

Numerical Simulation on Methane Steam Reforming in Grille-sphere Composite Packed Bed with Axial Variable Diameter Configuration Particle

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Thermochemical energy storage is an important energy storage technology, which has become a focus of technology in recent years. The methane steam reforming reaction is a thermochemical energy storage reaction, and it is the main method for industrial hydrogen production. The methane steam reforming reaction is a strongly endothermic reaction. In the present study, the simulation of the methane steam reforming reaction in the reactors is commonly calculated. There are two main methods of simulation: macro-scale simulation and pore-scale simulation. Equivalent media model of macro-scale simulation is adopted. This method has advantages of less calculation time and highly accurate results. The structure of the packed bed has an important influence on the reaction performance. The grille-sphere composite packed bed has good reaction performance. The axially varying particle size in a single channel of the grid has the effect of improving the reaction performance. In this article, the equivalent medium model simulation was used to verify the performance advantage of the axially-varying particle in the whole grid- particle composite packing bed. This work has great significance in guiding industrial production.

1. Introduction

Thermochemical energy storage is one of the three major energy storage technologies. It is considered to have good application prospects in solar energy storage and high-temperature waste heat recovery. Thermochemical energy storage technology has advantages: wide temperature, high energy density and feasibility for energy storage and transport. Methane steam reforming reactions are strong endothermic reactions. There are five species participated in reactions, including methane (CH₄), hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂) and water vapour (H₂O). Methane steam reforming reactions are suitable for thermochemical energy storage because of the high calorific value of its production hydrogen. In Malaysia, people store the waste heat of palm combustion into hydrogen through the methane steam reforming. Methane steam reforming reactions have also been widely used to store solar energy. Lu et al. (2016) found that methane steam reforming in a packed bed reactor store high-temperature thermal energy efficiently. Yu et al. (2015) studied solar thermochemical energy storage in a packed bed reactor heated through experiments. Wang et al. (2014) produced hydrogen via methane steam reforming reactions using concentrated solar irradiation as a heat source.

Packed beds are widely used as chemical reactions reactor where the particles act as catalysts. In the reactor, There are fluid flow process, heat transfer process and mass transfer process accompanied by chemical reactions. The randomly packed bed is commonly used in industry because of its simple packing and low cost. In the methane steam reforming reactor, the packed bed is adapted to low tube-to-particle diameter ratio (N₀). However, this situation brings a significant wall effect which can lead to flow uneven and hotspot unpredictable. Recently many scholars have done many studies to reduce the wall effect in the randomly packed bed. According to Zobel et al. (2014), homogeneous void fraction distribution in the radial direction can improve the lateral dispersion and heat transport. The results showed that void fraction distribution depends on the wall structure. And wave-like orthogonal wall structure can bring a homogeneous void fraction distribution. Yang et

al. (2016) proposed a radially layered packing structure, which is composed of small particles in the close wall region and large particles in the central region. The new packing structure changes the porosity distribution along a radial direction and reduces the wall effect.

Many scholars have studied methane steam reforming reactions to improve the efficiency of the reactions. They put forward various methods of numerical simulation. There are two main methods of methane steam reforming numerical simulation: Macro-scale model simulation and pore-scale model simulation. In the macro-scale model simulation, many scholars have achieved many results recently. Mokheimer et al. (2014) used a two-dimensional axisymmetric homogeneous model to simulate the methane steam reforming reactions and studied the effect of different operating parameters on methane conversion. In order to study the performance of energy storage, Yuan et al. (2017) adapted macro-scale numerical simulation to simulate methane steam reforming reactions. The experiments have also been used to verify the accuracy of the simulation. The results point out that energy storage efficiency depends on both the operating parameters and the porosity of packed beds. In the pore-scale model, there are many results worth concentrating on. Kuroki et al. (2009) proposed a high-fidelity CFD method to verify this method can predict the distribution of species both microscopically and macroscopically. Behnam et al. (2012) used the solid particle method to investigate flow process, heat transfer process and mass transfer process along with chemical reaction in the methane steam reforming reactions. The macro-scale simulation is used in this article and the homogeneous model to simulate the reaction in a methane steam reforming reformer channel. The different conditioners are adapted to study the effect on the performance of reactions, and the new structures are proposed. There are four structures of the reactor in simulation for comparing the performance of reactions. And the new structures have good performance in simulation. The results of the simulation can guide industrial production.

2. Methodology

2.1 Physical model

The whole reactor can be treated as many channels combined in geometry. In order to reduce calculation time, only a representative channel of the whole packed bed is selected. According to Mokheimer et al. (2014) and Yuan et al. (2017), this method can be considered feasible. The diagram is shown in Figure. 1. There are four different structures in this study. These different structures have the same 76.8 mm stacking section. For different structures, they have the same square reactor pipe whose side length is 12.7 mm, and the different catalyst particle diameter. The inlet is set as velocity inlet, and the outlet is set to pressure outlet.

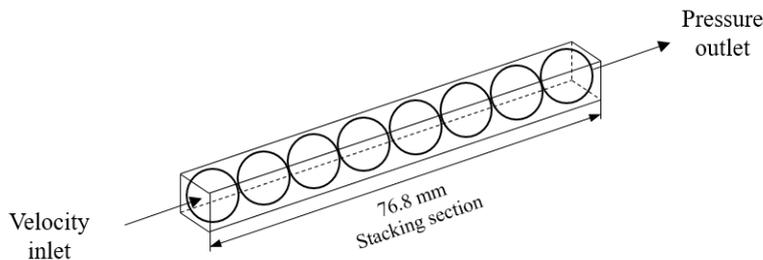


Figure 1: Diagram of the representative channel

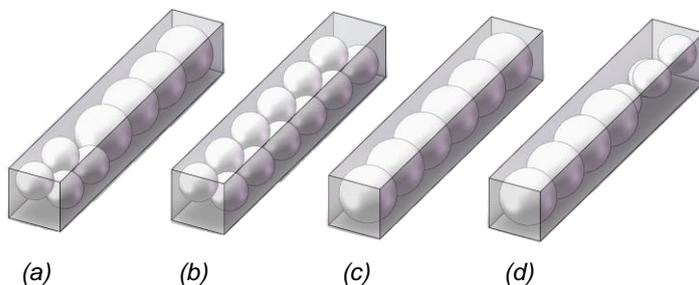


Figure 2: Diagram of four different structures: (a) S1 (b) S2 (c) S3 (d) S4

The different diameter catalyst particle is chosen for different N, which is the pipe-to-particle ratio. In the first structure (S1), there are four big particles and four small particles orderly packed in the stacking section, and

the N is mixed 1 and 1.5. In the second structure (S2), there are twelve small particles orderly packed, and the N is 1.5. In the third structure (S3), there are six big particles orderly packed, and the N is 1. In the fourth structure (S4), it has the same orderly packed particles as S1, but inlet and outlet are opposite to S1. The length of the stacking section is taken first structure as standard. S2, S3 are existing structures for study methane steam reforming. S1, S4 are new structures in this paper for study methane steam reforming. The four structures are shown in Figure. 2.

2.2 Governing equations and reaction kinetics

In a homogeneous model, particle packed area is regarded as a porous medium, and the grille area is treated as a solid area Mokheimer et al. (2014) used this model to simulation the methane steam reforming reactions. The model has been validated in the previous study, and the details are shown in Qian et al. (2019). The governing equations of the equivalent medium model are as follows.

Continuity equation:

$$\frac{\partial u_i}{\partial x_i} = 0 \quad (1)$$

Momentum equation:

$$\rho_f \frac{\partial u_i u_j}{\partial x_j} = -\frac{\partial p}{\partial x_j} + \frac{\partial}{\partial x_j} \left[\mu \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \right] + S_i \quad (2)$$

Where U_i represents velocity component, ρ_f represents the density of the fluid, μ is the dynamic viscosity of a fluid. The momentum source term is consists of viscous term and inertial terms, its expression is:

$$S_i = -\left(\frac{\mu}{\alpha} \mu_i + C_2 \frac{1}{2} \rho_f u_i^2 \right) \quad (3)$$

Where α represents permeability, C_2 represents inertial drag coefficient, ρ_f represents fluid density.

Energy equation:

$$\rho_f \frac{\partial u_i T}{\partial x_i} = \frac{\partial}{\partial x_j} \left(\frac{k_{\text{eff}}}{c_p} \frac{\partial T}{\partial x_j} \right) - \frac{\partial}{\partial x_j} \left(\sum_m h_m J_{mj} \right) + S_h \quad (4)$$

Where h_m represents formation standard enthalpy of substance m , J_{mj} represents substance m diffusion flux in direction j , k_{eff} represents thermal conductivity of porous medium area.

Mass equation:

$$\frac{\partial}{\partial x_j} (\rho_f u_j Y_m) = -\frac{\partial}{\partial x_j} (J_{mj}) + R_m \quad (5)$$

Where Y_m represents the quality score of substance m , R_m represents generation or consumption rate of substance m , J_{mj} represents substance m material flux in direction j .

Methane steam reforming reactions mainly include the following chemical equations: the kinetics model of Hou and Hughes (2001) is used, and the reactions occur on a nickel-alpha alumina (Ni/ α -Al₂O₃) catalyst. The reaction rate formulas are listed below, and parameters are taken from the original reference.

$$r_1 = \frac{k_1 \left(\frac{P_{\text{CH}_4} P_{\text{H}_2\text{O}}^{0.5}}{P_{\text{H}_2}^{1.25}} \right) \left(1 - \frac{P_{\text{CO}} P_{\text{H}_2}^3}{K_{\text{P}_2} P_{\text{CH}_4} P_{\text{H}_2\text{O}}} \right)}{\left(1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}} P_{\text{H}}^{0.5} + K_{\text{H}_2\text{O}} \left(P_{\text{H}_2\text{O}} / P_{\text{H}_2} \right) \right)^2} \quad (6)$$

$$r_2 = \frac{k_2 \left(\frac{P_{CO} P_{H_2O}^{0.5}}{P_{H_2}^{0.5}} \right) \left(1 - \frac{P_{CO} P_{H_2}}{K_{P2} P_{CO} P_{H_2O}} \right)}{\left(1 + K_{CO} P_{CO} + K_H P_H^{0.5} + K_{H_2O} \left(P_{H_2O} / P_{H_2} \right) \right)^2} \quad (7)$$

$$r_3 = \frac{k_2 \left(\frac{P_{CH_4} P_{H_2O}}{P_{H_2}^{1.75}} \right) \left(1 - \frac{P_{CO} P_{H_2}^4}{K_{P3} P_{CH_4} P_{H_2O}^2} \right)}{\left(1 + K_{CO} P_{CO} + K_H P_H^{0.5} + K_{H_2O} \left(P_{H_2O} / P_{H_2} \right) \right)^2} \quad (8)$$

Where r_1 , r_2 and r_3 are reaction rates of various reactions, k_1 , k_2 and k_3 are reaction rate constants of various reactions K_{P1} , K_{P2} and K_{P3} are equilibrium constants of various reactions, K_{CO} , K_H and K_{H_2O} are adsorption coefficients of various species, P_{CH_4} , P_{H_2} , P_{CO} , P_{CO_2} and P_{H_2O} are partial pressure of different species.

2.3 Boundary conditioners

This study simulates the methane steam reactions with the homogeneous model. There are two groups of cases adapted. The inlet velocity, inlet temperature, wall temperature, inlet CH_4 mass fraction and Inlet H_2 mass fraction are the mainly boundary conditioners. In the first group cases, the inlet velocity is taken as an independent variable, and the details of boundary conditioners are shown in Table 1. In the second group cases, the inlet temperature is taken as an independent variable, and the details of boundary conditioners are shown in Table 2. Four structures are compared in performance of the reactions.

Table 1: Simulation boundary conditioner of the first group of cases

Case	1	2	3	4
Inlet velocity (m/s)	1	1.5	2	2.5
Inlet temperature (K)	798			
Wall temperature (K)	798			
Inlet CH_4 mass fraction	0.220931			
Inlet H_2 mass fraction	0.034688			

Table 2: Simulation boundary conditioner of the second group of cases

Case	1	2	3	4
Inlet temperature (K)	798	850	900	950
Inlet velocity (m/s)	2			
Wall temperature (K)	798			
Inlet CH_4 mass fraction	0.220931			
Inlet H_2 mass fraction	0.034688			

3. Results and discussion

The outlet hydrogen mass fraction and outlet methane conversion are concentrated on. In the first group of cases, outlet hydrogen mass fraction and outlet methane conversion both increase with a temperature rising. The new structure S1 and previous structure S2 have the best performance. The S1 has an obvious improvement compared with other structures at the temperature of 950 K. The results are shown in Figure 3. In the second group of cases, the independent variable is inlet velocity. With the inlet velocity increasing, outlet hydrogen mass fraction and outlet methane conversion both decrease. The previous structure S2 has the best performance in four structures. The new structures S1, S4 have moderate performance. The results are shown in Figure 4. The outlet temperature increase with the inlet temperature is rising, and the outlet temperature decrease with the inlet velocity rising. The new structure S4 has the best performance in two groups of cases. The lower the outlet temperature is, the higher the heat absorption efficiency is. The new structure S1 has a different growth trend compared with others in the second group of cases. The results are shown in Figure 5.

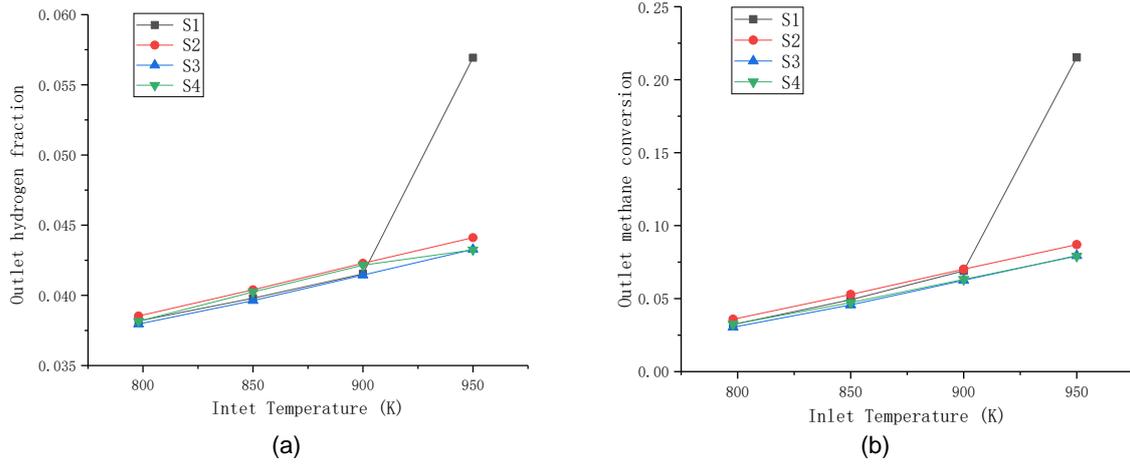


Figure 3: (a) Hydrogen mass fraction of outlet and (b) Methane conversion of outlet

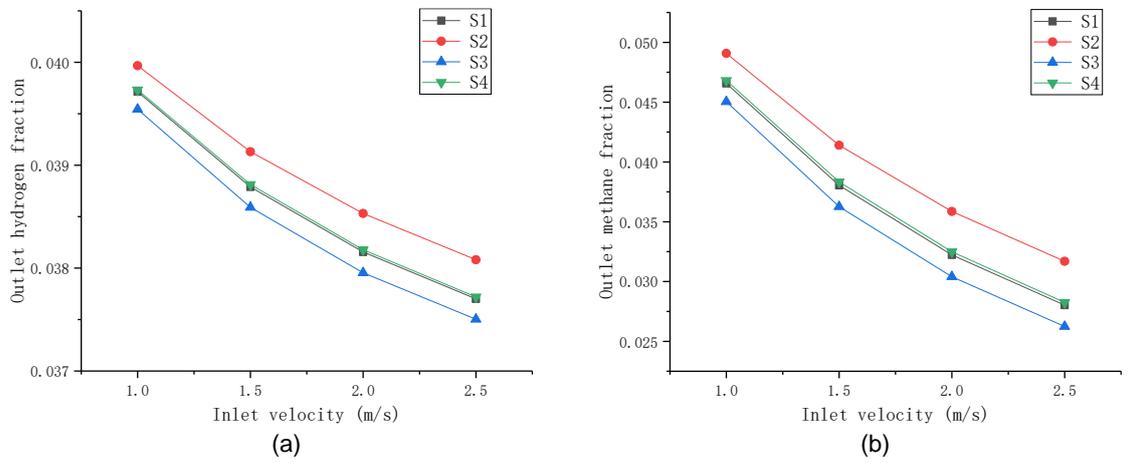


Figure 4: (a) Hydrogen mass fraction of outlet and (b) Methane conversion of outlet

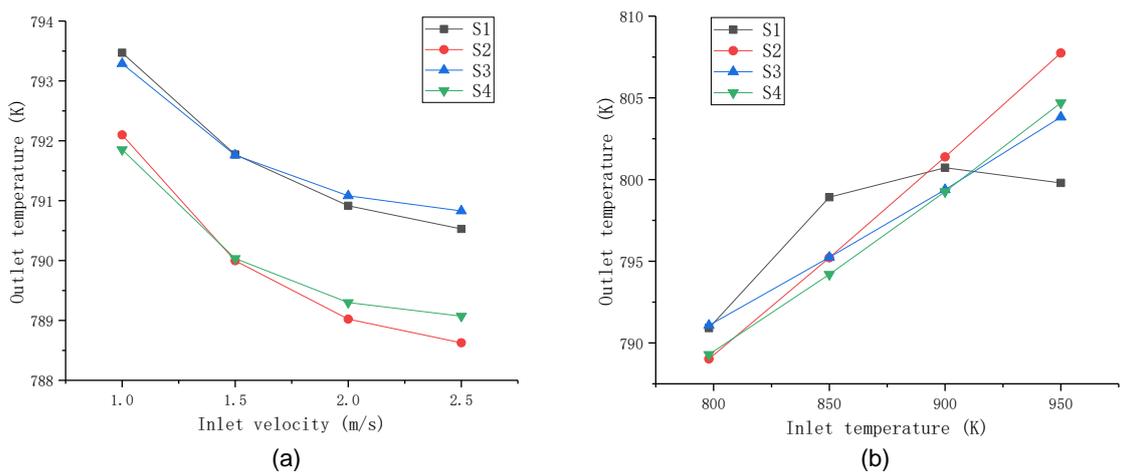


Figure 5: (a) Outlet temperature change with inlet velocity rising and (b) Outlet temperature change with inlet temperature rising

4. Conclusions

- (i) Outlet hydrogen mass fraction and outlet methane conversion both increase with the temperature rising.
- (ii) With the inlet velocity increasing, outlet hydrogen mass fraction and outlet methane conversion both decrease.
- (iii) The outlet temperature increase with the inlet temperature rising, and the outlet temperature decrease with the inlet velocity rising

The new structures can improve the efficiency of heat absorption. It can bring more benefit in the hydrogen industry.

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