

KINETIC MODELING STUDY OF H₂S PYROLYSIS

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Abstract

This article proposes a detailed kinetic scheme for the pyrolysis of H₂S. The H₂S pyrolysis is involved in different processes such as, for instance, Claus process, coal gasification and hydro-desulfurisation. Moreover, the H₂S pyrolysis is an important key-step for a new and promising route to reduce CO₂ by means the oxi-reduction reaction between H₂S and CO₂. For these reasons, there is the interest in a better understanding of the reactions involved in H₂S pyrolysis. The kinetic scheme, used in this work, differs from the literature ones since it involves the presence of light and heavy hydrocarbons, ammonia, and other species usually present in H₂S containing feedstocks. Aiming at a hierarchical validation of the mechanism, different experimental conditions of H₂S pyrolysis are analyzed. In particular, the scheme is in comparison with experimental data of pure pyrolysis, of pyrolysis with S₂ addition, and the effect of H₂S on the pyrolysis hydrocarbons is also investigated.

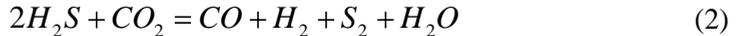
1. Introduction

The presence of hydrogen sulfide as a common byproduct in oil refineries and the strict legislation that limits its release into the atmosphere have triggered renewed interest in the modeling of sulfur chemistry. Moreover, H₂S is a poison for industrial catalysts and its combustion products are responsible for the acid rains. The most important and spread neutralization method is based on the Claus process. The thermal stage of this process promotes the conversion of H₂S into elemental sulfur by a controlled oxidation at high temperatures (800-1500 °C). This process involves several reactions such as oxidation and pyrolysis reactions of H₂S [1]. The overall global reaction:



is, in reality, a complex radical mechanism with many elementary processes where various reactive systems are coupled by common intermediate radicals [2]. Basing on recent advances [3], it could be also possible to convert H₂S and CO₂ into valuable products and specifically into syngas according to the oxi-reduction

reaction [4]:



whenever it takes place into a regenerative thermal reactor and at specific operating conditions. Such a technology allows to enable some energy sources currently still unexploited due to their relevant content in sulfur, such as some crude oils, natural gases, and coal sources. For example, the Sulcis coal in Italy has the 7 to 9% w/w of sulfur content [5]. To study in depth this technology, it is mandatory to analyze the H₂S pyrolysis, considered the initial step of the overall conversion system.

2. Kinetic Mechanism and Comparison with Literature Data

Glassman [6] discussed and reviewed the major characteristics of sulfur fuels oxidation mechanism including their interactions with N compounds as well as the formation and the oxidation of CS and COS. Glarborg et al. [7] developed a detailed reaction mechanism of H/S/O system. The aim was from one side to analyzing the interactions of SO₂ with the radical pool under combustion conditions and from the other to evaluating the effect of sulfur components on NO_x formation. Very recently, Bongartz [8] revised the kinetics of sulfur compounds with attentions to the oxy-fuel combustion of sour gas (mixture of natural gas, CH₄, CO₂, and H₂S). They construct the mechanism by combining the CH₄ sub-mechanism AramcoMech by Metcalfe et al. [9] with an optimized mechanism of H₂S oxidation, originally taken from the work of Zhou et al. [10]. In this work, the oxidation and combustion of methane and light hydrocarbons with a kinetic scheme of sulfur compounds originally developed to model Claus process reaction furnaces [2].

2.1. H₂S pyrolysis in plug-flow reactor

Hawboldt et al. [11] performed experiments of H₂S pyrolysis in isothermal plug-flow reactors at temperatures between 850-1150 °C and residence times of 50-1500 ms. The cracking experiments were performed under H₂S concentrations from 0.5-2.5% with the balance N₂. The quartz reactors are 5 mm in diameter with reactor lengths from 1.5 to 15.0 m. In the re-association (reverse) experiments, the H₂ was varied from 0.5-1.0%, sulfur 1.0-3.0%, always with N₂. Panel a) of Figure 1 shows the comparison between experimental data and model predictions in terms of H₂S conversion versus contact time along the reactor, at different temperatures. Panel b) of the same figure shows the hydrogen conversion at different temperatures and different contact times. The agreement between experimental data and model predictions is satisfactory

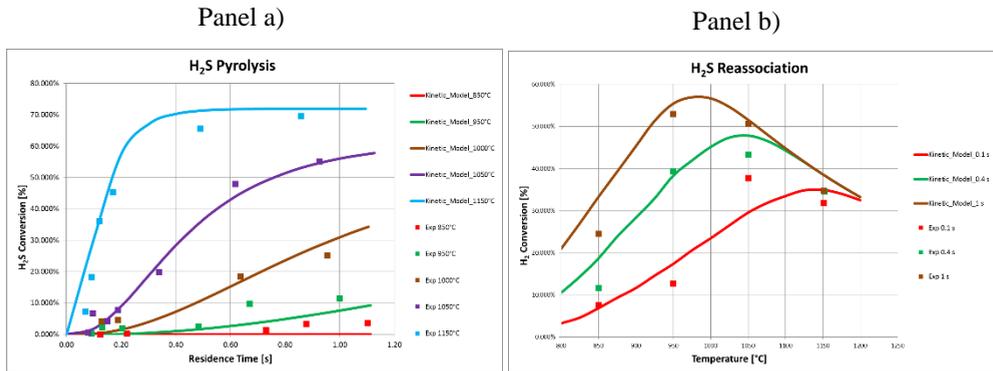


Figure 1. Panel a) H₂S conversion versus contact time along the reactor. Panel b) H₂ conversion versus temperature at different contact times. [11]

2.2. H₂S pyrolysis in jet-stirred reactors, also in presence of S₂

Binoist et al. [1] studied the pyrolysis of hydrogen sulfide diluted in argon (95 vol %) at residence times between 0.4 and 1.6 s in a continuous perfectly mixed quartz reactor at temperatures of 800-1100 °C. The addition of elemental sulfur to H₂S allowed demonstrating a clear kinetic auto-acceleration effect.

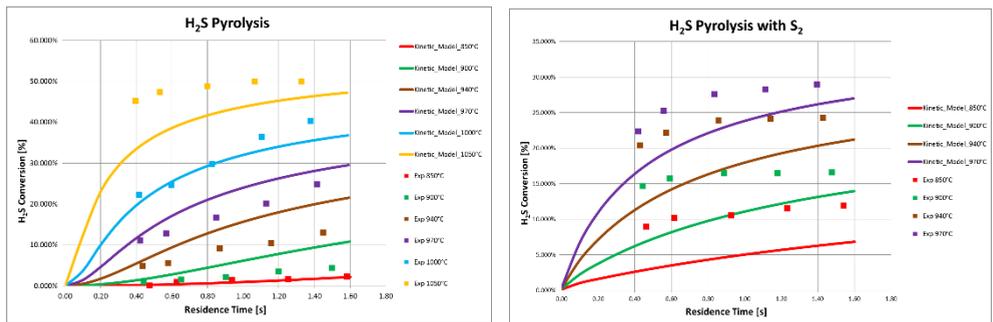


Figure 2. H₂S conversion versus residence time in JSR [1].

Figure 2 show the comparisons between experimental data and model predictions, without (H₂S/Ar=.05/.95) and with the elemental sulfur addition (H₂S/S/Ar=.033/.017/.95). The model systematically under-predicts the high temperature conversion of hydrogen sulfide, especially when elemental sulfur is added to the reacting mixture.

2.3. CH₄ pyrolysis in presence of H₂S and S₂

The kinetics of CH₄-S₂ and CH₄-H₂S reactions was investigated by Karan et al. [12] in a high-temperature flow reactor with pressures of 1-1.5 atm, at temperatures of 800-1250 °C, and residence times of 90-1400 ms. The methane-sulfur interactions are very rapid, resulting in complete sulfur consumption with CS₂ and

H_2S formation in less than 100 ms at 1100 °C. At temperatures higher than 1000 °C, H_2S decomposes with a corresponding CS_2 formation. Figure 4 and Figure 5 show the satisfactory comparisons between experimental data and model predictions.

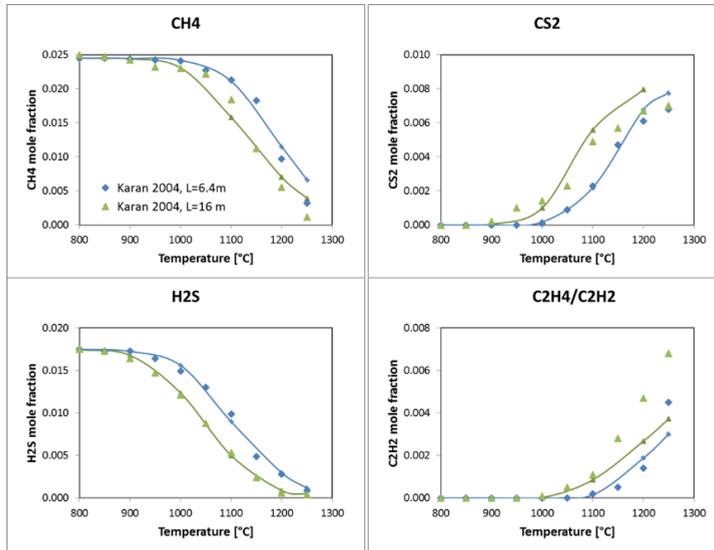


Figure 3. $\text{CH}_4\text{-H}_2\text{S}$ pyrolysis [12]. Comparisons between experimental data (symbols) and model predictions (lines) with two different reactor lengths.

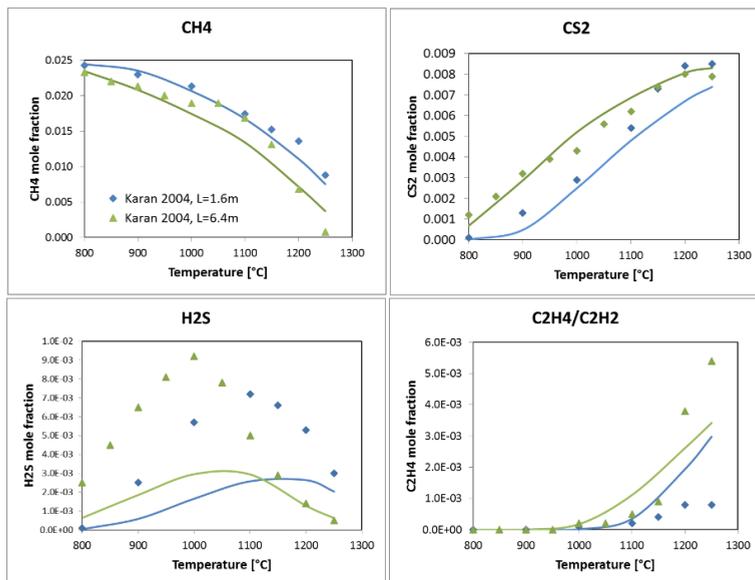


Figure 4. CH₄-S₂ pyrolysis [12]. Comparisons between experimental data (symbols) and model predictions (lines) with two different reactor lengths.

2.4. H₂S effect on hydrocarbon pyrolysis

Rebick [13] studied the pyrolysis of n-hexadecane in the presence of 0-0.6 atm of H₂S in a quartz flow reactor at 500 °C. Partial pressure of n-C₁₆H₃₄ varied from 0.08 to 0.4 atm. These data are consistent with a mechanism in which H₂S promotes the conversion with the H transfer from hexadecane to alkyl radicals produced during the pyrolysis. Figure 5 shows the predicted n-C₁₆H₃₄ conversion with and without the hydrogen sulfide addition. The promoting effect of H₂S addition are evident, even if this effect is lower than the experimental one. This deviation seems to indicate a slightly lower reactivity of the hydrogen atoms of H₂S, and/or a lower abstraction capability of SH radicals.

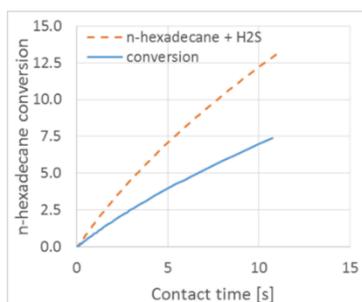


Figure 5. Predicted n-C₁₆H₃₄ conversion at 500 °C.

3. Conclusions and future developments

Preliminary studies on H_2S pyrolysis are demonstrating that relatively high temperatures are enough to decompose a large part of H_2S . In order to use this kinetic model for reliable predictions in a more complex process environment to predict and optimize the operating condition of the overall technology of oxy-reduction of H_2S and CO_2 to syngas it is necessary to analyze and critical revise oxidation conditions. Therefore, new experimental data both in pyrolysis and oxidation conditions are necessary to improve and verify the prediction of the kinetic scheme. The experimental work in the tubular reactor of Sotacarbo could be useful to better clarify system reactivity and could be crucial for future development of kinetic scheme. The reactor is a plug-flow in quartz with 5 cm diameter and 785 cm^3 volume. As reported in Figure 6, the reactor internal is also disposed for a catalytic filling allowing in this way to study not only the thermal but also the catalytic behavior of this reaction system.

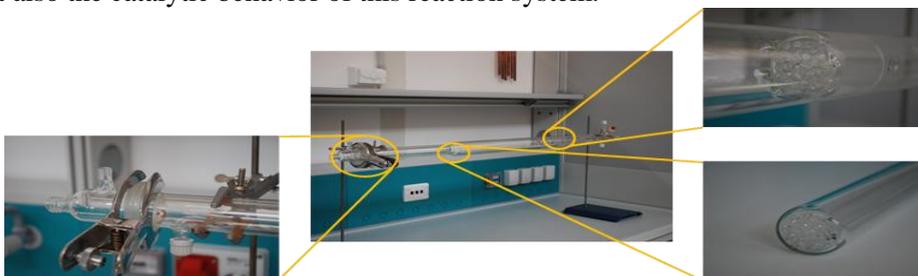


Figure 6. Experimental apparatus adopted to validate the H_2S pyrolysis model.

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