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Steam Reforming of Methane in Metal-foam Filled Reactor

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Abstract

As a unique porous media, open-cell metal foams with high porosity, high specific surface area and strong heat transfer capability is highly potential to be used to increase the conversion rate of methane to hydrogen. Steam reforming of methane in metal-foam filled reactor was studied in this paper. An innovative chemistry model was developed in which the reactive rate J and volume expanding rate δ were associated with partial pressure, density and concentration in the chemical reactions. While reactive heat addition and mass diffusion were considered as inner thermal sources in the temperature equation for fluid. The methane conversion rate and distribution of fluid temperature were investigated. It was found that metal foams improved the conversion by its higher thermal conductivity of solid matrix, bigger cell size and smaller cell ligament diameter. It was demonstrated that higher average temperature along the flow direction is caused by metal foams. The peak section-average temperature of fluid appeared close to the entrance of the reactor and increased simultaneously with the increasing of conversion of methane to hydrogen. It is explained that moving of the chemical equilibrium of steam reforming was due to better endothermic reaction and longer contacting time of amount of substance with metal-foam filled in the reactor.

Introduction

Steam methane reforming (SMR) is widely used for producing hydrogen, through which about 50% of hydrogen demand in chemical manufacturing and petroleum refining is satisfied [1]. However, heat and mass diffusion in the process of steam methane reforming was relatively limited [2]. Open-cell metal foams could be used for addressing the above limitations, since the complex 3-D matrix of open-cell metal foams could thin both velocity and heat boundary layers of the flowing fluid [3-4]. By sintering open-cell metal foams in a chemical reactor, the conversion rate of hydrogen by SMR is largely improved.

The chemical kinetics for steam reforming was found in [5-9]. Conventional wisdom showed that steam methane reforming included more than two reactions, through which both CO and CO_2 were formed during the hydrogen production [5]. To investigate the further kinetics, Lin et al [6] regarded the SMR as combination of steam reforming and water gas shift reactions. Craciun et al [7] argued that SMR occurred through a bi-functional mechanism consisting of reactions of oxygen from ceria and the dissociated methane on the previous metal. While Abashar [8-9] established mathematical model of fluidized bed membrane reactors for SMR based on the four-step reaction mechanism. All of the above researchers considered SMR as multi-step reactions, leading to complexity of predicting the conversion rate. However, due to the use of various catalysts, the reactive processes were largely shortened. As a result, SMR can be regarded as one-step reactions. Nevertheless, performance of SMR is highly dependent on the catalyst used in the reactions, owing to its effect on the endothermic characteristics of the reactions. By using catalysts, the reactive temperature was reduced [10] and the heat transfer and dynamic response during the reactions were improved [11].

Thermal performance of SMR in porous-media supported reactor was extensively studied [1, 12-15]. Yu et al [1] analysed the performance of porous ceramic membrane for hydrogen production by SMR. Raviraj et al [12] studied the conversion of methane to hydrogen in a porous media reactor. Levent [13] investigated the distribution of concentration and temperature in porous catalyst. Luna [14] reported the performance of the SMR in the range of 773-873K, using alumina-titania as the catalyst. Yang et al [15] investigated the influence of temperature, ratio of H_2O and CH_4, porosity of porous media on methane steam reforming in planar porous support of solid oxide fuel cell. However, most of the studies were based on one-dimensional heat transfer model, and presented vague information about the influence of reactive heat and mass diffusion in SMR.

In this study, a two-dimensional model was established for the SMR in a metal-foam supported reactor. Special attention was paid on processing the reactive heat and variable density of reactants. Parametric study was carried out for exploring the achieving optimal conversion rate of SMR in metal-foam filled reactor.

Theoretical Models

Chemical Kinetics Model

Under certain thermal conditions, steam reforming of methane can be described as a reversible chemical reaction as shown in equation (1) (Abashar [3, 4]):

$$CH_4 + H_2O = CO + 3H_2 + 206kJ/mol \tag{1}$$

The mixture of the reactants was regarded as an ideally flowing system under the hypothesis of continuous reactions. No lag or deposit was proposed in metal-foam filled reactor. As a result, the reactive rate was formulated in equation (2) by Abashar [4]:

$$\mathrm{J} = \rho \cdot \frac{k}{P_{H_2}{}^{2.5}} \left(P_{CH_4}.P_{H_2O} - \frac{P_{H_2}{}^{3}.P_{CO}}{K}\right) / DEN^2, mol/(kg.s) \tag{2}$$

In the formula, $\rho, P_{CH_4}, P_{H_2O}, P_{CO}, P_{H_2}$ are density of the reactive fluid mixture, partial pressure of CH_4, H_2O, CO, H_2, respectively; k represents the rate constant; K is the equilibrium constant of the above reaction. Detailed calculations of parameters were listed in Abashar [4]. However, partial pressure, temperature and density of the reactants were not mentioned in the literature.

The physical properties of the mixed reactants could be obtained in terms of ideal gas state equations and Dalton's law of partial pressure. For steam reforming of methane in metal foams, the volume expanding was described in equation (3):

$$\sum_i \varphi_i \cdot A_i = \sum_j \eta_j \cdot B_j \tag{3}$$

In which A_i, B_j are reactants and products while φ_i, η_j denote volume coefficients for the above reactants and products. Volume expanding rate δ demonstrated the variation of the total volume, resulting in changing pressure and density during the reaction, which was defined as in equation (4):

$$\delta = \frac{1}{\varphi_i} \cdot (\sum_j \eta_j - \sum_i \varphi_i) \tag{4}$$

For steam reforming in Eq. (1), volume expanding rate was calculated as $\delta = 2$. Ideal gas equation and Dalton's law of partial pressures were formulated as equation (5) and (6):

$$\rho = \frac{P}{R_g T} \tag{5}$$

$$\frac{P_i}{P_{io}} = \frac{n_i}{n_{io}} \cdot \frac{V_0}{V_i} \cdot \frac{T_i}{T_0} \tag{6}$$

In which P, T, R_g, are the whole pressure, temperature and universal gas constant, respectively; While P_i and P_{io}, n_i and n_{io}, V_i and V_0, T_i and T_0, are the partial pressure, the amount of substance, gas volume, and temperature at time t and 0, respectively. Due to no lag and deposit in the reactor, equation (7) ~ (9) can be obtained:

$$\frac{n_i}{n_{io}} = 1 - \alpha_i \tag{7}$$

$$\frac{V_0}{V_i} = \frac{1}{1 + \xi_i \cdot \alpha_i} \tag{8}$$

$$\xi_i = \omega_{i0} \cdot \delta \tag{9}$$

In which α_i, ξ_i, ω_{i0} are conversion rate of component i, rate of expansion based on component i, and initial fraction of component i. It was noted that all the properties of reactants were associated with the reactive rate J in metal-foam filled reactor. Therefore, it is necessary to figure out the reactive rate in prior to obtain the thermal properties of the mixture. According to chemical kinetics, reactive rate was expressed as equation (10):

$$J = -\frac{n_{io}}{S_o} \cdot \frac{d\alpha_{CH_4,i}}{dz} = \frac{dC_{CH_4}}{dz} \cdot \bar{u} \tag{10}$$

In which, S_o is the section area of the reactor; $C_{CH_4,i}$ represents the concentration of methane at time t; while $\overline{u}$ is the average velocity of the mixed gas. One could see that both of heat and mass diffusions had significant effects on determining the value of conversion rate.

Heat Transfer Model in metal foams

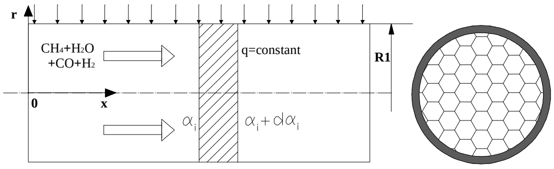

Figure 1. schematic model of the reactor

Figure 1 showed a schematic diagram of a cylinder-shape reactor with high porosity metal foams sintered inside. Due to heat absorption from the wall and effect of catalyst supported by metal foams, reaction of SMR proceeded when the mixture of methane and steam flowed through the reactor.

In metal-foam fill reactor, the governing equations for velocities and solid matrix of metal foams were proposed by Zhao [3-4]:

$$\frac{\partial(\rho_f u^2)}{\partial x} + \frac{1}{r}\frac{\partial(r\rho_f uv)}{\partial r} = -\varepsilon^2 \frac{\partial p}{\partial x} + \frac{\partial}{\partial x}(\mu_f \varepsilon \frac{\partial u}{\partial x}) + \frac{1}{r}\frac{\partial}{\partial r}(r\mu_f \varepsilon \frac{\partial u}{\partial r}) - \frac{\mu_f \varepsilon^2}{K}u - \frac{\rho_f \varepsilon^2 C_I}{\sqrt{K}}u^2 \tag{11}$$

$$\frac{\partial(\rho_f uv)}{\partial x} + \frac{1}{r}\frac{\partial(r\rho_f v^2)}{\partial r} = -\varepsilon^2 \frac{\partial p}{\partial r} + \frac{\partial}{\partial x}(\mu_f \varepsilon \frac{\partial v}{\partial x}) + \frac{1}{r}\frac{\partial}{\partial r}(r\mu_f \varepsilon \frac{\partial v}{\partial r}) - \frac{\mu_f \varepsilon^2}{K}v - \frac{\rho_f \varepsilon^2 C_I}{\sqrt{K}}v^2 \tag{12}$$

$$0 = \frac{\partial}{\partial x}[(k_{fe} + k_d)\frac{\partial T_s}{\partial x}] + \frac{1}{r}\frac{\partial}{\partial r}[(k_{fe} + k_d)\frac{\partial T_s}{\partial r}] - \mathrm{h}_{\mathrm{sf}}\, a_{sf}(T_s - T_f) \tag{13}$$

Which are momentum equations and energy equation for solid matrix (metal foams). Calculations for all of the involved parameters could be found in [3-4].

Due to the heat and mass diffusion in the reaction, thermal source term should be added in energy equation for fluid consisting of the reactants. The reactive heat of the steam reforming was supposed to be absorbed by the fluid mixture completely. As a result, the thermal source term caused by reactive heat could be calculated in terms of volume-averaging method, as shown in equation (14):

$$\mathrm{Q}_{\mathrm{rea}} = J \times \Delta H / C_f \tag{14}$$

Similarly, another thermal source term due to mass diffusion was formulated as in equation (15):

$$\mathrm{Q}_{\mathrm{mass}} = \Sigma \frac{k_{fi}}{C_{fi}} \frac{\partial Y_i}{\partial x} \frac{\partial T_f}{\partial x} \tag{15}$$

Therefore, energy equation for fluid temperature was written as equation (16):

$$\frac{\partial(\rho_f u T_f)}{\partial x} + \frac{1}{r}\frac{\partial(r\rho_f v T_f)}{\partial r} = \frac{\partial}{\partial x}(\frac{k_{fe} + k_d}{C_f}\frac{\partial T_f}{\partial x}) + \frac{1}{r}\frac{\partial}{\partial r}(r\frac{k_{fe} + k_d}{C_f}\frac{\partial T_f}{\partial r}) + h_{sf}\ \mathrm{a}_{\mathrm{sf}}(T_s - T_f)/C_f - J \cdot \Delta H / C_f - \sum_i \frac{k_{fi}}{C_{fi}}\frac{\partial Y_i}{\partial x}\frac{\partial T_f}{\partial x} \tag{16}$$

The code for two-dimensional numerical model was developed based on SIMPLER algorithm. Boundary conditions for the reaction in metal-foam filled tube were shown in table 1.

Position	Velocity		Temperature	
$x = 0$	$u = u_{in}$	$v = v_{in}$	$T_f = T_{f\,in}$	$\frac{\partial T_s}{\partial x} = 0$
$x = L$	$\frac{\partial u}{\partial x} = 0$	$\frac{\partial v}{\partial x} = 0$	$\frac{\partial T_f}{\partial x} = 0$	$\frac{\partial T_s}{\partial x} = 0$
$r = 0$	$\frac{\partial u}{\partial r} = 0$	v	$\frac{\partial T_f}{\partial r} = 0$	$\frac{\partial T_s}{\partial r} = 0$
$r = R$	$u = 0$	$v = 0$	$q = k_{fe}\frac{\partial T_f}{\partial r} + k_{se}\frac{\partial T_s}{\partial r} = 0$ $T_s = T_f$	

Table 1. Boundary conditions

Results and Discussion

Characteristics of reaction

An example of conversion rate of the SMR and section-average temperature of reactants was shown in Fig.2. The reactor was 100 mm long with a radius of 10mm. The reactants were fully mixed before entering the cylinder-shape reactor. The inlet temperature was equal to 823 K, while gauge pressures were set as 1 bar and

0.5 bar in different cases. The constant heat flux at the wall of the reactor was 5000 W/m^2, which was used to promote the endothermic reaction.

One could see that the conversion rate increased sharply within the first 10% of distance along the axial direction, indicating crucial effects of catalyst and metal-foam as the catalyst support on shortening the reacting time (figure 2(a)). A peak section-average temperature of the reactants was observed at the same location, as more heat was absorbed and accumulated to push the reaction rightwards (figure 2(b)).

With the proceeding of the reaction, concentrations of the reactants and products were close to an approximate equilibrium, leading to difficulty of producing more hydrogen. As a result, the subsequent improvement of conversion rate became much slower. The section-average temperature dropped down quickly and increased gradually in the following reacting time.

Under a gauge pressure of 0.5 bar, the conversion rate of CH_4 was around 50%; while it was over 90% when the gauge pressure was improved to 1 bar. This indicated a positive effect of gas pressure on hydrogen production. The temperature of the reactants was improved in the process of reaction, since the supplied heat flux on the wall was bigger than the heat absorption and mass diffusion.

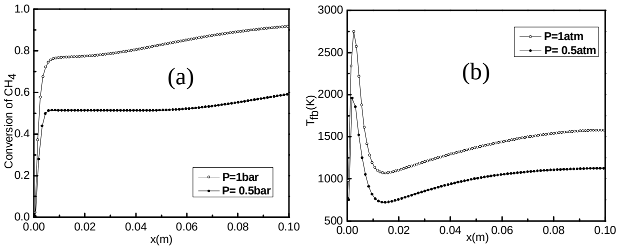

Figure 2. Characteristics of the SMR reaction in metal-foam filled reactor: (a) Conversion rate; (b) Section-average temperature

Parametric study

The influence of pressure at the entrance of the reactor was also shown in figure 2. It was shown that conversion of methane increased with the increase of inlet pressure. The reason was that both the concentration of methane and steam became bigger due to an increased pressure of the mixed gas. As a result, chemical equilibrium moved rightwards, resulting in a larger conversion of methane to hydrogen. The average temperature of fluid was higher when pressure at inlet was improved.

The influence of Re of the mixed reactants at the inlet of the reactor was demonstrated in Figure.3. The conversion rate of methane to hydrogen was found to increase in the case of reduced Re (figure 3 (a)). This was attributed to the shorter contacting time as the fluid velocity dropped with a decreased Re. It was highlighted that the average temperature with higher Re (e.g. Re=500) maintained an approximate value of the initial temperature of 773 K (figure 3 (b)). As a result, the endothermic reaction had a low conversion rate of less than 10%. This indicated the gas velocity need to be restrained for promoting the reaction of methane to hydrogen. However, Re should be larger than the minimum value to fulfil the assumptions of ideally flowing system due to the hypothesis of continuous reactions.

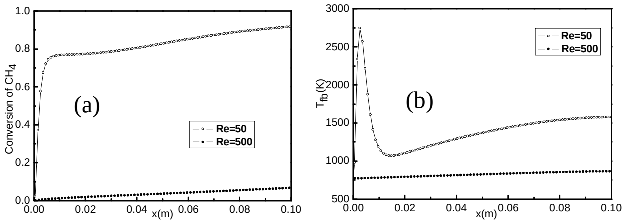

Figure 3. Effect of Re with the variation of gas velocity

The effect of Re could also be demonstrated by changing the value of the reactor radius. The continuous equation could be written as in equation (17):

$$\rho_f \cdot u \cdot \frac{\pi}{4} \cdot R^2 = C = const \tag{17}$$

Re was formulated as:

$$\mathrm{Re} = \frac{\rho_f \cdot u \cdot 2R}{\mu} = \frac{8C}{\pi \cdot \mu \cdot R} \tag{18}$$

Consequently, with the increase of the reactor radius, Re was reduced. As a result, the conversion rate and section-average temperature were enlarged, which was accordant with the analysis above (figure 4). It was noted that the improvement of the conversion rate was limited. This was because Re under both cases was still in a suitable range that had no negative influence on the reactive proceeding.

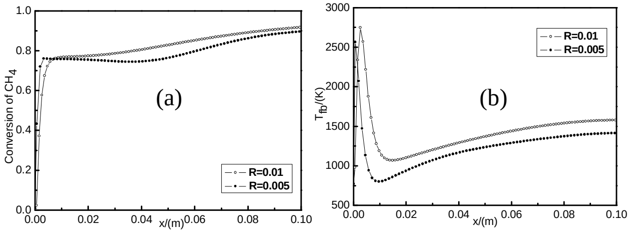

Figure 4. Effect of Re with the variation of reactor radius

The molar concentrations of the reactions have significant influence on the proceeding of the reaction. In the case under consideration, the amount of substance of methane was kept the same, while that of steam was changed under different cases. By changing the ratio of methane to steam from 1:1 to 1:2, the concentration of steam was increased, resulting in the rightward-move of the chemical equilibrium. Both the conversion rate of methane to hydrogen and the average temperature were improved (figure 5). It was pointed out that effect of ratio of reactions on the reaction was actually determined by the variations of concentration of each reactant before the reaction.

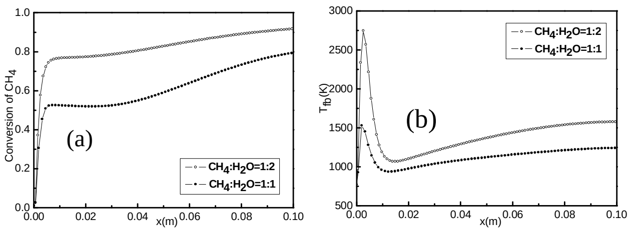

Figure 5. Effect of reactant concentrations

As mentioned above, SMR was significantly affected by the heat flux on the wall due to the endothermic characteristics of the reaction. By increasing the heat flux from 500 W/m^2 to 5000 W/m^2, the conversion rate of methane at the outlet of the reactor was improved from 50% to 90% (figure 6 (a)). The temperature of the reactants was not explicitly improved with a small heat flux on the wall (figure 6 (b)).

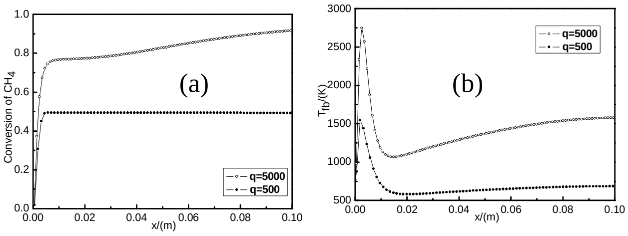

Figure 6. Effect of heat flux on the wall of the reactor

Improvement by Metal Foams

Because of the metal foams used as the catalyst support, the contacting surface area between the mixed reactants and the catalyst is largely increased. This positive effect of metal foams can be further promoted by optimizing the typical parameters of metal foams, such as porosity, pore density and relative thermal conductivity ratio.

The effects of porosity and pore density on the conversion rate of methane to hydrogen were shown in figure 7 (a) and (b), respectively. One could see that with increasing of porosity or decreasing of pore density, the conversion rate of methane to hydrogen was improved. It was explained that heat transfer performance became better in a reactor filled with metal foams that had a bigger cell size (d_p) and a smaller cell ligament diameter (d_f).

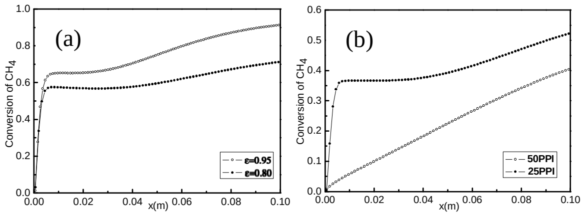

Figure 7. Improvement by metal foams: (a) Porosity and (b) Pore density

Conclusions

A chemistry and heat transfer model was established for simulating the steam reforming of methane in metal-foam filled reactor. The following conclusions were obtained:

(1) One-step chemical reaction was reasonable due to the use of catalyst and catalyst support (metal foams) for shortening the reacting time;
(2) The conversion rate increased sharply within the first 10% of the axial distance of the reactor due to the crucial promotion effect of catalyst and metal foams; A peak section-average temperature of the reactants was observed at the same location, due to the explosive heat absorption;
(3) Shifting of the chemical equilibrium was the criteria of affecting the conversion rate of methane. With increasing of inlet pressure, concentration of reactants and heat flux on the wall, or decreasing of Re of the flow in the reactor, the equilibrium moves rightwards, leading to an improved conversion rate;
(4) Open-cell metal foams used as the catalyst support play a positive role for improving the heat and mass transfer in the reactor. This effect can be promoted by using metal foams with bigger pore size (d_p) and smaller fibre diameter (d_f).

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