Carbon disulfide production via hydrogen sulfide methane reformation

H. Hosseini, M. Javadi, M. Moghiman, M. H. Ghodsi Rad

Abstract— Carbon disulfide is widely used for the production of viscose rayon, rubber, and other organic materials and it is a feedstock for the synthesis of sulfuric acid. The objective of this paper is to analyze possibilities for efficient production of CS_2 from sour natural gas reformation (H_2SMR) ($2H_2S+CH_4 = CS_2 + 4H_2$) . Also, the effect of H_2S to CH_4 feed ratio and reaction temperature on carbon disulfide production is investigated numerically in a reforming reactor. The chemical reaction model is based on an assumed Probability Density Function (PDF) parameterized by the mean and variance of mixture fraction and β-PDF shape. The results show that the major factors influencing CS_2 production are reactor temperature. The yield of carbon disulfide increases with increasing H_2S to CH_4 feed gas ratio ($H_2S/CH_4 \leq 4$). Also the yield of C(s) increases with increasing temperature until the temperature reaches to 1000°K, and then due to increase of CS_2 production and consumption of C(s), yield of C(s) drops with further increase in the temperature. The predicted CH_4 and H_2S conversion and yield of carbon disulfide are in good agreement with result of Huang and T-Raissi.

Keywords— Carbon disulfide, sour natural gas, H_2SMR, probability density function.

I. Introduction

Carbon disulfide is a volatile liquid with a pungent smell and is widely used for the production of viscose rayon, rubber, and other organic materials. It has been known for its toxicity to animals and aqueous organisms. It is one of the sulfur-containing compounds that is produced via hydrogen sulfide methane reformation. Carbon disulfide (CS_2), a valuable product that is more desirable than elemental sulfur as a feedstock for the production of sulfuric acid (H_2SO_4). Furthermore, CS_2 can be hydrogenated to produce gasoline–range hydrocarbon liquid fuels [1]. It also has been useful as substrate probes for enzyme activities [2] and can greatly reduce the lifetime of the ammonia synthesis catalyst [3]. Carbon disulfide is classified as a hazardous pollutant and is emitted by either natural or industrial sources. direct

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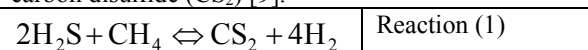
conversion of methane and hydrogen sulfide, which are the main components of sour gas that called sub-quality natural gas (SQNG), has widely been studied in order to obtain more valuable chemical products such as carbon disulfide [4]. At oil flow stations it is common practice to flare or vent sub quality natural gas, which is produced along with crude oil [5]. Gas flaring has also been blamed for environmental and human health problems such as acid rain, asthma, skin and breathing diseases [6]. The removal of H_2S from SQNG is expensive and not commercially viable for large-scale plants. In a reactor, hydrogen sulfide methane reformation produces carbon, sulfur and CS_2[7]. The purpose of this paper is to assess production of carbon disulfide from sub-quality natural gas (SQNG) using a 3D numerical technique that employs the model of probability density function for modeling of turbulent-chemistry interaction leading to production of carbon disulfide.

II. Reforming reactor Geometry

The reactor used in this investigation is a small-scale axial flow reactor identical by Gruenberger [5]. The basic geometry of the reactor is shown in Fig. 1. In the inlet, the tangentially injected hot gases (without oxidant) enters to reactor through two tangential inlets. Then, the highly swirling hot gases mix with the sub-quality natural gas injected radially into the reactor in the proximity of the mixing zone. vigorous mixing of the SQNG fuel with the hot gases as a result of sudden increase in the tube diameter at the exit of the choke leading to thermal decomposition of CH_4+H_2S and carbon disulfide formation [8].

iii. CHEMICAL REACTION MODELING

H2S can react with methane, according to Reaction (1), producing not only 4 mol of hydrogen, but also 1 mol of carbon disulfide (CS_2) [9].

$2H_2S + CH_4 \Leftrightarrow CS_2 + 4H_2$	Reaction (1)

H2SMR (Reaction (1)) proceeds via H_2S and methane pyrolysis according to following reactions (2, 3):

$$H_2S \rightarrow \frac{1}{2}S_2 + H_2 \qquad \text{Reaction (2)}$$

$$CH_4 \rightarrow C(S) + 2H_2 \qquad \text{Reaction (3)}$$

Since reaction 2 is highly endothermic, temperatures in excess of 1500°K is required for achieving reasonable rates [7], and, as reaction 3 is mildly endothermic, it requires temperatures higher than 850°K to proceed at reasonable rates [10].

IV. TURBULENCE CHEMISTRY INTERACTION

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 handling of large numbers of reacting species, including intermediate species. Transport equations are solved for the mean mixture fraction $\bar{f}$, its variance $\overline{f'^2}$ and for enthalpy $\bar{h}$. Calculations and PDF integrations are performed using a preprocessing code, assuming chemical equilibrium between 30 different species. The results of the chemical equilibrium calculations are stored in look-up tables which relate the mean thermochemical variables (species mass fractions, temperature and density) to the values of $\bar{f}$, $\overline{f'^2}$ and $\bar{h}$ [11].

V. NUMERICAL SOLUTION PROCEDURE

Fluent CFD software has been used to model the furnace employing solution-adaptive grid refinement technique to solve the 3D problem. The 3D volume grid is represented in Fig 2. A grid dependence study was conducted to arrive at the appropriate size of the grid for optimal accuracy and efficiency. In the optimal grid, the domain is discretized into a grid of 20493 nodes and 82745 tetrahedral cells. The conservation equations for mass, momentum, energy, Reynold's stresses, dissipation rate, mixture fraction and its variance are solved by finite-volume analysis, using a second-order upwind scheme for discretisation of the convective terms in the transport equations.

The RNG $k - \varepsilon$ model is used for modeling of dissipation rate and turbulence kinetic energy. The conventional wall-function approach is used in the near-wall region. At the inlet boundary, conditions are specified once and did not need updating during the course of the solution procedure. At the outlet boundary, zero gradient conditions are applied. We assumed an adiabatic boundary condition at the wall of the furnace.

VI. result

Numerical calculations were performed on the axial flow gas furnace described by Gruenberger [5] as shown in Fig. 1. The inlet gas flow rate is 0.019 m^3/s. Figs. 3 and 4 show the effect of H$_2$S to CH$_4$ ratio and temperature on CH$_4$ and H$_2$S conversions given by [9]:

$$CH_4 \ conversion = \frac{[CH_4]_0 - [CH_4]}{[CH_4]_0} \times 100 ,$$

$$H_2S \ conversion = \frac{[H_2S]_0 - [H_2S]}{[H_2S]_0} \times 100$$

where $[CH_4]_0$ and $[H_2S]_0$ denote the initial (input) concentration of CH$_4$ and H$_2$S in feed gas, respectively. $[CH_4]$, $[H_2S]$, are equilibrium concentration of CH$_4$ and H$_2$S at reactor outlet, respectively. H$_2$S decomposition is the limiting step in the H$_2$SMR process as it proceeds by the sequential reaction involving H$_2$S pyrolysis to form sulfur diatomic gas (S$_2$) (Reaction (2)), followed by S$_2$ reaction with CH$_4$ to produce carbon disulfide (CS$_2$) and H$_2$. Figs. 3 and 4 depict that the CH$_4$ and H$_2$S conversions drop with decreased H$_2$S/CH$_4$ ratio in feed gas; this can be attributed to the endothermic nature of H$_2$S and CH$_4$ decomposition reactions. For higher values of temperature CH$_4$ conversion $(\geq 800^\circ K)$ and H$_2$S conversion $(\geq 1200^\circ K)$ sharply increases with increased temperature due to the endothermicity of CH$_4$ and H$_2$S thermolysis. Fig. 3 shows that CH$_4$ conversion reaches 100% at temperatures above $1100^\circ K$. This is in accord with the results of Huang and T-Raissi [9].

Figs. 5 , 6 depict the yields of sulfur and carbon as a function of H$_2$S to CH$_4$ feed ratio and reactor temperature at the outlet of the reactor, that S$_2$ and C(s) yield is defined as:

$$S_2(\%) = \frac{2[S_2]}{[H_2S]_0} *100, \quad C(s)(\%) = \frac{[C(s)]}{[CH4]_0} *100$$

Where [X] denote the equilibrium molar concentrations of species X [9].

The figure reveals that for high values of H$_2$S to CH$_4$ ratio and reactor temperatures, CH$_4$ and H$_2$S convert mostly to S$_2$ and C(s). It can be seen that for higher values of temperature (and high H$_2$S/CH$_4$), yield of S$_2$ and C(s) are quite high. This is due to increased of CH$_4$ and H$_2$S conversion. Fig 5 shows that carbon yield increases with increasing temperature until the yield reaches a maximum value (at 1000°K), and then drops with further increase in the temperature for H$_2$S to CH$_4$ ratio ranging from 0.1 to up. In lower temperature than 1000∘K, hydrogen and carbon is produced by CH$_4$ decomposition. As shown in Fig .7 , CS$_2$ yields depend not only on the temperature, but also on the H$_2$S/CH$_4$ feed ratio. In lower temperature than 1000∘K, the yield of carbon disulfide (CS$_2$) approaches zero (Fig. 7). This is in accord with results of Huang and T-Raissi [9].

$$CS_2 \ (\%) = \frac{[CS_2]}{[CH_4]_0} \times 100$$

Where [CS$_2$] denote the equilibrium molar concentrations of Carbon disulfide.

Vii. CONCLUSION

The production of carbon disulfide from sour natural gas containing methane (CH$_4$) and hydrogen sulfide (H$_2$S) has been analyzed. Based on the presented results, the following conclusions may be drawn:

- CS$_2$ yields depend not only on the temperature, but also on the H$_2$S/CH$_4$ feed ratio.
- The carbon disulfide yield increases with increasing H$_2$S to CH$_4$ feed gas ratio.
- In lower temperature than 1000°K, the yield of carbon disulfide (CS$_2$) approaches zero.
- The maximum yield of C(s) is in 1000°K, then reduces sharply due to increasing of CS$_2$ production.
- Results show that the yield of S$_2$ reaches to 0.8 above 1800°K and it has not completed yet.

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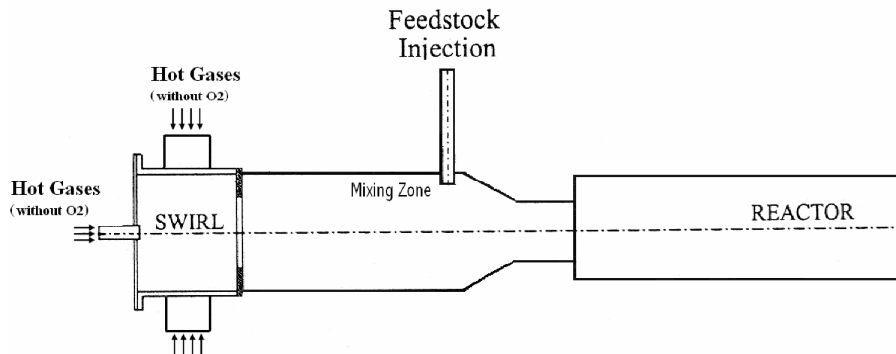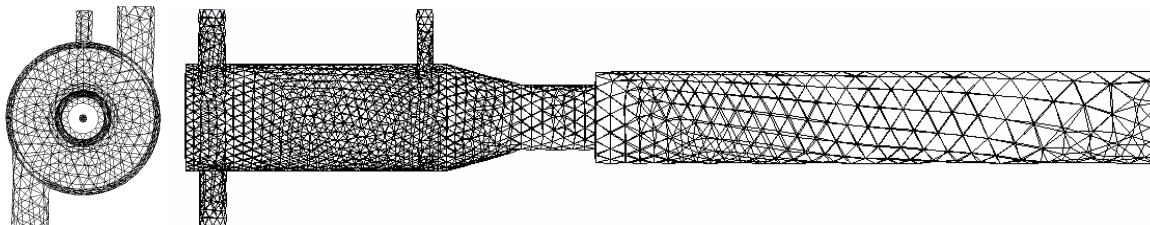
Figure 1. Reforming reactor
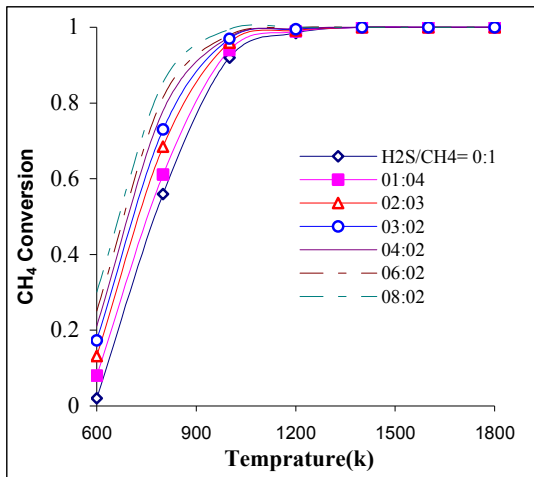

Figure 2. Three-dimensional tetrahedral grid

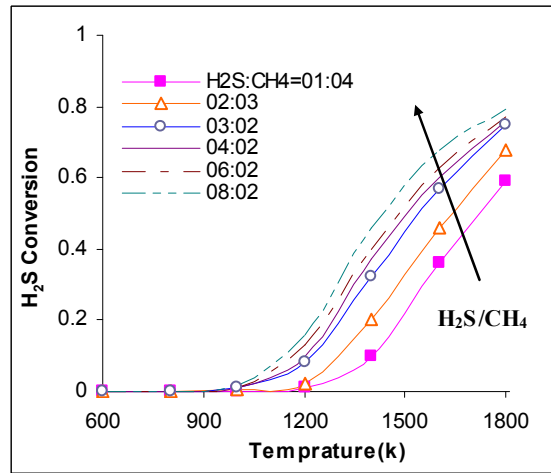Fig. 3. The effect of temperature and H_2S/CH_4 ratio on CH_4 conversion

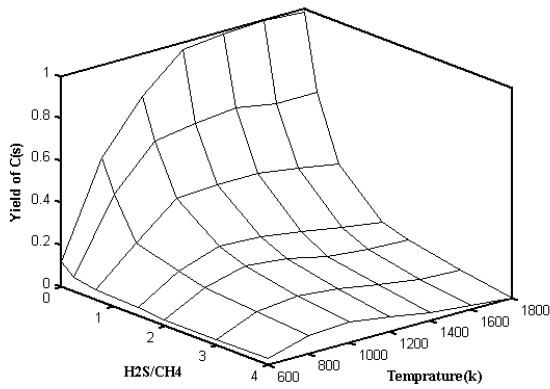Fig. 4. The effect of temperature and H_2S/CH_4 ratio on H_2S conversion

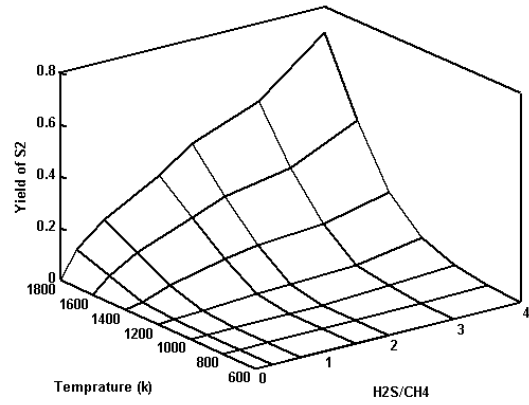Fig. 5. Yield of C(s) as a function of temperature and H_2S/CH_4 ratio

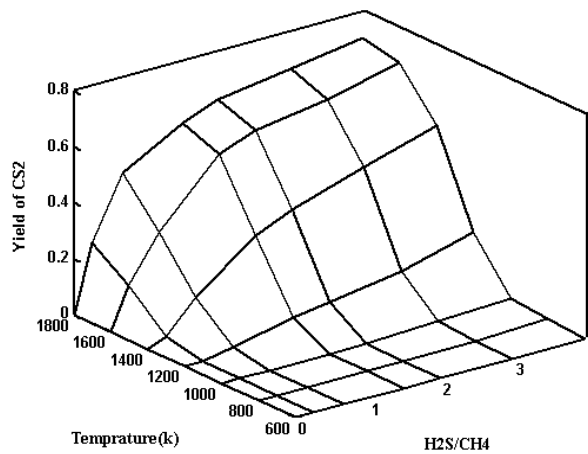Fig. 6. Yield of S_2 as a function of temperature and H_2S/CH_4 ratio

Fig. 7. Yield of CS_2 as a function of temperature and H_2S/CH_4 ratio