KINETIC MODELING STUDY OF H\textsubscript{2}S PYROLYSIS

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Abstract
This article proposes a detailed kinetic scheme for the pyrolysis of H\textsubscript{2}S. The H\textsubscript{2}S pyrolysis is involved in different processes such as, for instance, Claus process, coal gasification and hydro-desulfurisation. Moreover, the H\textsubscript{2}S pyrolysis is an important key-step for a new and promising route to reduce CO\textsubscript{2} by means of the oxi-reduction reaction between H\textsubscript{2}S and CO\textsubscript{2}. For these reasons, there is the interest in a better understanding of the reactions involved in H\textsubscript{2}S 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 H\textsubscript{2}S containing feedstocks. Aiming at a hierarchical validation of the mechanism, different experimental conditions of H\textsubscript{2}S pyrolysis are analyzed. In particular, the scheme is in comparison with experimental data of pure pyrolysis, of pyrolysis with S\textsubscript{2} addition, and the effect of H\textsubscript{2}S 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, H\textsubscript{2}S 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 H\textsubscript{2}S 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 H\textsubscript{2}S [1]. The overall global reaction:

\[ 2H_2S + O_2 = S_2 + 2H_2O \]  \hspace{1cm} (1)

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 H\textsubscript{2}S and CO\textsubscript{2} into valuable products and specifically into syngas according to the oxi-reduction
reaction [4]:

$$2H_2S + CO_2 = CO + H_2 + S_2 + H_2O$$  \(2\)

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 H$_2$S 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 SO$_2$ 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, CH$_4$, CO$_2$, and H$_2$S). They construct the mechanism by combining the CH$_4$ sub-mechanism AramcoMech by Metcalfe et al. [9] with an optimized mechanism of H$_2$S 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. H$_2$S pyrolysis in plug-flow reactor

Hawboldt et al. [11] performed experiments of H$_2$S 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 H$_2$S concentrations from 0.5-2.5% with the balance N$_2$. 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 H$_2$ was varied from 0.5-1.0%, sulfur 1.0-3.0%, always with N$_2$. Panel a) of Figure 1 shows the comparison between experimental data and model predictions in terms of H$_2$S 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.
2.2. \( \text{H}_2\text{S} \) pyrolysis in jet-stirred reactors, also in presence of \( \text{S}_2 \)

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 \( \text{H}_2\text{S} \) allowed demonstrating a clear kinetic auto-acceleration effect.

2.3. \( \text{CH}_4 \) pyrolysis in presence of \( \text{H}_2\text{S} \) and \( \text{S}_2 \)

The kinetics of \( \text{CH}_4 \)-\( \text{S}_2 \) and \( \text{CH}_4\)-\( \text{H}_2\text{S} \) 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 \( \text{CS}_2 \) and...
H₂S formation in less than 100 ms at 1100 °C. At temperatures higher than 1000 °C, H₂S decomposes with a corresponding CS₂ formation. Figure 4 and Figure 5 show the satisfactory comparisons between experimental data and model predictions.

**Figure 3.** CH₄-H₂S pyrolysis [12]. Comparisons between experimental data (symbols) and model predictions (lines) with two different reactor lengths.
2.4. \( \text{H}_2\text{S} \) effect on hydrocarbon pyrolysis

Rebick [13] studied the pyrolysis of \( \text{n-hexadecane} \) in the presence of 0-0.6 atm of \( \text{H}_2\text{S} \) in a quartz flow reactor at 500 °C. Partial pressure of \( \text{n-C}_{16}\text{H}_{34} \) varied from 0.08 to 0.4 atm. These data are consistent with a mechanism in which \( \text{H}_2\text{S} \) promotes the conversion with the H transfer from hexadecane to alkyl radicals produced during the pyrolysis. Figure 5 shows the predicted \( \text{n-C}_{16}\text{H}_{34} \) conversion with and without the hydrogen sulfide addition. The promoting effect of \( \text{H}_2\text{S} \) 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 \( \text{H}_2\text{S} \), and/or a lower abstraction capability of \( \text{SH} \) radicals.

**Figure 5.** Predicted \( \text{n-C}_{16}\text{H}_{34} \) conversion at 500 °C.
3. Conclusions and future developments

Preliminary studies on H₂S pyrolysis are demonstrating that relatively high temperatures are enough to decompose a large part of H₂S. 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 H₂S and CO₂ 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 cm³ 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 H₂S pyrolysis model.](image)

References


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