A multiscale modeling of fixed bed catalytic reactors

H.M. Park

Department of Chemical and Biomolecular Engineering, Sogang University, Seoul, South Korea

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ABSTRACT

The packed bed may be viewed as consisting of two distinct fields, i.e., one existing on the macroscale and the other existing on the microscale levels. The macroscale describes phenomena occurring in the bed dimension and the microscale for those occurring in the intraparticle dimension. The macroscale temperature and concentration fields are found from a hypothetical continuum model of particle-fluid heterogeneous media. Each macroscale differential volume element contains several catalyst pellets, each of which is a microscale continuum embedded in a gross macroscale external fields. The boundary conditions of the microscale fields at the catalyst surfaces are provided by the solution of the macroscale model equations, while the heat and mass source terms of the macroscale model equations are determined by the microscale heat and mass transfer and chemical reactions within the catalyst pellets. In the present investigation, we have considered the HPPO process in which the propene oxide is produced by oxidizing propene with hydrogen oxide using the titanium silicalite-1(TS-1) catalysis. The set of six partial differential equations for the macroscale field coupled with the set of five partial differential equations for the microscale field at each macroscale point is solved employing the numerical Green's function technique to overcame the inherent numerical instability in this coupled PDE system. The effects of pellet size, intra-pellet diffusivity and conductivity on the reactor yield and catalyst effectiveness factor are investigated.

1. Introduction

Tubular packed beds have been employed as catalytic reactors in the chemical industries for a long time. For the design and efficient operation of these reactors, it is important to secure a reliable model that takes care of the heterogeneous discrete system consisting of solid pellets of catalyst and flowing gas or liquid [1–5]. A packed bed or a fixed bed is composed of randomly packed catalyst pellets around which the reactant and product flow in a random manner. The reactant and product fluids also permeate through each of these catalyst pellets [6]. Therefore, the fixed bed packed with permeable catalysts may be viewed as consisting of two fields, i.e., those existing on the macroscale and microscale levels. The macroscale temperature and concentration distributions are found by assuming that the heterogeneous system consisting of the solid particles and ambient fluid may be treated as though it were homogeneous, i.e., and a hypothetical continuum is assumed. If the macroscale temperature and concentration profiles are smooth, the concept of a differential volume balance may be adopted to derive the macroscale conservation equations. On

the viewpoint of microscale, each macroscale differential volume element contains several catalyst pellets, each of which is a microscale continuum embedded in a gross macroscale external fields. An accurate and reliable model must consider a resistance to heat and mass transfer between the catalyst surface and the macroscale field and the microscale intraparticle heat and mass transfer as well as chemical reactions in the permeable pellets. The boundary conditions of the microscale fields at the catalyst surfaces are provided by the solution of the macroscale model equations, while the heat and mass source terms of the macroscale model equations are determined by the heat and mass transfer and chemical reactions within the catalyst pellets. It is a typical multiscale problem [7–10].

Since the numerical solution of the macroscale and the microscale governing equations, which must be solved at each grid point of the macroscale fields, demands such a tremendous amount of computer time that we are forced to find out an approximate method. A traditional approximate method for this purpose is the concept of the effectiveness factor [6]. The effectiveness factor is defined as the ratio of the actual overall rate of reaction to the rate of reaction that would result if the entire interior surface were exposed to the external pellet surface condition. Employing the effectiveness factor, the source terms in the macroscale balance

E-mail address: hmpark@sogang.ac.kr

equations, which are determined by the reaction rate within the catalyst pellets, can be obtained using the macroscale temperature and concentration of fluid stream surrounding the pellets, and thus we can circumvent the need of solving the microscale governing equations within the catalyst pellets. However, the effectiveness factors of catalyst pellets are found analytically under the steady state conditions [2,6]. If the macroscale temperature and concentration fields vary temporally as in the case of unsteady operation, it is not appropriate to adopt the effectiveness factor, and we have to solve the microscale governing equations for the pellets and adopt the multiscale model [11]. The multiscale model can predict the unsteady as well as steady behavior of the packed bed catalytic reactor reliably with accuracy.

2. A multiscale model for a fixed bed packed with permeable catalyst pellets

Consider the following chemical reaction of HPPO process [12,13], where the propene oxide (C^s) is produced by oxidizing propene (A^s) with hydrogen oxide (B^s) using the titanium silicalite-1 catalyst. The fixed bed is packed with spherical catalysts, within which the following reaction occurs.

$$A^s(\equiv CH_3CH{=}CH_2) + B^s(\equiv H_2O_2) \rightarrow C^s(\equiv CH_3CHCH_2O) + D^s(\equiv H_2O)$$
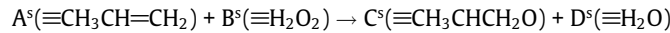
The empirical reaction rate is given by:

$$(-r_{cat}) = A^{rr}e^{-E_a/T}(B^s)^{0.32}(A^s)^{0.68} \tag{1}$$

where A^{rr} is the Arrhenius factor and E_a is the activation energy divided by the gas constant. Fig. 1 depicts the packed catalytic bed under consideration. The macroscale and microscale balance equations for the multiscale model may be summarized as follows. The macroscale concentrations of each species are A^l, B^l, C^l and D^l, the macroscale temperature field is T and the coolant temperature in the reactor is T^r. The microscale concentrations of each species in the catalyst pellet are A^s, B^s, C^s, and D^s, the microscale temperature is T^s. And $A^s_s, B^s_s, C^s_s, D^s_s$, and T^s_s designate values of the corresponding microscale variables at the pellet boundary. The parameters ε^l is the bed porosity, u^l the axial fluid velocity, K^{ls} the fluid-pellet mass transfer coefficient, a^{ls} the fluid-pellet interfacial area per bed volume, h^s the fluid-pellet heat transfer coefficient, D^s_e the diffusivity in the pellet, k^s the thermal conductivity in the pellet, ρ^l fluid density, ρ^r coolant density, U the overall heat transfer coefficient of cooling coil, d_t the diameter of cooling coil, L the bed height, C^l_p fluid heat capacity, C^s_p pellet heat capacity, ρ^s the pellet bulk density, $\triangle H_R$ the heat of reaction, z the dimensionless macroscale axial coordinate, L is the bed length, r is the dimensionless microscale radial coordinate and R_p is the radius of catalyst pellets.
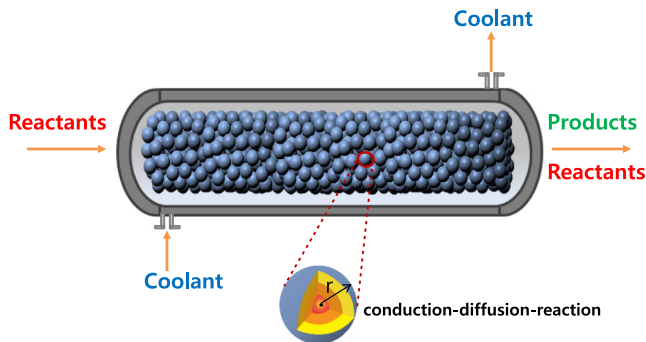

Fig. 1. A fixed-bed catalytic reactor.

The dimensionless coordinates z and r are related with the dimensional ones z^* and z^* as follows.

$$z \equiv z^*/L; \quad r \equiv r^*/R^p \tag{2}$$

The governing conservation equations are as follows:

(Governing equation of macroscale concentration: ϕ^l is one of A^l, B^l, C^l, D^l)

$$\varepsilon^l \frac{\partial \phi^l}{\partial t} = -\frac{u^l}{L}\frac{\partial \phi^l}{\partial z} - (K^{ls})a^{ls}(\phi^l - \phi^s_s)$$

$$\cdot \phi^l|_{z=0} = \phi^{l,f}$$

$$\cdot \phi^l(z, t=0) = \phi^{l,0}(z) \tag{3}$$

where $\phi^{l,f}$ is the inlet concentration, $\phi^{l,0}(z)$ is the initial concentration and ϕ^s_s is one of $A^s_s, B^s_s, C^s_s, D^s_s$.

(Governing equation of macroscale temperature T)

$$\varepsilon^l \rho^l C^l_p \frac{\partial T}{\partial t} = -\frac{\varepsilon^l \rho^l C^l_p u^l}{L}\frac{\partial T}{\partial z} + h^s a^{ls}(T^s_s - T) - \frac{4U}{d_t}(T - T^r)$$

$$\cdot T|_{z=0} = T^f$$

$$\cdot T(z, t=0) = T^0(z) \tag{4}$$

(Governing equation of coolant temperature T^r)

$$\rho^r C^r_p \frac{\partial T^r}{\partial t} = -\frac{\rho^r C^r_p u^r}{L}\frac{\partial T^r}{\partial z} + \frac{4U}{d_t}(T - T^r)$$

$$\cdot T^r|_{z=0} = T^{r,f}$$

$$\cdot T^r(z, t=0) = T^{r,0}(z) \tag{5}$$

(Governing equation of microscale concentration ϕ^s : ϕ^s is one of A^s, B^s, C^s, D^s)

$$\frac{\partial \phi^s}{\partial t} = \frac{D^s_e}{R^2_p}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \phi^s}{\partial r}\right) \mp (-r_{cat})(\rho^s)$$

$$\cdot \frac{D^s_e}{R_p}\frac{\partial \phi^s}{\partial r}|_{r=1} = (K^{ls})(\phi^l - \phi^s_s)$$

$$\cdot \frac{\partial \phi^s}{\partial r} = 0 \quad \text{at} \quad r = 0 \tag{6}$$

where the minus sign in front of the reaction term $(-r_{cat})$ is for the reactants (A^s, B^s) and the plus sign for the products (C^s, D^s).

(Governing equation of microscale temperature T^s)

$$\rho_s C^s_p \frac{\partial T^s}{\partial t} = \frac{k^s}{R^2_p}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T^s}{\partial r}\right) + (-r_{cat})(\rho^s)(-\Delta H_R)$$

$$\cdot \frac{k^s}{R_p}\frac{\partial T^s}{\partial r} = h^s(T - T^s_s) \quad \text{at} \quad r = 1$$

$$\cdot \frac{\partial T^s}{\partial r} = 0 \quad \text{at} \quad r = 0 \tag{7}$$

In the above equations, z is the macroscale variable and r is the microscale variable. The typical parameter values are specified in Appendix A.

The microscale concentration equations, Eq. (6), contain source terms due to the chemical reaction. Nonlinear reaction term in Eq. (6) can be removed by introducing the following auxiliary variables, E^s, F^s and G^s, and the corresponding auxiliary variables for fluids, E^l, F^l, G^l;

$$E^s \equiv A^s - B^s \quad (\text{if } A^s < B^s, \quad \text{then redefine } E^s \equiv B^s - A^s);$$

$$F^s \equiv A^s + C^s; \quad G^s \equiv A^s + D^s;$$

$$E^l \equiv A^l - B^l; \quad F^l \equiv A^l + C^l; \quad G^l \equiv A^l + D^l \tag{8}$$