

Parameter Analysis and Numerical Simulation of Hydrogen Production by Steam Reforming of Dimethyl Ether

Lei Guo*, Cong Li

School of Mechanical and Automotive Engineering, Shanghai University of Engineering Science, Shanghai, China

Email: *939889358@qq.com

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Abstract

Hydrogen production through dimethyl ether steam reforming is an attractive option for mobile applications of hydrogen fuel cells. Hydrogen is a major trend in the future of energy development. It is not only pollution-free, but also has a high energy density. Therefore, research on hydrogen fuel cells is particularly important. In this paper, a numerical research on dimethyl ether steam reforming reaction in a reactor has been presented using a computational fluid dynamics. A three-dimensional reactor model developed by the commercial software COMSOL (version 5.2a) was used to simulate the reaction characteristics by modifying reforming conditions. The simulation results indicate the temperature distribution, mass distribution, and reveal the dependency of dimethyl ether reforming reaction rate on temperature, pressure, the length of the reactor. The yield of H₂ and conversion of dimethyl ether with different mass ratios and inlet temperature (200°C, 300°C, 400°C, 500°C) were examined. The governing equations in the model include conservations of mass, momentum, energy and chemical species.

Keywords

Dimethyl Ether, Steam Reforming, Computational Fluid Dynamics Modeling, Simulation

1. Introduction

As a result of rapid consumption of non-renewable energy, hydrogen is a fuel that is regarded as having the most development potential for this century because of its clean, efficient, and renewable characteristics. As a new type of portable power supply, hydrogen is the ideal fuel for PEMFC [1] [2] [3]. Among the various hydrocarbon feeds, for the advantages of high energy density, non-toxicity,

easy availability, safe storage, dimethyl ether (DME) is considered to be one of the ideal sources of hydrogen for FCV [4].

Several studies on kinetic models of DME steam reforming and steam reforming (SR) reaction have been presented [5]. Feng *et al.* [6] presented a kinetic rate of total combustion of DME based on copper-based catalyst. Seunghyeon Choi *et al.* investigated the DME ATR reaction with different types of precious metal (Pt, Rh, Ru)-supported CGO catalysts [7]. Derek Creaser *et al.* developed a global kinetic model for the autothermal reforming of dimethyl ether (DME) over a Pd-Zn/Al₂O₃ catalyst on a cordierite monolith [8]. M.H. Akbari *et al.* presented a numerical investigation of catalytic autothermal reforming of methane in a surface microreactor [9]. Francis A. Elewuwa *et al.* presented a computational parametric analysis of DME steam reforming in a large scale Circulating Fluidized Bed (CFB) reactor [10] [11]. Chang-Feng Yan *et al.* designed a micro-reactor with catalyst coated on nickel foam support to enhance the heat and mass transfer during dimethyl ether (DME) steam reforming, and investigated the effect of Cr promoter on performance of steam reforming of dimethyl ether in a metal foammicro-reactor [12] [13]. Manoj Kumar Moharana developed an ethanol-based distributed hydrogen production device of the order of 1 kW using steam reforming of ethanol [14].

In this paper, a simpler kinetic equation was used to replace the previous complex kinetic equations to better describe and analyze the reaction mechanism of hydrogen production from dimethyl ether steam reforming, a three-dimensional SR reactor model was developed to investigate the influence of variation parameters on the performance of reactor. The effects of temperature of reactant gas, steam to DME ratio on the hydrogen production of outlet, DME conversion and average outlet temperature of reformer bed were analyzed.

2. Numerical Model

2.1. Model

The simulated reactor consists of following dimensions: catalytic bed, insulating jacket. There formation chemistry occurs in a catalytic bed, and the reactant gas flow through the inlet of the reactor. The reactor had a diameter of 30 mm and a length of 150 mm.

2.2. Model Assumptions

The reaction flow was assumed to be steady, laminar and incompressible. The gas mixture was supposed to be an ideal gas. The mixture consists of six species: DME, CO, H₂, CO₂ and H₂O. A three-dimensional model has been constructed end used in this analysis.

2.3. Governing Equations

The governing equations are set up on the basis of ideal gas mixture, including the conservations of mass, momentum, energy and chemical species.

The flow of gaseous species through the reformer bed is described by Darcy's Law [15]

$$\nabla \cdot \left(\rho \left(-\frac{\kappa}{\eta} \nabla p_{sr} \right) \right) = 0 \quad (1)$$

In the above equation, ρ denotes the gas density, η is the viscosity, κ is the permeability of the porous medium, and P_{sr} is the pressure in the reformer bed.

The equation [15] for the average temperature distribution in the porous bed is given by

$$Q = (\rho C_p)_t \frac{\partial T_{sr}}{\partial t} + \nabla \cdot (-k_{sr} \nabla T_{sr}) + (\rho C_p)_f u \cdot \nabla T_{sr} \quad (2)$$

The volumetric heat capacity of the bed is expressed as follows [15]

$$(\rho C_p)_t = \varepsilon (\rho C_p)_f + (1 - \varepsilon) (\rho C_p)_s \quad (3)$$

Here, the indices "f" and "s" denote fluid and solid phases, respectively, and ε is the volume fraction of the fluid phase. Furthermore, T_{sr} is the temperature and k_{sr} is the thermal dispersion of the reformer bed. Q represents a heat source, and u is the fluid velocity.

The mass-balance equations [15] for the model are the Maxwell-Stefan diffusion and convection equations at steady state as

$$R_i = \nabla \cdot \left(\rho \omega_i u - \rho \omega_i \sum_{j=1}^n \tilde{D}_{ij} \left(\nabla x_j + (x_j - \omega_j) \frac{\nabla p}{p} \right) - D_i^T \frac{\nabla T}{T} \right) \quad (4)$$

In the equation above, ρ denotes the density, ω_i is the mass fraction of species i , x_j is the molar fraction of species j , D_{ij} is the ij component of the multicomponent Fick diffusivity. D_i denotes the generalized thermal diffusion coefficient, T is the temperature, and R_i is the reaction rate.

2.4. Chemical Kinetics

Steam reforming of DME involves many reactions with different rates, in this paper, following reactions are analyzed:

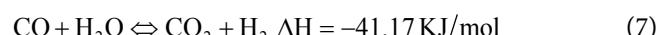
DME hydrolysis



MeOH steam reforming



Water gas shift



In this paper, the kinetic models of total DME reforming reactions used in this study are given as follows

1) Dimethyl ether hydrolysis into methanol

$$R_1 = \frac{k y_{\text{DME}} y_{\text{H}_2\text{O}}}{\left(1 + K_{\text{H}_2\text{O}} y_{\text{H}_2\text{O}} \right)^2} \quad (8)$$

where, y was the mole fraction, k was the rate constant.

2) Methanol steam reforming reaction

$$R_2 = (1 - \varepsilon) \rho_s k_R C_{\text{CH}_3\text{OH}} \quad (9)$$

where, ρ_s was catalyst density, k_R was the reforming rate constant, $C_{\text{CH}_3\text{OH}}$ was the molar concentration of methanol, ε was porosity.

3) Water-gas shift

$$R_4 = C_{\text{WGS}} k_{\text{WGS}} \left(p_{\text{CO}} p_{\text{H}_2\text{O}} - p_{\text{CO}_2} p_{\text{H}_2} / K_{eq} \right) \quad (10)$$

where, k_{WGS} and K_{eq} were the rate constant and the equilibrium constant of the WGS reaction.

For the reaction of DME hydrolysis, the rate constant K can be calculated by Arrhenius equation as follows.

$$K = A e^{-\frac{E}{RT}} \quad (11)$$

To avoid correlation between the pre-exponential factors and activation energies of the Arrhenius equation, the rate constant k at an average temperature T of 300°C and the activation energy were used as fitting parameters. Thus, for parameter fitting purposes, the Arrhenius equation was reformulated, equation is as follows

$$k_1 = k_{m1} \left(\frac{E_{A1}}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) \right) \quad (12)$$

The calculation of A is given by

$$A = \frac{k_{m1}}{\frac{E_{A1}}{R} e^{\frac{E_{A1}}{RT}}} \quad (13)$$

The formula of adsorption equilibrium constant is as follows

$$K_j = K_{mj} \exp \left(\frac{\Delta H_{\text{adj}}}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) \right) \quad (14)$$

where Δ'_{jk} is adsorption enthalpy, K_{mj} was the adsorption equilibrium constant at the average temperature.

2.5. Boundary Conditions

The inlet and outlet boundary conditions describe a pressure drop across the bed. All other boundaries are impervious, corresponding to the condition [15]

$$-\frac{\kappa}{\eta} \nabla p_{sr} \cdot n = 0 \quad (15)$$

Convective heat transport at the outlet is assumed to be dominant [15]

$$n \cdot (k_{sr} \nabla T_{sr}) = 0 \quad (16)$$

At the outlet, the convective flux condition is used [15]:

$$n \cdot \left(\left(-\rho \omega_i \sum_{j=1}^n D_{ij} \left(\nabla x_j + (x_j - \omega_j) \frac{\nabla p}{p} \right) \right) - D^r \frac{\nabla T}{T} \right) = 0 \quad (17)$$

3. Solution Method

In order to solve the non-linear equations, a computational fluid dynamics (CFD) code was developed based on the finite volume method using the SIMPLE algorithm for the coupling of pressure and velocity domains. As is shown in **Figure 1**, the simulated fluidized porous zone is 0.15 m in length and 0.033 m in radius. The shell is 0.003 m in thickness. The maximum element size is 0.015 m, and minimum element size is 0.0075 m.

4. Results and Discussion

4.1. Experiment and Validation

To verify the availability of the simulation model, an experiment for DME auto-thermal reforming was set up. The system was shown in **Figure 2**, the water measured by the metering pump is fully vaporized in the evaporator, and the air, DME and water were preheated to 500 degrees. Then, the mixed gas flowed into the reactor through a mass flow controller, and the reactor was filled with a CuO/ZnO/Al₂O₃ + ZSM5 catalyst. Finally, the reactants and products flowed into gas chromatography (GC-9900) linked to a computer so as to measure components.

The most important performance indexes of dimethyl ether reforming reaction mainly include dimethylether conversion rate, production rate of hydrogen. The DME conversion and the hydrogen yield are defined as follows

$$\text{DME conversion: } X_{\text{DME}} = \frac{F_{\text{DME,in}} - F_{\text{DME,out}}}{F_{\text{DME,in}}} \times 100\% \quad (18)$$

$$\text{Hydrogen production: } Y = \frac{F_i}{F_0 \cdot v_i} \quad (19)$$

Compared to the experimental reactor, the performance of the reactor used in the simulation is analyzed. The operating conditions are equal to those of simulations. The ratio of steam to DME varied from 1 to 4, the inlet temperature was 773 K. The DME conversion and volume content of H₂ were shown in **Table 1** and **Table 2** respectively. The result of the experiment was approximate to the

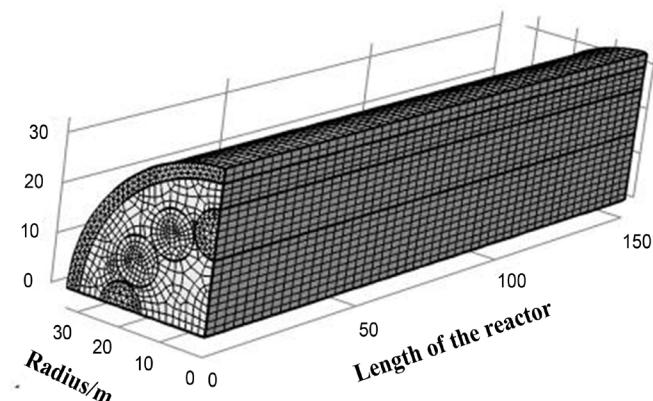
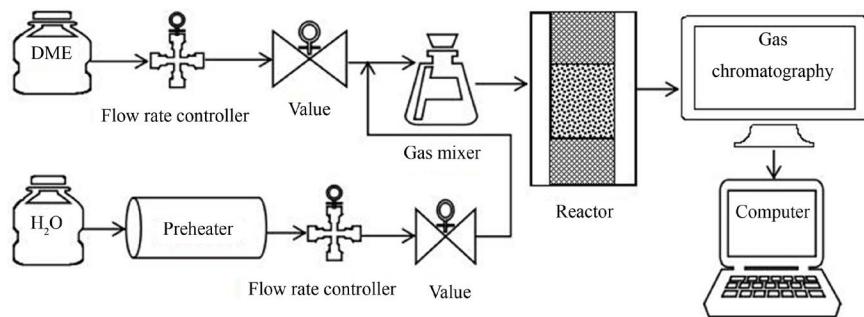


Figure 1. Geometry and mesh size of the reactor.

**Figure 2.** Schematic diagram of experimental.**Table 1.** Comparison of experimental and simulated values of DME conversion.

	DME conversion Steam:DME = 0.5:0.5	DME conversion Steam:DME = 0.75:0.25	DME conversion Steam:DME = 0.8:0.2
Simulated data	18.27%	42.88%	54.79%
Experimental data	17.28%	41.53%	53.18%

Table 2. Comparison of experimental and simulated values of H₂ production.

	H ₂ production Steam:DME = 0.5:0.5	H ₂ production Steam:DME = 0.75:0.25	H ₂ production Steam:DME = 0.8:0.2
Simulated data	17.22%	42.74%	52.41%
Experimental data	16.34%	41.21%	51.68%

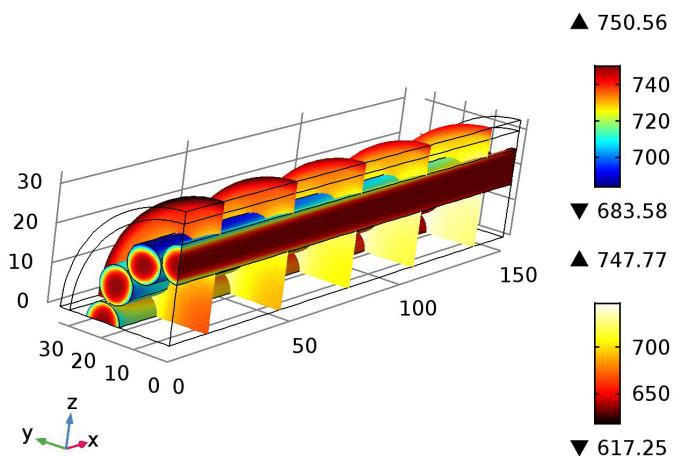
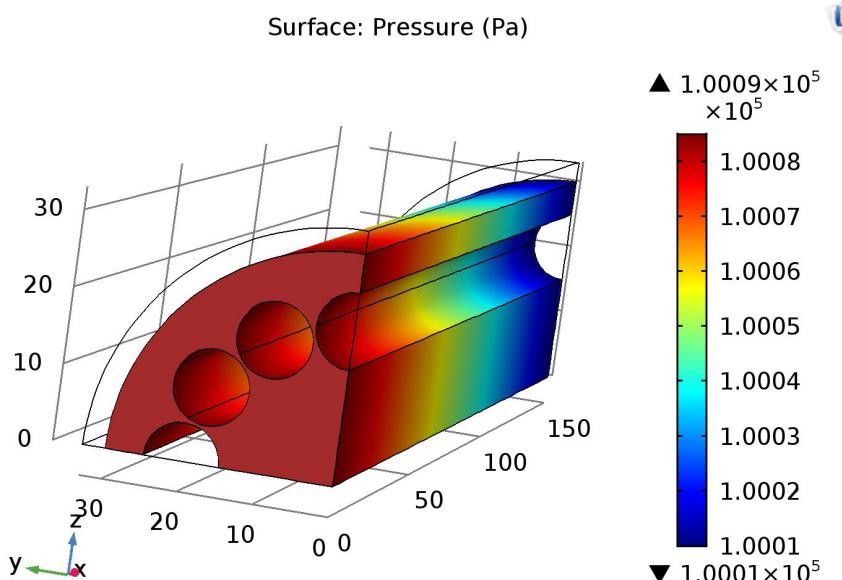
result of simulation, the lower hydrogen production of experiment was probably due to hydrogen spillover or hydrogen leak. The experiment temperature was lower than the theoretical value may be caused by the incomplete adiabatic, and the wall heat dissipation. The comparison between the data collected by the experiment and the simulation results verified that the present simulation can describe the reforming reaction in details.

4.2. Study of Parameters

In this section, the influence of parameters including H₂O/DME molar ratio, the inlet temperature of mixture gas on the reaction rate has been analyzed. The simulation results indicate the temperature distribution of the reactor, DME conversion and hydrogen production of the reforming reaction. The simulation conditions were as follows: the ratio of steam to DME is 3, **Figure 3** was the temperature distribution of the reactor. The inlet mixture gas temperature of the reformer bed was 750 K, and decreases along the reaction bed because of the endothermic hydrolysis reaction, finally, the average outlet temperature of reformer bed was 683 K.

The pressure distribution in the reforming reactor is shown in **Figure 4**. The pressure at the inlet of the reactant is 1.0009×10^5 Pa, and the pressure at the outlet is 1.0001×10^5 Pa. After calculation, the pressure drop loss during the

Surface: Temperature (K) Slice: Temperature (K)

**Figure 3.** The temperature distribution of the reactor.**Figure 4.** The pressure distribution of the reforming reactor.

reaction is $8 \times 10 - 4$ Pa, which is much lower than 10% of the pressure drop in the reforming reactor. Since the pressure drop within the system is very low, it is feasible to assume that the gas is ideally incompressible at the beginning of the model establishment.

4.3. Effects of Temperature

Figure 5(a) and **Figure 5(b)** are simulations performed under the reaction conditions of a water ether molar ratio of 0.75:0.25, a heat pipe inlet flow rate of 10 m/s, and a standard atmospheric pressure, indicating dimethyl ether. The variation of conversion rate and hydrogen yield at different inlet temperatures. The varying temperature values were 573 K, 623 K, and 673 K, respectively. As can be

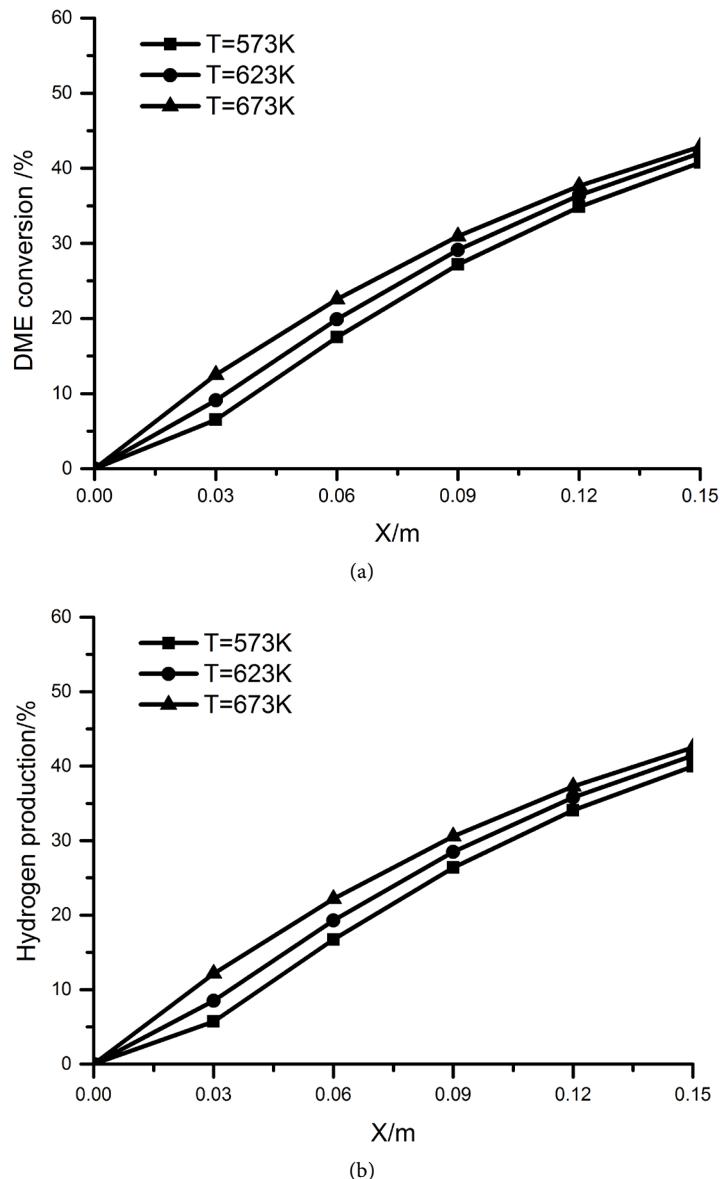


Figure 5. DME conversion and Hydrogen production as a function of heat tubes inlet temperature along the axial length: (a) DME conversion (b) Hydrogen production.

seen from **Figures 3-5**, as the temperature at the inlet of the reactor increases, the conversion of dimethyl ether and the yield of hydrogen are significantly improved. This is due to the hydrogen production of dimethyl ether by steam reforming. Generally, it is an endothermic reaction. Appropriately increasing the inlet temperature is beneficial to increase the forward reaction rate of the reaction, and the reaction proceeds toward the direction of hydrogen production, thereby improving the conversion efficiency of dimethyl ether and the yield of hydrogen.

The water ether molar ratio is a major operating parameter that affects the hydrogen production of dimethyl ether by steam reforming. **Figure 6(a)** and **Figure 6(b)** are simulated simulations of the heat pipe inlet flow rate of 10 m/s,

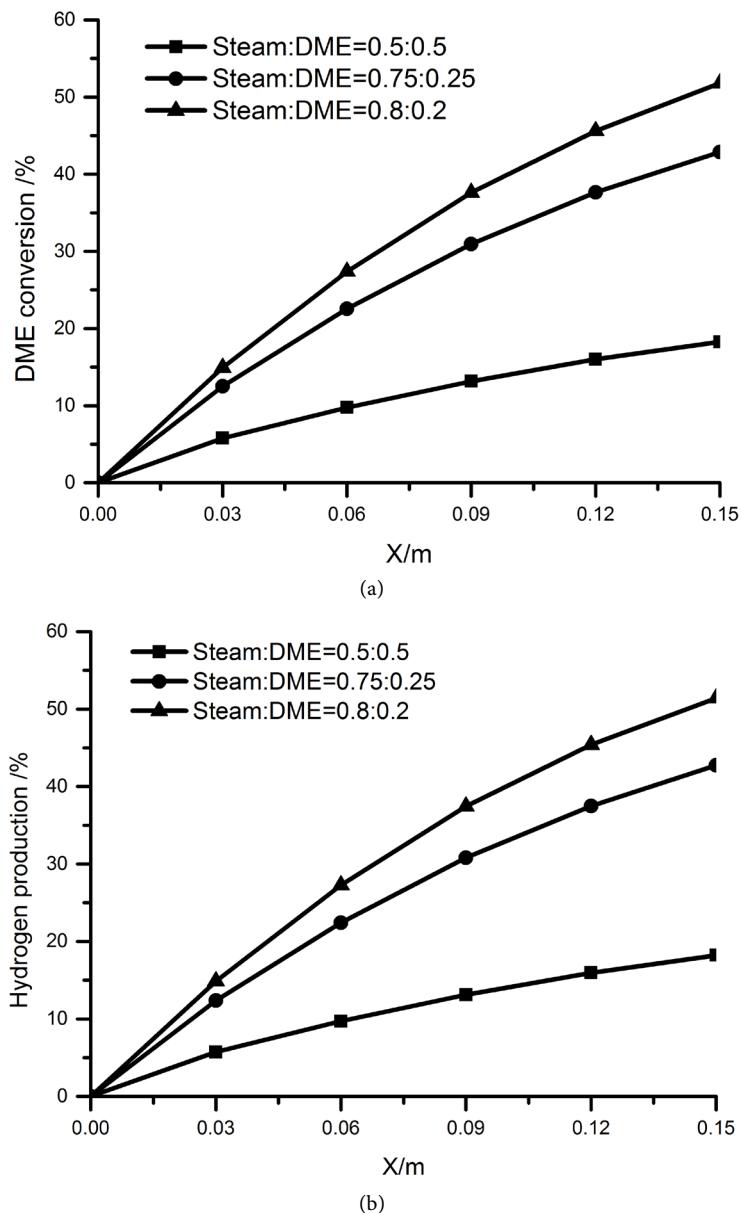


Figure 6. DME conversion and Hydrogen production as a function of steam to DME ratio (a) DME conversion (b) Hydrogen production.

reforming reaction bed temperature of 673 K, a standard atmospheric pressure, showing dimethyl ether conversion and hydrogen. The variation of the yield under different water ether molar ratios (1, 2, 4). It can be clearly seen from the figure that appropriately increasing the ratio of the molar mass of water vapor to dimethyl ether is advantageous for improving the hydrogen production efficiency of the reformer and increasing the conversion rate of dimethyl ether. However, from the principle of chemical reaction, the molar ratio of water ether is not as large as possible. As the molar mass of water vapor increases, the temperature in the reactor will also decrease, because the entire reforming reaction is endothermic. Therefore, there is a great influence on the reaction rate of the

positive reaction, which in turn affects the conversion of dimethyl ether and the hydrogen yield.

5. Conclusions

In this study, catalytic steam reforming of DME is simulated using a three-dimensional CFD model. The simulation model introduced in software COMSOL (version 5.2a) can reveal the temperature distributions in the reactor and the hydrogen production and DME conversion properly. On the basis of the model, we investigated the DME SR reaction on different temperatures, various ratios of steam to DME.

The model can accurately describe the reaction mechanism of hydrogen production from dimethyl ether steam reforming. At the same time, the established reaction kinetic equation is simple, but from the simulation results, the dimethyl ether obtained by using this kinetic equation can be seen. Ether conversion and hydrogen yield are relatively low. Therefore, on the basis of the simplicity of the kinetic equation, how to improve the reaction efficiency is the place to be studied in the follow-up work.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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