A High-Fidelity CFD Model of Methane Steam Reforming in a Packed Bed Reactor

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A novel high-fidelity CFD model is proposed for the process optimization and intensification of methane steam reforming in a packed bed reactor. The random packing of spherical particles is constituted by simulating a dumping of particles into the annular reactor by a commercial code based on discrete element method (DEM). The complex spatial geometry between hundreds of particles is created associated with a developed interparticle bridge method, which eliminates the interparticle and particle-wall contact regions by assuming that the small gaps between the particles are stagnant and would not affect the reactor behavior. The conservation equations of mass, momentum, energy and chemical species are fully solved by employing a commercial CFD code based on finite volume method. A newly coded subroutine is incorporated into the CFD code to evaluate the reaction rates according to the species partial pressures and temperature on each surface cell covering the particles. The values of reaction, equilibrium and adsorption constants are specified based on the experiments in the literature. According to the reaction rates, the mass and heat sources are given to each fluid cell on the surface cell. It is verified that the developed CFD model is capable of predicting the distributions of species and temperature microscopically as well as macroscopically for methane steam reforming. The present DEM–CFD procedure enables one to investigate the behavior of packed bed reactor in detail once the catalyst is characterized in a conventional way. Therefore it would become a powerful tool to optimize and intensify any process in a packed bed reactor where the plug flow assumption is invalid.

Introduction

A packed bed with a low tube-to-particle diameter ratio is often employed for methane steam reforming (MSR) that is highly endothermic and hence requires a large heat flux (Dixon et al., 2003). In the reactor the gas temperature may consequently vary within a catalyst scale. The invalidity of plug flow assumption is also implied by a discrepancy of Ergun equation in predicting a pressure loss in the narrow bed (Eisfeld and Schnitzlein, 2001). In optimizing such a reactor, a conventional analytical or numerical approach assuming a uniform porous medium encounters a difficulty in evaluating the reaction rate since it would considerably vary over the particle due to temperature and velocity variation as well as resultant species distribution. In addition, the approach might be insufficient to optimize a blending manner of adsorbent in a sorption-enhanced reactor (Xiu et al., 2003) without additional modeling of species transport induced by the additives.

A recent high-fidelity CFD model for the packed bed, whose computational domain consists of connecting spaces between many particles each shaped without geometrical simplification, is apparently a potential tool for the given purposes. The previous hi-fi models were able to contain only tens of spheres in a short tube (Nijemeisland and Dixon, 2004; Guardo et al., 2006). The particles were packed regularly or irregularly in the tube so that they were strictly in contact. To avoid the generation of extremely fine or skew mesh around the contact point, the contact point itself was eliminated by expanding or shrinking the particles after the particle arrangement. However, the fine mesh is still necessary to fill the gaps between the particles created by the shrinkage or the spaces around the overlapped face generated by the expansion. The necessity of fine mesh in those regions may limit the number of particles and the treatment methods for the contact point may prevent the truly irregular bed from being constituted numerically. Since the scale of simulation and the reality of packing structure are important factors for the practical application, the hi-fi CFD model should be improved regarding these issues.

Further, it is desired to fully solve the flow of mass, momentum and heat around the particles with the catalytic reactions for predicting the distribution of species and temperature in the bed as well as the macroscopic reactor behavior. To the authors’ knowledge, however, the degree of coupling or the scale of simulation is still limited. Dixon et al. (2003) coupled heat transfer with gas flow by giving a heat flux on particles according to reac-
tion rates in the literature. Freund et al. (2003) solved first flow field and subsequently mass transport with a simple reaction by fixing the flow field. Recently, Dixon et al. (2007) performed a fully coupled simulation with intraparticle MSR reactions in the 120° wall segment model consisting of 8 spheres within 2 layers.

Provided that MSR reactions are modeled as surface reactions, as experienced in this study, it seems that the difficulties of complete coupling arise from the contact regions, where the flow of heat tends to be stagnant leading to poor convergence in case.

For the process optimization and intensification, in this study, the reaction model of MSR is incorporated into a hi-fi CFD model, associated with an interparticle-bridge method (Ookawara et al., 2007). The novel CFD model resolves the above difficulties since it can fully solve the flow of mass, momentum and heat with the reactions around hundreds of particles randomly packed in a reactor by excluding the contact regions. For the model validation, the predicted species fractions are compared with the experiments (Hoang et al., 2005).

1. Numerical Methods

1.1 DEM simulation

A packed bed is practically constituted by dumping particles into a reactor. The reactor for catalyst characterization is often an annular tube, in whose inner pipe a thermocouple is installed. In this study, the dumping procedure is simulated by discrete element method (DEM). Theuerkauf et al. (2006) reported that DEM provided a tool with which radial porosity distributions to any tube to particle diameter ratio can be calculated. It was shown that overall porosity as well as radial porosity distributions predicted by DEM was in reasonable agreement with experimental results. In this study, therefore, a commercial DEM code EDEM1 (DEM Solutions Ltd., 2007) is employed for constituting the packing. In the simulation, the particle diameter is identical with that of spherical catalyst (1.75 mm) utilized in the experiments (Hoang et al., 2005). The properties of density, shear modulus, Poisson’s ratio and restitution coefficient of typical glasses are specified so that the magnitudes are realistic. The coefficients of static and rolling frictions are the values to attain an appropriate overall porosity in a pipe with a low tube-to-particle diameter ratio (Ookawara et al., 2007). It is expected that a packing with appropriate porosity distribution can be constituted by controlling the overall porosity even in an annular tube owing to the capability of DEM. The annular with same material properties is defined in the direction of gravity (9.8 m/s²). The inner and outer diameters are defined as 2 and 10 mm that are identical with those of the reactor in the literature (Hoang et al., 2005). The annular height is defined as 50 mm.

The spherical particles are randomly generated in the annular with a downward initial velocity of 0.1 m/s. The 550 of particles are generated over the domain in 2 s at a constant rate. The particles freely fall with interparticle and particle-to-wall collisions under the gravity. The particle motion and collisions are simulated based on Hertz–Mindlin model (Mindlin, 1949) at a time interval of 1.5 × 10⁻⁷ s. The velocities of all the particles are monitored and the simulation is terminated when the maximum velocity sufficiently becomes small. Figure 1 shows a series of snapshots of the DEM simulation. It can be seen that the damping into the annular is well simulated. It is confirmed that the maximum particle velocity becomes a value less than 10⁻⁸ m/s at 2.5 s and it remains constant afterward, i.e., the packing is completed and stable. Subsequently, all the center coordinates of the particles are retrieved at the time.

1.2 Geometry and mesh generation

The coordinates are sorted according to y-coordinates and the lower 349 particles are selected so that the bed height becomes 25 mm. Based on the coordinates, the 349 of spherical elements are shaped by a mesh generator GAMBIT2 (Ansys Inc., 2006).

Figure 2 depicts the geometry and mesh of packed bed model. The packing is placed at the middle of the annular with a height of 65 mm. The particles in contact or near contact are cylindrically bridged so that the cylinder axis lies on the line connecting the particle centers. The contact zones between the particle and the inner/outer wall of the annular are similarly treated. In this interparticle bridge method, it is assumed that the bridging zone is sufficiently negligible within the stagnant region, which was experimentally and numerically observed near the contact point in a regular packing (Suekane et al., 2003; Gunjal et al., 2005). The bridging makes a giant volumetric element. The CFD domain is then created by subtracting the giant element from a pillar element. The triangular surface mesh is first created on the side wall of the bridge. The particle surface is subsequently covered by the triangular mesh. The tetrahedral volume mesh is finally generated from these surface meshes. The adopted mesh density is determined to attain the sufficient accuracy based on our previous study (Kuroki et al., 2007).
1.3 Governing equations for CFD simulation

The conservation equations for mass, momentum, energy and chemical species are fully solved by employing a CFD code FLUENT6 (Ansys Inc., 2006), which is based on finite volume method. The conditions of steady, laminar and no interphase-mass-transfer reduce the governing equations as follows. The gravity effect is not considered in the simulations.

**Conservation of mass:**

\[ \nabla \cdot (\rho \bar{\nabla}) = 0 \]  
(1)

**Conservation of momentum:**

\[ \nabla \cdot (\rho \bar{v} \bar{u}) = - \nabla p + \nabla \cdot (\bar{\tau}) \]  
(2)

The stress tensor is;

\[ \bar{\tau} = \mu \left[ \left( \nabla \bar{\nabla} + \nabla \bar{\nabla}^T \right) - (2/3) \nabla \cdot \bar{v} I \right] \]  
(3)

where \( \mu \) is the molecular viscosity, \( I \) is the unit tensor.

**Conservation of energy:**

\[ \nabla \cdot (\bar{\nabla} (\rho E + p)) = \nabla \cdot \left[ k \nabla T - \sum_i h_i \bar{J}_i + (\bar{\tau} \cdot \bar{v}) \right] + S_h \]  
(4)

where \( k \) is the conductivity, \( \bar{J}_i \) is the diffusion flux of species \( i \), \( S_h \) is the heat of chemical reaction. In Eq. (4),

\[ E = \sum_i Y_i h_i + \frac{v^2}{2} \]  
(5)

where \( Y_i \) is the mass fraction of species \( i \). The sensible enthalpy \( h_i \) is;

\[ h_i = \int_{T_{ref}}^{T} c_{p,i} dT \]  
(6)

where \( c_{p,i} \) is the specific heat capacity defined as a polynomial function of the temperature, \( T_{ref} \) is 298.15 K. The diffusion flux, which arises due to concentration gradients, is expressed as;

\[ \bar{J}_i = -\rho D_{i,m} \nabla Y_i \]  
(7)

where \( D_{i,m} \) is the diffusion coefficient for species \( i \) in the mixture evaluated based on the binary mass diffusion coefficient \( D_{ij} \) of component \( i \) in component \( j \) as;

\[ D_{i,m} = (1 - X_i) / \sum_{j \neq i} (X_j / D_{ij}) \]  
(8)

The \( X_i \) is the mole fraction of species \( i \). The \( S_h \) is the source of energy due to chemical reactions.

\[ S_h = -\sum_i \left( h_i^0 R_i / M_i \right) \]  
(9)

where \( h_i^0 \) is the enthalpy of formation of species \( i \) and \( R_i \) is the volumetric rate of creation of species \( i \).

**Equation of state:**

The density is calculated based on the incompressible ideal gas law as

\[ \rho = \frac{p_{op}}{(RT/M_w)} \]  
(12)

where \( R \) is the universal gas constant, \( M_w \) is the molecular weight of the gas, \( p_{op} \) is the operating pressure specified as 150 kPa in this study.

1.4 Material properties

The mixture thermal conductivity and viscosity are

\[ k = \sum_i \sum_j X_i k_{ij}, \mu = \sum_i \sum_j X_i \mu_{ij} \]  
(13)

where

\[ \phi_{ij} = \left[ \frac{1}{8} \left( \frac{\mu_i}{\mu_j} \right)^{1/2} \left( \frac{M_{w,j}}{M_{w,i}} \right)^{1/4} \right]^2 \]  
(14)

The thermal conductivity \( k_i \) of species \( i \) is;

\[ k_i = \frac{15}{4} \frac{R}{M_{w,i}} \frac{\mu_i}{\mu} \left[ \frac{4}{15} \frac{c_{v,i} M_{w,i}}{R} \right] + \frac{1}{3} \]  
(15)

The molecular viscosity \( \mu_i \) of species \( i \) is;

\[ \mu_i = 2.67 \times 10^{-6} \sqrt{M_{w,i} T / \left( \sigma_{\mu,i}^2 \Omega_{\mu,i} \right)} \]  
(16)
where the collision integral for viscosity $\Omega_{\text{li,j}}$ is the function of reduced temperature $T^*$.  

$$T^* = T / (e / k_B)$$

(17)

The $\sigma_i$ and $(e / k_B)$ are the Lennard–Jones parameters for species $i$. The binary mass diffusion coefficient is:

$$D_{ij} = 0.00188 \left[ T^3 \left( \frac{M_{w,i}^{-1} + M_{w,j}^{-1}}{M_{w,i}} \right) \right]^{1/2} / \rho \sigma_{ij}^2 \Omega_D$$

(18)

where the diffusion collision integral $\Omega_D$ is the function of the dimensionless temperature $T_D^*$:

$$T_D^* = T / (e / k_B)_{ij}$$

(19)

where

$$(e / k_B)_{ij} = \sqrt{(e / k_B)_i (e / k_B)_j}, \sigma_{ij} = (\sigma_i + \sigma_j) / 2$$

(20)

1.5 Reaction model for methane steam reforming

In this study modeled is a part of reaction zone in the packed bed reactor utilized for the characterization of sulfide nickel catalyst (Hoang et al., 2005). It is assumed that the influences of bed beyond and below the modeled packing are negligible. The surface reactions 1 to 3 below are to be considered on the catalyst (Xu and Froment, 1989; Hoang et al., 2005).

**Reaction 1**: $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$

**Reaction 2**: $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$

**Reaction 3**: $\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$

The reactions 1 and 3 are strongly endothermic ($\Delta H_{298} = 206.1$ kJ/mol and $165.0$ kJ/mol) while the reaction 2 is slightly exothermic ($\Delta H_{298} = -41.15$ kJ/mol). The rate expressions $R_1$ to $R_3$ for the reactions 1 to 3 are expressed by Eqs. (21) to (24), where the rate constants $k_j (j = 1–3)$, equilibrium constants $K_{eqj} (j = 1–3)$ and adsorption constants $K_i$ ($i = \text{CH}_4, \text{H}_2\text{O}, \text{CO}, \text{H}_2$) are the functions of temperature (Hoang et al., 2005). This reaction kinetics with the rate expressions is widely accepted in the literature (Ding and Alpay, 2000; Xiu et al., 2003) and hence it is adopted in this study.

$$R_1 = \frac{k_1}{p_{\text{H}_2}^{2.5}} \left( p_{\text{CH}_4} p_{\text{H}_2\text{O}} - \frac{p^3_{\text{H}_2} p_{\text{CO}}}{K_{\text{eq1}}} \right) \times \frac{1}{\text{DEN}^2}$$

(21)

$$R_2 = \frac{k_2}{p_{\text{H}_2}} \left( p_{\text{CO}} p_{\text{H}_2\text{O}} - \frac{p_{\text{H}_2}^4 p_{\text{CO}_2}}{K_{\text{eq2}}} \right) \times \frac{1}{\text{DEN}^2}$$

(22)

$$R_3 = \frac{k_3}{p_{\text{H}_2}^{3.5}} \left( p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2 - \frac{p^4_{\text{H}_2} p_{\text{CO}_2}}{K_{\text{eq3}}} \right) \times \frac{1}{\text{DEN}^2}$$

(23)

$$\text{DEN} = 1 + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{H}_2} p_{\text{H}_2} + K_{\text{CH}_4} p_{\text{CH}_4}$$

$$+ K_{\text{H}_2\text{O} p_{\text{H}_2} / p_{\text{H}_2}}$$

(24)

For the rate constants, the values were given in the unit of [mol/(kg-cat-s)] (Hoang et al., 2005). Since the weight of used catalyst is known, the molar rates of creation/destruction over the whole reactor can be evaluated in the unit of [mol/s] by multiplying the weight with the original rate constants. In this study, the rate over the reactor is divided by the sum of catalyst surface area, which can be estimated from the particle diameter and the voidage. The unit for the re-defined rate constants then becomes [mol/(m$^2$-s)], i.e., the reaction rates can be expressed in terms of the molar flux through the particle surface. The newly defined constants $k_{oj}$ [mol/(m$^2$-s)] in Eq. (25) are $1.02 \times 10^{11}$ Pa$^{0.5}$, $1.93 \times 10^{-3}$ Pa$^{-1}$, and $2.41 \times 10^8$ Pa$^{-0.5}$ for reactions 1, 2 and 3, respectively.

$$k_j = k_{oj} \times e^{-E_j / RT}$$

(25)

A user defined subroutine is newly developed to evaluate the reaction rates $R_1$ to $R_3$ based on the partial pressures and temperature on each surface cell covering particles. According to the reaction rates, mass and heat sources are given to each fluid cell on the surface cell by Eqs. (9) and (10).

1.6 Numerical conditions

As an initial inlet boundary condition, a velocity of gas mixture is specified so that the molar flow rates of methane and water become 0.00250 mol/s and 0.00875 mol/s, which are identical with the values in the experiments (Hoang et al., 2005). The three operational temperatures of 773, 973 and 1073 K are examined in this study. The particle $Re$ numbers at the inlet become around 300 for all the conditions and the $Re$ decreases along the reactor length. The reactor is in a laminar regime and the adopted mesh density is sufficient for predicting the transport phenomena in the given $Re$ conditions (Kuroki et al., 2007). The operational temperature values are specified as the gas temperature at the inlet and also specified on the inner and outer sidewalks below the packing. The incoming heat fluxes of 20, 60 and 85 kW/m$^2$ are specified at the outer sidewalk of the packing at the temperature conditions of 773, 973 and 1073 K, respectively. The uniform heat-flux boundary condition is modeled in this study so that a proper amount of heat is given to the reactor in total based on enthalpy balance between the reactor inlet and outlet in the experiments (Hoang et al., 2005). This is possible since mass flow rates of methane and water at the inlet and all species fractions at the outlet were given in their work. The zero-heat flux condition is specified on the other walls.

The average values of predicted species fractions, temperature and velocity at the bed outlet are specified as inlet boundary conditions in the subsequent simulation. By repeating the procedure, the distribution of species is predicted through 150-mm reaction zone.

2. Results and Discussion

Figure 3 shows the distribution of temperature and species fractions over the cross-sectional plane of first 25 mm portion of the reactor obtained at the operational temperature of 973 K. It can be seen that the temperature steeply changes at the very inlet of catalyst zone. The
temperature boundary layer apparently forms around first 2 to 3 particle layers, where the temperature difference reaches about 100 K. The concentration boundary layer of each species is also observed in this region. The extremely high reaction rate is caused by a low fraction of H\textsubscript{2} in the region. The temperature is also high within a particle scale near outer wall through the bed as expected from the given huge heat flux. As a result, CH\textsubscript{4} and H\textsubscript{2}O tend to be consumed along the outer wall while H\textsubscript{2} is accordingly formed in the region as well as CO and CO\textsubscript{2}.

Figure 4 indicates the average molar fraction of each species at the given axial positions at the operational temperature of 973 K. It can be also seen that the methane steam reforming predominantly takes place near the inlet and the downstream reaction is relatively slow. Associated with Figure 3 and the rate expressions of R\textsubscript{1} to R\textsubscript{3}, it can be easily understood that H\textsubscript{2} would be more rapidly formed at the inlet region provided that the bulk proper-
ties are utilized in evaluating the reaction rates because of the higher temperature and lower H\textsubscript{2} fraction compared with those in the boundary layers. On the other hand, it is expected that the low reaction rates at the downstream do not cause the significant variation of temperature and species fractions in the boundary layer, which assures the validity of rate expressions based on the bulk properties. It seems that the rate expressions are not sufficient only for the first 2 to 3 particle layers.

Figure 5 shows the temperature distribution of gas, inner and outer walls as well as sphere surface along the reactor length at the operational temperature of 973 K. It can be seen that the temperature difference between the gas and sphere surface is about 10 K except near the inlet zone. The result supports above discussion on the negligible boundary-layer-effect at the downstream. It is further noticed that the heat flux determined based on the enthalpy balance attains the desired operational temperature only on the outer wall. The temperature difference of about 100 K between inner and outer walls significantly causes a difference in the reaction rates. In other words, there is a possibility that the reaction near the outer wall is dominant and the inward portion does not sufficiently work in the reactor.

These results well demonstrate that the present CFD model will be useful, for instance, to determine the optimum particle-to-tube diameter ratio based on the temperature distribution. For the process intensification, it is possible to specify different boundary condition on each particle surface such as catalyst and adsorbent as shown in previous study (Ookawara et al., 2007).

It is further confirmed that the predicted species fractions at the reactor outlet remarkably agree with the experimental values (Hoang et al., 2005) as shown in Figure 6. The higher operational temperature results in the better agreement. This is probably because the reactions well proceed at the higher temperature until the methane is almost depleted within the reactor length. It is expected that the insufficient H\textsubscript{2} yield at the lower temperature will be numerically corrected by evaluating the reaction rates
The model is applicable to any reactions in the packed bed particles in the domain without geometrical simplification. Random packing containing hundreds of spherical particles bridge method enables one to flexibly constitute the species with equation of state. The developed interparticle equations of mass, momentum, energy and chemical in annular tube and a CFD code to fully solve conservation of mass, momentum, energy and chemical species with equation of state. The developed interparticle-bridge method enables one to flexibly constitute the random packing containing hundreds of spherical particles in the domain without geometrical simplification.

It is shown that the rate expressions, which are experimentally determined in a conventional way, can be incorporated into the present CFD model by converting the unit of rate constant to \( \text{mol/(m}^2\text{s)} \). Therefore, the CFD model is applicable to any reactions in the packed bed reactor once the catalyst is experimentally characterized.

The present study also demonstrates that the novel hi-fi CFD model incorporating surface reaction can accurately predict species and temperature distributions microscopically as well as macroscopically for the methane steam reforming. The design and operation can be optimized and intensified based on the considerable information obtained by the CFD model. The model would be more useful by developing an adsorbent boundary condition to be specified on the particle and by increasing the scale of simulation in future, which mainly depends upon a promising increase of computational resources.

Conclusions

The present study describes a novel numerical methodology to optimize and intensify packed bed reactors for methane steam reforming in narrow beds where plug flow assumption is invalid. The method employs a DEM code to realistically constitute a random packing in annular tube and a CFD code to fully solve conservation equations of mass, momentum, energy and chemical species with equation of state. The developed interparticle bridge method enables one to flexibly constitute the random packing containing hundreds of spherical particles in the domain without geometrical simplification. It is shown that the rate expressions, which are experimentally determined in a conventional way, can be incorporated into the present CFD model by converting the unit of rate constant to \( \text{mol/(m}^2\text{s)} \). Therefore, the CFD model is applicable to any reactions in the packed bed reactor once the catalyst is experimentally characterized.

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