.** Comparison of equilibrium data (dashed lines), model prediction (lines) and experimental results (symbols) at reactor temperature equal to 1373 K and different O<sub>2</sub>/H<sub>2</sub>S molar ratio in terms of H<sub>2</sub>S conversion (red), SO<sub>2</sub> selectivity (blue) and H<sub>2</sub> yield (green).



**Figure 3.** Comparison of equilibrium data (dashed lines), model prediction (lines) and experimental results (symbols) at  $O_2/H_2S$  equal to 0.2 and different reactor temperature in terms of  $H_2S$  conversion (red),  $SO_2$  selectivity (blue) and  $H_2$  yield (green).

Reported results underline the model ability to predict the  $O_2/H_2S$  effect on product composition within the investigated range, whereas further improvements are required for the estimation of reactor temperature effect on  $SO_2$  selectivity and  $H_2$  yield, particularly at reaction temperature lower than 1100 K.

Discrepancies among experimental results and model prediction of  $SO_2$  and  $H_2$  concentration may be due to the adopted kinetics parameters of Claus reaction, which were developed under conditions far from those studied in this work.

## Conclusion

A new kinetic model was developed and validated in order to reproduce the experimental data of the oxidative decomposition of  $H_2S$ . Results indicate that the model can predict the  $H_2S$  and  $O_2$  conversion in several investigated conditions, whereas further improvement are needed to guarantee an acceptable product composition estimation, especially at reactor temperature below 1100 K. Authors suggest as possible explanation of reported discrepancies among experimental data and model predictions the lack of knowledge of  $H_2S$  chemistry under the investigated conditions. Hence, further development on reaction mechanism at low temperature and low oxygen content are suggested.

## References

- [1] Clark, P. D., Dowling, N. I., and Huang, M. , "Production of  $H_2$  from catalytic partial oxidation of  $H_2S$  in a short-contact-time reactor," *Catal. Commun.*, vol. 5, no. 12, pp. 743–747, (2004).
- [2] Palma, V., Vaiano, V., Barba, D., Colozzi, M., Palo, E., Barbato, L., Cortese, S., "H<sub>2</sub> production by thermal decomposition of  $H_2S$  in the presence of oxygen," *International Journal of Hydrogen Energy*, vol. no. 40, 106-113, (2015).

- [3] University of California at San Diego, "Chemical-Kinetic Mechanisms for Combustion Applications." [Online]. Available: <http://web.eng.ucsd.edu/mae/groups/combustion/mechanism.html>.
- [4] Leeds University, "Sulphur mechanism. Version 5.2," (2005).
- [5] Zhou, C. R., Sendt, K., and Haynes, B. S., "Experimental and kinetic modelling study of H<sub>2</sub>S oxidation," *Proc. Combust. Inst.*, vol. 34, no. 1, pp. 625–632, (2013).
- [6] Salzano E., Cammarota F., Di Benedetto A., Di Sarli V., Explosion behaviour of Hydrogen-Methane/Air mixtures, *Journal of Loss Prevention in the Process Industries*, 25, 443-447 (2012).
- [7] Salzano E., Basco A., Cammarota F., Di Sarli V., Di Benedetto A., Explosions of Syngas/CO<sub>2</sub> Mixtures in Oxygen-Enriched air, *Industrial & Engineering Chemistry Research*, 51, 7671–7678 (2012).
- [8] Barba, D., Cammarota, F., Vaiano, V., Salzano, E., and Palma, V., "Experimental and numerical analysis of the oxidative decomposition of H<sub>2</sub>S," *Fuel*, vol. 198, pp. 68–75, (2017).
- [9] GASEQ, A Chemical Equilibrium Program for Windows. Available at: <http://www.c.morley.dsl.pipex.com>, last download, (2015).
- [10] Goodwin, D. G., "An Open Source, Extensible Software Suite FOR CVD Process Simulation," (2003).
- [11] Chamberlin, D. S., and Clarke, D., "Flame speed of hydrogen sulfide," *Proc. Symp. Combust.*, vol. 1–2, pp. 33–35, (1928).
- [12] Cohen L., "Burning velocities of hydrogen sulfide in air and in oxygen," *Fuel*, (1955).
- [13] Gibbs, G. J., and Calcote, H. F., "Effect of Molecular Structure on Burning Velocity.", (1959)
- [14] Flockenhaus C, "Rates of flame propagation of hydrogen sulphide/air mixtures," *Gaswaerme International*, vol. 18, no. 4, (1969).
- [15] Patryl, L., and Galeriu, D., "Statistical Performances measures - models comparison," (2011).
- [16] Patel, V. C., and Kumar, A., "Evaluation of three air dispersion models: ISCST2, ISCLT2, and SCREEN2 for mercury emissions in an urban area," *Environ. Monit. Assess.*, vol. 53, no. 2, pp. 259–277, (1998).