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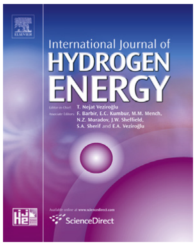

Experimental and modeling study of hydrogen production from catalytic steam reforming of methane mixture with hydrogen sulfide

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ABSTRACT

Experimental and theoretical studies of steam methane reforming reactions with different amount of hydrogen sulfide in the feed gas are presented. A two dimensional pseudo-heterogeneous model is developed to simulate methane steam reforming reactions in a packed bed tubular reactor. This model is based on mole and energy balance equations for the catalyst and the fluid phases. Attention is given to the analysis of sulfur negative effects on reforming process. A parametric study is done and effects of different steam to carbon ratios, space velocities, temperatures and different amount of sulfur on methane conversion and temperature distribution within the reactor are investigated. The results are verified comparing to the experimental results. It is shown that even presented in the gas at very low concentration levels (ppm), sulfur drastically decreases the conversion of methane. The obtained results play a key role in design and optimization of an actual reactor.

Introduction

In the latest years, the environmental problems derived from useful energy generation sources and from the increment of fossil fuels prices, have enhanced the development of new technologies for energy production. Steam reforming of methane produced by biomass gasification is one of the most employed processes to produce hydrogen and synthesis gas [1–4]. Synthesis gas, constituted by different quantities of carbon monoxide and hydrogen, can also be used to produce high purity hydrogen streams and chemical products, [5]. The steam reforming reactions are industrially operated at a high temperature up to 900 °C over nickel-alumina or noble metal based catalysts, because a reasonable conversion of methane is required in this endothermic process, [6–8]. Sulfur, on the other hand, which also is incorporated in the biomass structure, is released into the product gas during gasification as hydrogen sulfide. It is generally recognized that sulfur can have devastating effects on the catalytic activity of supported metal particles. Many catalytic reactions are poisoned by even trace quantities of sulfur containing molecules such as hydrogen sulfide. Since, synthesis gas produced by steam reforming of low hydrocarbons are further used in the

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synthesis to mixed alcohols or Fischer–Tropsch products, it is of interest to investigate steam reforming process without cleaning the gas and desulfurization prior to the reactor.

Even though, different methods have been used to address and simulate the steady state and non-steady state operation of catalytic steam reformers, and several comprehensive reviews have been written about reforming of methane [9–21], there is no mechanism available which covers steam reforming of methane including sulfur and published papers are very few in numbers, [22–30]. This work considers a two dimensional pseudo-heterogeneous model to mathematically simulate steam reforming of methane in a fixed bed reactor including reasonable amount of hydrogen sulfide. Using the same inlet and process condition for experiments, makes it possible to compare the modeling and experimental results and see how well the modeling predict the experimental results. Moreover, a parametric study is done to investigate the effects of different reforming parameters such as sulfur, space velocity, steam to carbon ratio and temperature on process efficiency.

Mathematical model

Steam reforming of methane involves, two reversible endothermic reforming reactions, (1, 3) coupled with exothermic water gas shift reaction, (2) [31],:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^0_{298} = +206 \text{kJ/mol} \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0_{298} = -41 \text{kJ/mol} \tag{2}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H^0_{298} = +165 \text{kJ/mol} \tag{3}$$

The kinetic model for methane steam reforming reactions on a nickel catalyst is based on a Langmuir–Hinshelwood reaction mechanism and the intrinsic kinetic expressions reported by Xu and Froment are adopted [10,11],:

$$R_1 = \frac{\frac{k_1}{P_{H_2}^{2.5}}\left[P_{CH_4}P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_1}\right]}{DEN^2} \tag{4a}$$

$$R_2 = \frac{\frac{k_2}{P_{H_2}}\left[P_{CO}P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_2}\right]}{DEN^2} \tag{4b}$$

$$R_3 = \frac{\frac{k_3}{P_{H_2}^{3.5}}\left[P_{CH_4}P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_3}\right]}{DEN^2} \tag{4c}$$

$$DEN = 1 + K_{CH_4}P_{CH_4} + K_{CO}P_{CO} + K_{H_2}P_{H_2} + \frac{K_{H_2O}P_{H_2O}}{P_{H_2}} \tag{4d}$$

Rate constants of the above equations are described by Arrhenius type functions [31],:

$$k_1 = 9.49 \times 10^{16} \exp\left(-\frac{28,879}{T}\right) \frac{\text{kmol kpa}^{0.5}}{\text{kg h}} \tag{5a}$$

$$k_2 = 4.39 \times 10^4 \exp\left(-\frac{8074.3}{T}\right) \frac{\text{kmol kpa}}{\text{kg h}} \tag{5b}$$

$$k_3 = 2.29 \times 10^{16} \exp\left(-\frac{29,336}{T}\right) \frac{\text{kmol kpa}^{0.5}}{\text{kg h}} \tag{5c}$$

$K_{CH_4}, K_{H_2}, K_{CO}, K_{H_2O}$ are the constants which related to surface adsorption in equilibrium and are functions of temperature. The equilibrium constants for reactions (1–3) were calculated using the standard Gibbs energy of each reaction at the corresponding temperature and are defined as [31],:

$$K_1 = 10266.76 \times \exp\left(-\frac{26,830}{T} + 30.11\right); \text{kpa}^2 \tag{5d}$$

$$K_2 = \exp\left(\frac{4400}{T} - 4.063\right) \tag{5e}$$

$$K_3 = K_1K_2; \text{kpa}^2 \tag{5f}$$

Partial pressures of gases were correlated to their own concentrations by using the ideal gas law. The formation rate of each component was then calculated by using equations (1)–(5f). For example, for methane and carbon dioxide components the reaction rates are written as follow:

$$R_{CH_4} = -(R_1 + R_3) \tag{6a}$$

$$R_{CO_2} = (R_2 + R_3) \tag{6b}$$

Pseudo-heterogeneous model considers transport by plug flow and distinguishes between conditions in the fluid and in the solid (catalyst) phases. The continuity and energy balance equations for the fluid phase are written as [31],:

$$u_z\left(\frac{\partial C_i}{\partial z} + u_r\frac{\partial C_i}{\partial r}\right) = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_{er}\frac{\partial C_i}{\partial r}\right) + k_g a_v\left(C_S^s - C_i\right) \tag{7a}$$

$$\frac{\partial T}{\partial z} = \frac{I}{\rho_f C_p u_z}\left(\lambda_{er}\left(\frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2}\right) - h_f a_v\left(T - T_s^s\right)\right. \tag{7b}$$

Where, a_v is the specific surface area of the catalyst bulk per reactor volume. The energy transport in axial direction is dominated by the transport from axial convection, and thus axial conduction is neglected. With no radial convection, the only energy transport mechanism in radial direction is the effective conduction.

When resistance to heat and mass transfer inside catalyst pellets is important, the rate of reaction is not uniform throughout the particle. The catalyst phase mass and energy balance equations are written as [31],:

$$k_g a_v(C^sS - C_i) = \rho_c(1-\varepsilon)\eta_i R_i \tag{8a}$$

$$h_p a_v\left(T_s^s - T_f\right) = \frac{1}{r}\frac{\partial}{\partial r}\left(r\lambda_{er}{}^s\frac{\partial T_s}{\partial r}\right) + \rho_c(1-\varepsilon)\sum(\eta_i(-\Delta H_i)R_i \tag{8b}$$

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 [32,33],:

$$\frac{dp}{dz} = -\frac{f\rho_f {u_z}^2}{dp} \tag{9a}$$

$$f = \mu^2(\mu - 1)\left[1.75 + \frac{4.2(\mu - 1)}{\mu {Re_p}^{1/6}}\right] \tag{9b}$$