Sulfur Deactivation Effects on Catalytic Steam Reforming of Methane Produced by Biomass Gasification

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Abstract: Deactivation effects of hydrogen sulfide on steam reforming of methane have been investigated from the modeling view point. A pseudo homogeneous mathematical simulation is developed, to exactly model the process in a fixed bed tubular reactor filled with nickel catalyst particles. A Temkin like isotherm model for the sulfur coverage on the Ni surface is considered to describe sulfur deactivation and steam reforming in a combined kinetic equation. Hydrogen sulfide deactivates the catalysts and poisoning effects of sulfur on process efficiency, hydrogen production and temperature distribution within the reactor are investigated carefully.

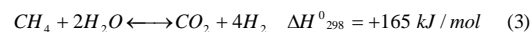**Keywords:** Methane, Reactor, Sulfur, Heat

1. Introduction

In today's energy supply system, electricity, gasoline, diesel fuel, and natural gas serve as energy carriers. These carriers are made by the conversion of primary energy sources, such as coal, petroleum, underground methane, and nuclear energy, into an energy form that is easily transported and delivered in a usable form to industrial, commercial, residential, and transportation end-users. In the latest years, the environmental and greenhouse problems derived from useful energy generation sources and the increment of fossil fuels prices have enhanced the development of new technologies for energy production [1]. In this sense, hydrogen and electricity play an important role in energy supply system in near future. In recent years, hydrogen has gained much research emphasis due to its wide range of energy applications. It is utilized predominantly for petroleum refining and the production of industrial chemical commodities such as ammonia. [2,3] Most of the hydrogen produced today is made via steam methane reforming, a process in which high-temperature steam (700°C–1000°C) is used to produce hydrogen from a methane source, such as natural gas or product gas from biomass gasification. Sulfur, on the other hand, which is incorporated in the biomass structure, is released into the product gas during gasification as hydrogen sulfide and deactivates nickel-based steam reforming catalysts by chemisorption on the metal surface. The metal sulfur bond is so strong that catalytic activity is substantially reduced, even at extremely low (ppb levels) gas-phase concentrations of hydrogen sulfide ,[4,5] Although several models have been purposed to address methane steam reforming reactions,[6-8], there are very few paper describing exactly the negative effects of sulfur on the process. This work uses finite element software COMSOL Multiphysics 4.2 to simulate a two dimensional pseudo homogeneous model describing methane steam reforming reactions in the presence of reasonable amount of hydrogen sulfide, which is typical for gasified biomass. Heat and mass transfer in the reactor are exactly modeled and effect of hydrogen sulfide on methane conversion, hydrogen yield and temperature distribution within the reactor are considered carefully.

2. Use of COMSOL Multiphysics

State of the art Comsol Multiphysics 4.2 is used to model the process. Heat transfer and chemical spices transport (transport of concentrated spices) interfaces in COMSOL, are used to solve partial differential mass and energy equations within the reactor. Pressure drop is modeled by Darcy law interface.

Methane steam reforming process is governed by two strongly endothermic reforming reactions coupled with exothermic water gas shift reaction,[9]:

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \qquad \Delta H^0_{298} = +206 \; kJ/mol \qquad (1)$$

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad \Delta H^0_{298} = -41 \; kJ/mol \qquad (2)$$

$$CH_4 + 2H_2O \longleftrightarrow CO_2 + 4H_2 \qquad \Delta H^0_{298} = +165 \; kJ/mol \qquad (3)$$

Several authors have proposed different kinetic expressions for the reforming reactions. Xu & Froment proposed a kinetic model using the Langmuir Hinshelwood methodology accounting for diffusional limitations, using a nickel based catalyst,[10,]:

$$R_1 = \frac{\frac{k_1}{P_{H2}^{2.5}}\left[P_{CH4}P_{H2O} - \frac{P_{H2}^3 P_{CO}}{K_1}\right]}{DEN^2} \tag{4a}$$

$$R_2 = \frac{\frac{k_2}{P_{H2}}\left[P_{CO}P_{H2O} - \frac{P_{H2}P_{CO2}}{K_2}\right]}{DEN^2} \tag{4b}$$
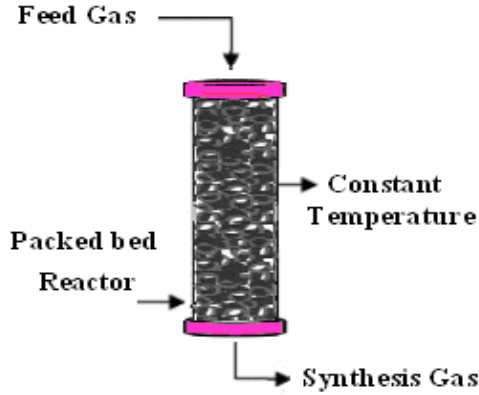
Figure 1. Schematic diagram of the packed bed catalytic reactor used for MSR reactions.

$$R_3 = \frac{\frac{k_3}{P_{H2}^{3.5}}\left[P_{CH4}P_{H2O}^2 - \frac{P_{H2}^4 P_{CO2}}{K_3}\right]}{DEN^2} \tag{4c}$$

$$DEN = 1 + K_{CH4}P_{CH4} + K_{CO}P_{CO} + K_{H2}P_{H2} + \frac{K_{H2O}P_{H2O}}{P_{H2}} \tag{4d}$$

$$K_1 = \frac{P^3_{H2}.P_{CO}}{P_{H2O}} \quad bar^2 \tag{4e}$$

$$K_2 = \frac{P_{H2}.P_{CO2}}{P_{co}.P_{H2O}} \tag{4f}$$

$$K_3 = K_1.K_2 \quad bar^2 \tag{4g}$$

Dependence of rate coefficients k_1, k_2, k_3 and adsorption coefficients of the gases $K_{CO}, K_{H2}, K_{CH4}, K_{H_2O}$ with temperature was described by an Arrhenius type function:

$$k_j = A_j \times e^{-E_j/RT} \qquad j = 1,2,3 \tag{5a}$$

$$K_i = B_i \times e^{-\Delta H_i/RT} \qquad i = CH_4, H_2, HO, CO, CO_2 \tag{5b}$$

The activation energies, enthalpies of adsorption and pre-exponential factors used in this work are from the work of Xu and Froment,[10]. The formation rate of each component was then calculated by using Eqs. (1)-(3) and (4a)-(5b); for example for methane and hydrogen components:

$$R_{CH4} = r_1 + r_3 \tag{5c}$$

$$R_{H2} = 3r_1 + r_2 + 4r_3 \tag{5d}$$

The continuity equation for each of the gas components and the energy equation can now be written as follow, [9]:

$$Der\left(\frac{\partial^2 C_i}{\partial r^2} + 1/r\frac{\partial C_i}{\partial r}\right) - u_s\frac{\partial C_i}{\partial r} - \varepsilon\rho_B r_i = 0 \tag{6a}$$

$$\lambda er\left(\frac{\partial^2 T}{\partial r^2} + 1/r\frac{\partial T}{\partial r}\right) - u_s\rho_g c_P\frac{\partial T}{\partial r} + \varepsilon\rho_B(-\Delta H)r_i = 0 \tag{6b}$$

The following boundary conditions are considered,[9]:

$$\begin{aligned}
at \quad z = 0 \qquad & C = C_0 \\
0 \le r \le R \qquad & T = T_0 \tag{7a}
\end{aligned}$$

$$\begin{aligned}
at \quad r = 0 \qquad & C = C_0 \\
r = R \qquad & \frac{\partial C}{\partial r} = 0 \tag{7b}
\end{aligned}$$

$$at \quad r = 0 \qquad \frac{\partial T}{\partial r} = 0 \tag{7c}$$

$$at \quad r = R \qquad \frac{\partial T}{\partial r} = -\frac{h_w}{\lambda_{er}}(T_R - T_w) \tag{7d}$$

Methane conversion and Hydrogen yield are calculated as follow:

$$xCH4 = (F^0CH4 - FCH4)/F^0CH4 \tag{8}$$

$$H2\ Yield = 0.25.FH2_{out}/F^0CH4 \tag{9}$$

D_{er} is based upon the superficial flow velocity and is calculated according to the Delgado,[11]. Wall heat transfer coefficient and effective thermal conductivity are calculated using the correlations reported by Peters and Achenbach,[12,13]. Momentum equation which shows the pressure distribution in the packed bed reactor was described by the Tallmadge, who proposed an extension of Ergun's equation under higher Reynolds numbers: [14,15]:

$$\frac{dp}{dz} = -\frac{f\rho_g u_s^2}{dp} \tag{10a}$$

$$f = \frac{(1-\upsilon)}{\upsilon^3}\left[1.75 + \frac{4.2(1-\upsilon)}{Re^{1/6}}\right] \tag{10b}$$

The intrinsic rate expressions of poisoned catalyst are compared to sulfur free catalyst rate by referring to free nickel surface and using a Maxted model for poisoning,[16]:

$$R_{sp} = R^0{}_{sp}(1-\theta_S)^3 \tag{11}$$

Where θ_s represents the sulfur coverage and rate expressions for sulfur free catalyst ($R^0{}_{sp}$) were discussed in previous sections. Hydrogen sulfide chemisorbs dissociatively on nickel surfaces. The thermodynamics of nickel sulfide phases indicates that the formation of bulk phase sulfide depends on H2S/H2 ratio and temperature. This can be described in terms of an adsorption isotherm and isosteric heat of chemisorption. The experimental data have shown that sulfur coverage is described by the so called Temkin isotherm,[16]:

$$\theta_S = 1.45 - 9.53.10^{-5}.T + 4.17.10^{-5}.T \ln\left(\frac{pH2S}{pH2}\right) \qquad (15)$$

The following values have been found to correlate the experimental data very well:

$\Delta H_0 = 280\, kJ/mol$, $\Delta S_0 = -19\, J/(mol\,K)$ and $a = 0.69$

3. Result and discussions

The numerical model presented in this work provides the temperature and concentration profiles along the reactor radial and axial coordinates for both cases, with and without presence of sulfur in the gas. Outside wall temperature of the reactor is kept constant at 1173 (K) .Figure (2) shows dry molar concentration of different spices of the gas 2(a) and methane conversion 2(b) along the reactor length without sulfur in the gas and compares the result to the case when sulfur is included. When sulfur is not included in the gas, it is shown that the concentration of methane decreased sharply at very close distance to the entrance of the reactor which corresponds to about 100 percent conversion of methane and highest level of hydrogen yield, Figure 3(a). Without presence of the sulfur in the gas, carbon monoxide concentration dropped and carbon dioxide concentration increases sharply at very close distance to the reactor entrance. Then, carbon monoxide gradually increases and carbon dioxide decreases along the axial bed of the catalyst.

2(a)
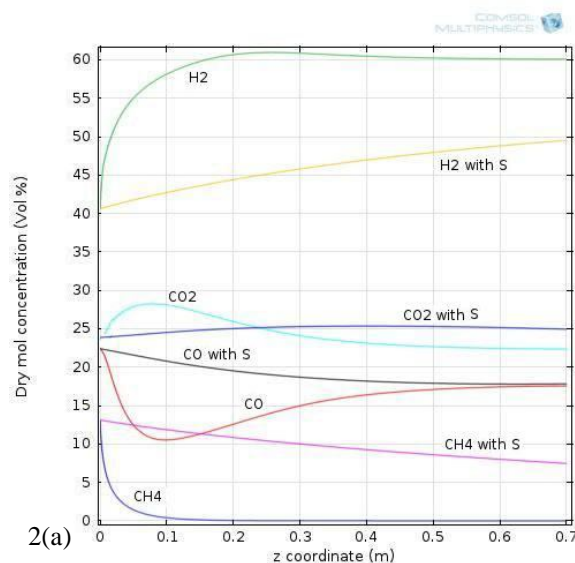
Figure 2.(a) Molar concentration of different spices in the reactor with and without sulfur included in the gas, wall temperature T=1173 (K).
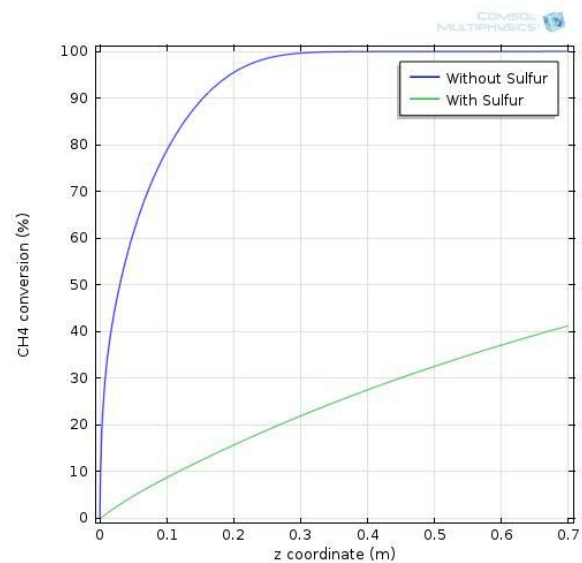

Figure 2.(b) Methane conversion in the reactor with and without sulfur included in the gas, wall temperature T=1173 (K).
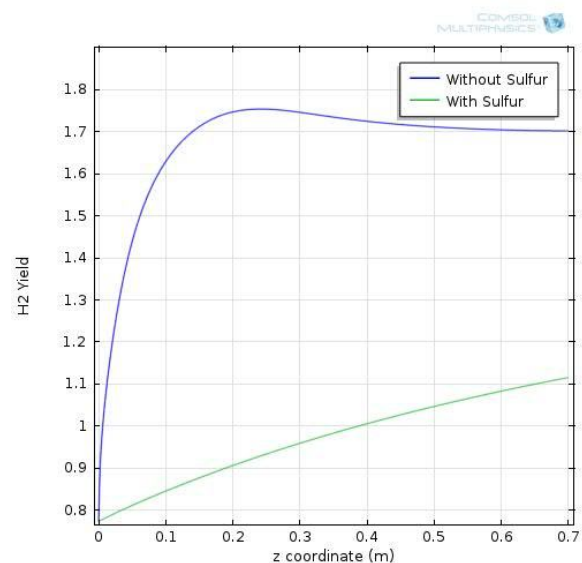
Figure 3(a) Hydrogen yield at the reactor outlet with and without sulfur included in the gas at reactor wall temperature T=1173 (K).

It is due to composition of the gas and the fact that the rate of water gas shift reaction is higher than reforming reactions and leads to decrease of carbon monoxide concentration (increasing carbon dioxide concentration) but later hydrogen reaction with carbon dioxide is suppressed and cause the water gas shift reaction to proceed in other direction. Due to the sulfur presence in the gas, carbon dioxide and carbon monoxide

concentrations increase and decrease uniformly along the reactor length, respectively. A sulfur negative effect on reforming reactions leads to around 60% reduction of methane conversion at the end of the reactor.
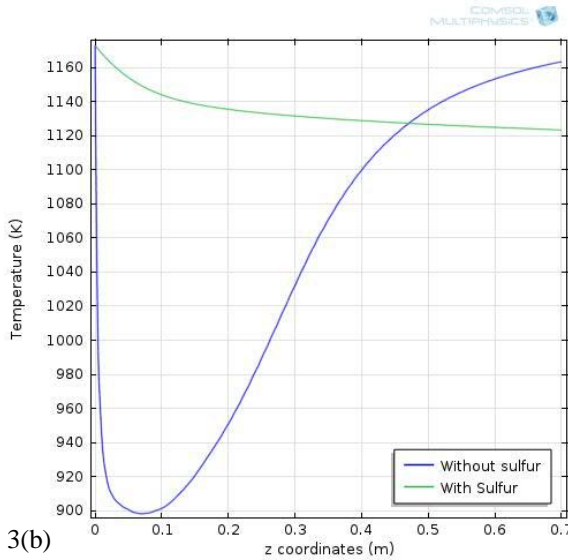
3(b)

Figure 3(b) Temperature distribution along the reactor bed with and without sulfur included in the gas at reactor wall temperature T=1173 (K).

In Fig. 3(b) the temperature distribution in the reactor is displayed. Predicting result shows that when sulfur is not presented in the gas, the temperature dropped drastically at the initial part of the reactor from the initial temperature of 1173 K to about 900 K and then increased gradually to 1073 K. This phenomenon is attributed to the large amount of heat required at the initial stage of the reactions due to the high endothermic nature of the reactions. The rising temperature after a sudden drop along the axial bed of the catalyst is due to the heat supplied by the outer surface of the reactor into the catalytic bed. Due to the completion of methane conversion close to the reactor entrance, more heat is available at the end of the reactor bed. Sulfur presence in the gas leads to catalyst deactivation and lower methane conversion rate. Therefore, temperature decreases gradually along the reactor bed. Pressure drop and velocity change along the reactor are shown in Figure 4(a,b) respectively. Pressure drop is about 120 mbar along the reactor length which increases the gas velocity according to the figure 4(b).

4(b)
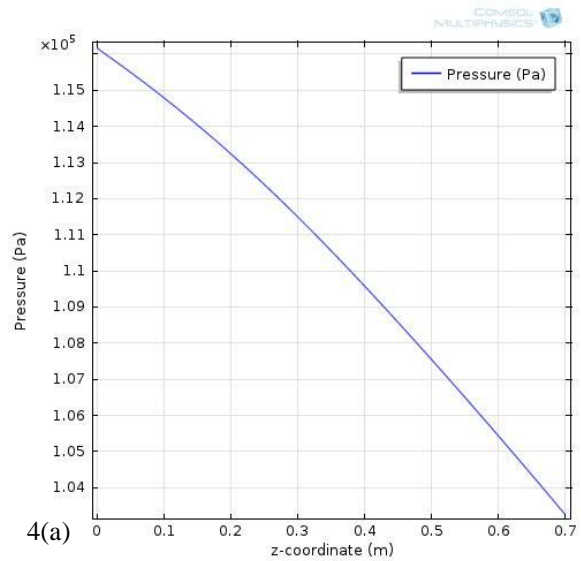
4(a)

Figure 4(a) Pressure drop along the reactor at reactor wall temperature T=1173 (K).
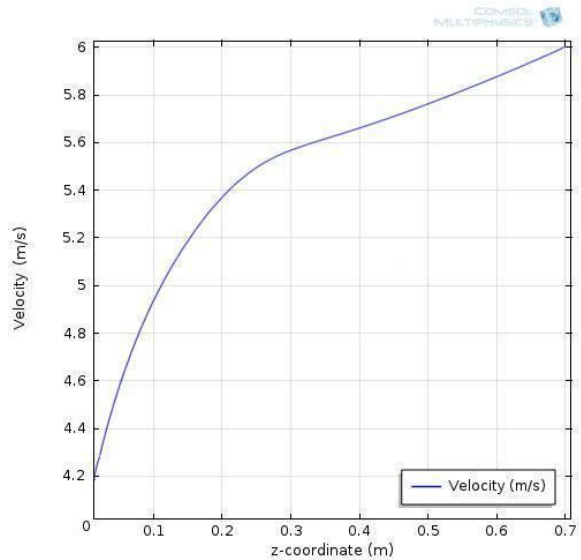
Figure 4. (b) Velocity change along the reactor at reactor wall temperature T=1173 (K).

4.Conclusion
State of the art finite element software, COMSOL Multiphysics 4.2 is used to model the steam reforming of methane in a fixed bed reactor and solve the system of differential equations. The profiles of reactor performance are simulated and sulfur effect on all species concentration and temperature distribution in the reactor was investigated. It is shown that even

when present in the hydrocarbon feedstock in small quantities, ppb levels, sulfur can have a significant effect in methane conversion, hydrogen yield and temperature distribution in the reactor.

5. References

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