A Numerical Study on Thermal Dissociation of H₂S

M. Moghiman, S. M. Javadi, A. R. Moghiman, and S. Baghdar Hosseini

Abstract—The main issue in sweetening natural gas is H_2S dissociation. The present study is concerned with simulating thermal dissociation of H_2S in industrial natural gas carbon black furnace. The comparison of calculated results against experimental measurements shows good agreement. The results show that sulfur derived from H_2S thermal dissociation peaked at φ=0.95. H_2S thermal dissociation is enhanced in equivalence ratio upper than 1 and H_2S oxidization is increased in equivalence ratio lower than 1. H_2 concentration of H_2S thermal dissociation is increased with increase of equivalence ratio up to 1. Also, H_2S concentration decreased in outlet as equivalence ratio increases. H_2S thermal dissociation to hydrogen and Sulfur reduces its toxic characteristics and make economical benefits.

Keywords—Equivalence ratio, H_2S, natural gas furnace, thermal dissociation.
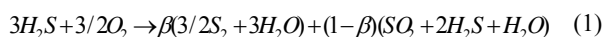
I. INTRODUCTION

THE acidic gas in oil and natural gas refinement consist of 80% CO_2 and 20% H_2S which emit to environment. Hydrogen sulphide is a byproduct from the sweetening of sour natural gas, the hydrodesulphurization of light hydrocarbons, and from the upgrading of heavy oils, bitumens and coals. It is usually separated from hydrocarbon gases by amine absorption. Considering to the poisonous behavior of H_2S and its influence on nature, it has to be further treated. H_2S is also an abundant source for potentially the cheapest Hydrogen. The petroleum industry spends a lot of money to produce Hydrogen from other sources for Sulfur removal from crude oils and refinery products. This creates more than 6 million tons per year of concentrated H_2S in which very weakly bonded Hydrogen is then stupidly burned to water. Controlling hydrogen sulfide concentrations is critical in many applications as it is one of the most malodorous compounds. The characteristic odor of H_2S is detected at a threshold of 0.0047 ppm. Hydrogen sulfide is reported to be toxic, harmful to human health, has damaging effects on many industrial catalysts, and is known to be a major source of acid rain when

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oxidized in the atmosphere. H_2S becomes harmful to human health when inhaled and can be deadly depending on the exposure concentration and duration of the exposure. Eye irritation starts to occur around 10-20 ppm. The risk of pulmonary edema is noticeable above 300 ppm. Exposure to concentrations over 1000 ppm might lead to death [1]. Hydrogen sulfide is corrosive and penetrates the lattice of some steels and makes them brittle, leading to sulphide stress cracking - a concern especially for handling acid gas and sour crude in the oil industry. In conclusion, H_2S thermal dissociation to hydrogen and Sulfur reduces its toxic characteristics and make economical benefits. This process operates in an industrial soot formation furnace. The objective of this study is to analyze the effect of the main feed stock's equivalence ratio on the efficiency of sulfur and other species production.

II. CHEMICAL REACTIONS

There are many approaches for H_2S dissociation. Among these are: photochemical, direct electrochemical, indirect electrochemical, claus process, thermal (catalytic and non-catalytic) and plasma systems [2]. The economics of such systems have been reviewed [3–6]. Photochemical methods were not very successful because of high energy costs and low conversion [6]. Electrolysis encounters many problems including sulfur passivation of the anode [7]. Electrochemical processes require chemical oxidants and have high electrical energy requirements [8].

H_2S dissociation for sulfur recovery in the Claus process consists of two stages. The first is a thermal step, in which H_2S is partially oxidized with air:

$$3H_2S + 3/2O_2 \rightarrow \beta(3/2S_2 + 3H_2O) + (1-\beta)(SO_2 + 2H_2S + H_2O) \quad (1)$$

This step occurs in a furnace at high temperatures of 1300–1700 K. The main product is sulfur (β = 55–70%); however, because of the high temperatures of the reaction, SO_2 is also formed. Consequently, a second step is necessary

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \quad (2)$$
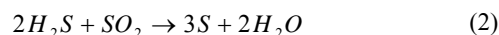
In order for (2) to occur at reasonable speeds, a catalyst is necessary. Even with the best catalyst, the reaction is not complete. Thus, it is operated in two or three stages with Intermediate sulfur condensation ultimately; all hydrogen in the H_2S is converted to water [9]. The Claus process is quite

sensitive to CO_2; generally the process cannot be sustained if CO_2 concentration in the gas exceeds 60%. In most of cases CO_2 is accompanying H_2S in natural gases as well as in other effluents and the both gases are hard to separate in order to satisfy such limitation. Also steam, hydrocarbons and NH_3 in the raw gas stream tend to poison or to plug the Claus catalyst. Moreover, large plants are required for this process to be economically feasible, additional tail gas treatment is necessary, controlling high temperature gas reaction and maintenance of the catalysts make the Claus process not flexible enough to immediately adjust to changes in the load, etc. This process is not economic when the price of sulphur (the primary product) is depressed, but nevertheless is practiced to dispose of the H_2S in an environmentally acceptable manner. Conversion of the hydrogen to water, however, is wasteful from the standpoint of thermodynamics because H_2S can be a cost effective source of hydrogen. The dissociation energy of H_2S (into hydrogen and sulfur) is only 0.2 eV/molecule. Compared to water, which has dissociation energy of 2.9 eV/ molecule, production of hydrogen from H2S is 15 times less costly. Therefore, the possibility to dissociate H_2S into sulfur and hydrogen is important commercially. Such prospects are particularly important for oil industry, which consumes large amounts of hydrogen in oil hydro-treatment for production of low sulfur fuels and could benefit from a low cost method of H2S dissociation. In general, thermal decomposition and plasma systems have more potential than other approaches because they have lower energy consumption [6]. Hydrogen sulfide dissociation, with hydrogen and elemental sulfur production, is slightly endothermic:

$$H_2S \rightarrow H_2 + S_{solid}, \Delta H = 20.6 kj/kmol = 0.2 eV/molecule \quad (3)$$
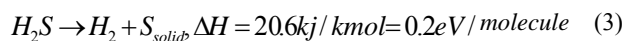
When the temperature in a system is increased to stimulate the dissociation, sulfur is not produced in the condensed phase. Instead, it forms as a gas, S8, which requires more energy. In addition, since the enthalpy of the gas-phase sulfur process exceeds that of the solid-phase sulfur process, the required temperature to stimulate dissociation is higher [10]. At these higher temperatures the only major sulfur containing product is gaseous S2. Thermodynamic equilibrium calculation indicates that conversion is fairly low, less than 20%, even at high temperatures, 1250 K, while energy cost is rather high, 4 eV per H2 molecule (Fig. 1). These results are in agreement with previous work [11-12]. The methods previously studied for H2S-dissociation do not allow a scale-up to industrial dimensions for fundamental reasons. A plasmachemical method for the continuous dissociation of H_2S which allows an essay scale-up might also be attractive for other plasmachemical syntheses and waste destruction. To make a process feasible for industrial application it must allow a continuous operation, require simple and inexpensive equipment and run at atmospheric pressure in order to achieve high mass through-puts.
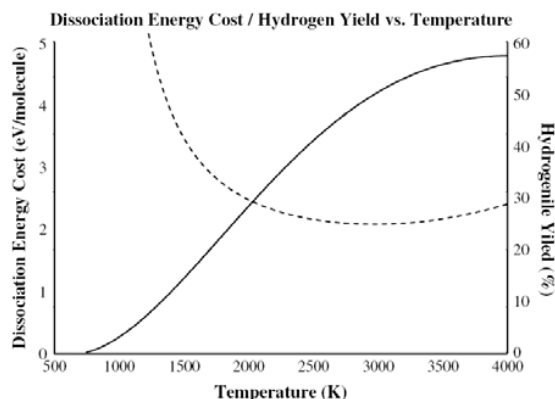

Fig. 1 Dissociation energy in eV per H_2 molecule (dashed line) and hydrogen yield in percent (solid line) depending on temperature at equilibrium conditions

Furthermore, there are physical and chemical limitations [13]. The dissociation of H_2S involves several steps, the balance being slightly endothermic. The first step of the dissociation of H_2S must have a higher energy requirement because the recombination reactions of the sulfur atoms of S_8-rings and of hydrogen atoms of H_2 are exothermic. Reported values for dissociation energies are:

$$HS - S : 377 Kj/mol = 3.9 Ev/mol$$
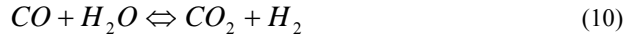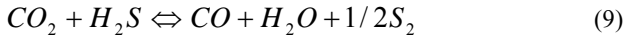$$H - S : 344 Kj/mol = 3.6 Ev/mol$$

$$\quad (4)$$
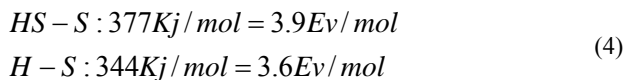
To make a continuous process possible, sulfur has to be removed from the reactor as a liquid or a vapor. Liquid sulfur (m.p. 119 °C) shows a peculiar temperature dependence of viscosity .there is a minimum at $\approx$ 156°C. However, H_2S has a strong effect on this minimum because polysulfanes H_2S_n are being formed. The boiling point of sulfur at atmospheric pressure is 444.6 °C [12]. H_2S thermal dissociation operates in a furnace with methane as main fuel. This process involves a series of complicated chemical reaction which control the dissociation of H_2S and CH_4. The simplified thermal decomposition reaction can be described by the following overall stoichiometric equation:

$$H_2S(g) \leftrightarrow H_2(g) + \frac{1}{2} S_2(g), \Delta H(25 °C) = 84.9 KJ/mol \quad (5)$$
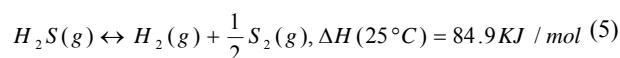
The reaction is highly endothermic and the equilibrium yields are poor. For example, at 860°C (1150 K) the conversion of H_2S is only 10% [5]. Above approximately 800°C there is a decreasing advantage to use a catalyst since the thermal reaction proceeds to equilibrium rapidly. Equilibrium is dependent on pressure, such that higher H_2S conversions are obtained at lower pressures. Depending on the temperature, the decomposition reaction has a varying potential to generate many molecular species of sulphur, including sulfanes. Above approximately 750°C Raymont [14] and Kaloidas and Papayannakos [12] have shown that diatomic sulphur (S_8) is the primary sulphur species. The

products must be quickly cooled (quenched) after leaving the reactor, as reaction (5) is reversible.

In H$_2$S thermal dissociation, other species are produced as follow:

$$H_2S \Leftrightarrow H_2 + 1/2S_2 \qquad (6)$$

$$H_2S + CO \Leftrightarrow H_2 + COS \qquad (7)$$

$$2CO + S_2 \Leftrightarrow 2COS \qquad (8)$$

$$CO_2 + H_2S \Leftrightarrow CO + H_2O + 1/2S_2 \qquad (9)$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad (10)$$

III. NUMERICAL SOLUTION PROCESS

The combustion model is based on the conserved scalar (mixture fraction) and prescribed probability density function (*pdf*) approach. Transport equations were solved for the mean mixture fraction $\overline{f}$, its variance $\overline{f'^2}$ and for enthalpy $\overline{h}$. The mean values of the reactive scalars have been obtained using a β-*pdf*. The chemistry calculations and the *pdf* integrations were performed using a preprocessing code, and assuming chemical equilibrium between 30 different species. The results of the chemistry calculations were stored in look-up tables which relate the mean thermochemical variables (species mass fractions, temperature and density) to the values of $\overline{f}$, $\overline{f'^2}$ and $\overline{h}$.

The mixture fraction / PDF method is used to model the turbulent chemical reactions occurring in the diffusion, combustion and thermal decomposition of natural gas in the carbon black furnace. This method, which assumes the chemistry is fast enough for a chemical equilibrium to always exist at molecular level, enables the handling of large numbers of reacting species, including intermediate species. In non-adiabatic systems, where change in enthalpy, due to heat transfer, affects the mixture state, the instantaneous thermo chemical state of the mixture, resulting from the equilibrium chemistry model, is related to a strictly conserved scalar quantity known as the mixture fraction, f, and the instantaneous enthalpy, $H^*, \phi_i = \phi_i(f, H^*)$. The effects of turbulence on the thermo chemical state are accounted for with the help of a probability density function (PDF):

$$\overline{\phi_i} = \int_0^1 \phi_i(f, \overline{H}^*) p(f) df \qquad (11)$$

As in carbon black furnaces, the heat transfer from walls is not high. For simplicity, it has been assumes that heat losses do not, significantly, impact on the turbulent enthalpy fluctuations. In this study, the β-probability density function used by Jones and McGurik [15] is used to relate the time-averaged values of individual species mass fraction, the temperature and the fluid density of the mixture to instantaneous mixture fraction fluctuations.

The β-probablity density function, in terms of the mean mixture fraction $\overline{f}$ and its variance $\overline{f'^2}$, can be written as:

$$P(f) = \frac{f^{\alpha-1}(1-f)^{\beta-1}}{\int_0^1 f^{\alpha-1}(1-f)^{\beta-1} df}, \quad 0 < f < 1 \qquad (12)$$

Where:

$$\alpha = \overline{f}\left[\frac{\overline{f}(1-\overline{f})}{\overline{f'^2}} - 1\right], \beta = (1-\overline{f})\left[\frac{\overline{f}(1-\overline{f})}{\overline{f'^2}} - 1\right]. \quad (13)$$

Using the unweighted averaging [16], the values of the two parameters $\overline{f}$ and $\overline{f'^2}$ at each point in the flow domain are computed through the solution of the following conservation equations [17]:

$$\frac{\partial}{\partial x}(\rho u_i \overline{f}) = \frac{\partial}{\partial x_i}(\frac{\mu_t}{\sigma_t}\frac{\partial \overline{f}}{\partial x_i}) \qquad (14)$$

$$\frac{\partial}{\partial x}(\rho u_i \overline{f'^2}) = \frac{\partial}{\partial x_i}(\frac{\mu_t}{\sigma_t}\frac{\partial \overline{f'^2}}{\partial x_i}) + C_g \mu_t\left(\frac{\partial \overline{f}}{\partial x_i}\right)^2 - C_d \rho \frac{\varepsilon}{k}\overline{f'^2} \quad (15)$$

Where the constants $\sigma_t, C_g(=2/\sigma_t)$ and C_d take the values 0.7, 2.86 and 2.0, respectively. The transport equation, which calculates the distribution of the instantaneous enthalpy, is as follows:

$$\frac{\partial}{\partial x}(\rho u_i \overline{H}^*) = \frac{\partial}{\partial x_i}(\frac{k_t}{c_p}\frac{\partial \overline{H}^*}{\partial x_i}) + \tau_{ik}\frac{\partial u_i}{\partial x_k} + S_h \qquad (16)$$

Where k_t is turbulent thermal conductivity and S_h includes the heat of the chemical reaction and radiation. The instantaneous enthalpy is defined as:

$$H^* = \sum_j m_j H_j = \sum_j m_j \left[\int_{T_{ref,j}}^T c_{p,j} dT + h_j^\circ(T_{ref,j})\right] \quad (17)$$

Where m_j is the mass fraction of species j and $h_j^\circ(T_{ref,j})$ is the formation enthalpy of species j at the reference temperature $T_{ref,j}$.

Fluent CFD software which allows one to model furnaces with complex geometry and solution – adaptive grid refinement, has been applied in this study to solve the 3D

problem. The 3D volume grid of thermal dissociation furnace is represented in Fig. 2.

Fig. 2 Three-dimensional grid of thermal dissociation furnace

To survey the effect of air-fuel ratio (main fuel) on the sulfur production efficiency and other products efficiency, the concentration of species has became dimensionless by the following formula:

$$H_2(\%) = \frac{[H_2]}{4/16*[CH_4]+([H_2S]_0-[H_2S])*2/34}*100 \quad (18)$$

$$H_2S(\%) = \frac{[H_2S]_0-H_2S}{[H_2S]_0}*100 \quad (19)$$

$$S_2(\%) = \frac{[S_2]}{[H_2S]_0*32/34}*100 \quad (20)$$

$$SO_2(\%) = \frac{[SO_2]*32/64}{[H_2S]_0*32/34}*100 \quad (21)$$

$$SO(\%) = \frac{[SO]*32/48}{[H_2S]_0*32/34}*100 \quad (22)$$

IV. RESULTS AND DISCUSSION

The comparison of calculated results and experimental measurements shows good agreement. Fig. 3 shows the relationship between temperature, and SO_2 and COS concentration. The concentration of SO_2 is increased with the increase of temperature and H_2S combustion while the COS concentration is decreased. Consumption rate of H_2S and S_2 production rate are shown in Fig. 4 H_2S combustion is tended to improve with rise of temperature, so the dissociation of H_2S is grown while its concentration is dropped. The concentration of S_2 is raised. Fig. 5 illustrate compares the predicted yields of S_2 and H_2S conversion with result of Towler and Lynn [18]. It shows that the yield of S_2 is increase with increase of temperature while H_2S yield is decreased. Fig. 6 shows the effect of equivalence ratio on production efficiency of S_2 and H_2S. It is seen that the amount of dissociated sulfur reaches its maximum at φ=0.95. The concentration of dissociated H_2S is decreased with increase of equivalence ratio. This is due to the fact that H_2S burns at low equivalence ratio however; H_2S exits the furnace without any chemical reaction at upper equivalence ratio. It also shows that the concentration of H_2 is increased with increase of equivalence ratio. At φ<1 H_2S thermal dissociation have an important role in production of H_2 while at φ>1 because of rich fuel-air mixture the production rate of H_2

increases. Fig. 7 shows the effect of equivalence ratio on production efficiency of SO_2 and SO. It can be seen that the efficiency of SO_2 and SO is decrease with increase of equivalence ratio as the amount of O_2 at higher equivalence ratio is decreased. Fig. 8 shows the effect of equivalence ratio on CO and CO_2 mole fractions. CO and COS mole fractions are increased with increase of equivalence ratio while the concentration of CO_2 has remained approximately constant.
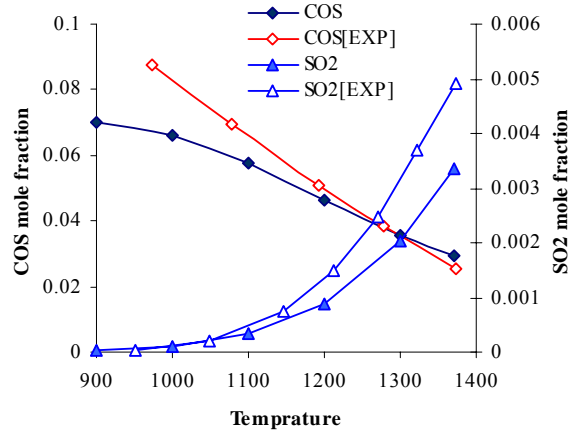

Fig. 3 Comparison of calculated results of SO_2 and COS with experimental results of Towler, and Lynn [18]
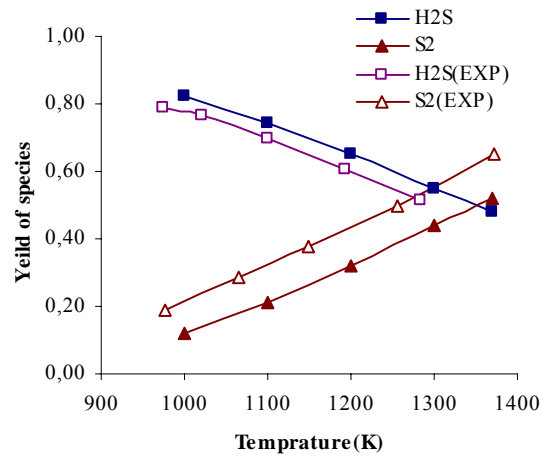

Fig. 4 Comparison of calculated results of H2S and S_2 withexperimental results of Towler, and Lynn [18]
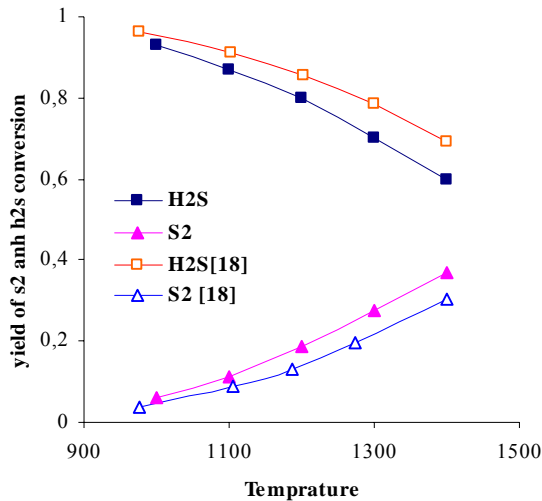
Fig. 5 Comparison of the predicted yields of S_2 and H_2S conversion with result of Towler and Lynn [18]
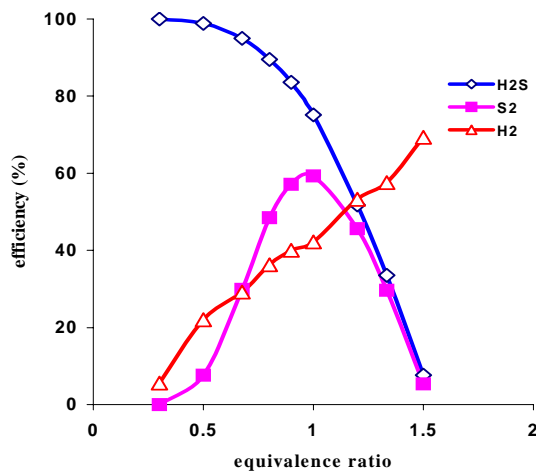

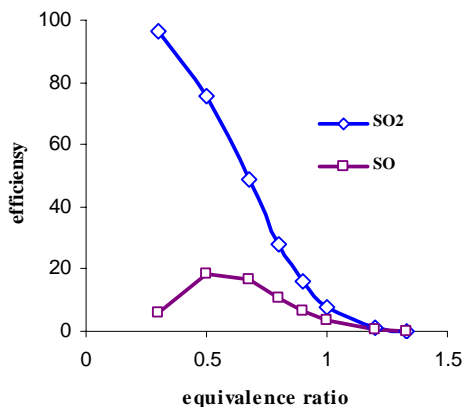Fig. 6 Effect of equivalence ratio on production efficiency of S_2 and H_2S

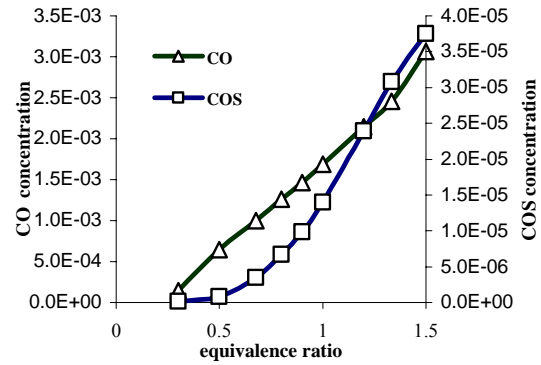Fig. 7 Effect of equivalence ratio on production efficiency of SO_2 and SO

Fig. 8 Effect of equivalence ratio on CO and COS mole fractions

V. CONCLUSION

The present study is concerned with simulating thermal dissociation of H_2S in industrial natural gas carbon black furnace. Fluent CFD software has been employed for numerical predictions. The comparison of calculated results against experimental measurements shows good agreement. The main results are summarized as follows:

- The concentration of H2S is decreased due to the increase of equivalence ratio.
- The concentration of sulfur is reached its peak at φ=0.95.
- H_2 concentration of H_2S thermal dissociation is increased with increase of equivalence ratio up to 1.
- H_2S is oxidized at low air-fuel ratio and is turned to SO_2 and a few amount of SO.
- The concentration of SO is peaked at φ=0.55.
- The concentration of SO_2 is increased due to decrease of equivalence ratio.
- CO and COS concentration is increased with increase of equivalence ratio.

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