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Analysis of the constant molar flow semi-batch vessel in contact with permeable core-shell composites

In-Soo Park†

Department of Fire and Disaster Prevention Engineering, Kyungnam University, Masan 631-701, Korea
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Abstract−An exact analytical solution was derived for the concentration of solute or the temperature of the fluid in a constant molar flow semi-batch well-stirred vessel in contact with permeable core-shell composites. The linear equilibria at both the fluid-particle interface and the core-shell interface are assumed and the extraparticle film resistance is included. Several particular solutions can be readily degenerated from the solution derived in this work. By taking the contact affinity at the core-shell interface to zero, the solution in case of impermeable core-shell composites can be degenerated. By taking both the contact affinity at the core-shell interface and the ratio of mass or thermal effective diffusivities in the core and the shell to unity or by taking the size of the core to zero, the solution in case of homogeneous particles can be degenerated. The solution for the batch vessel is also degenerated by the differentiation of the solution for the constant molar flow semi-batch vessel with respect to time.

Key words: Core-Shell Composite, Well-Stirred Vessel, Adsorption Vessel, Effective Diffusivity

INTRODUCTION

An adsorption vessel is one of the most basic devices in the study of adsorption engineering. Its performance depends largely on the intraparticle diffusion, which is dictated by the structure and the properties of adsorbent particles. When homogeneous adsorbents are loaded in the adsorption vessel, we have one of the classical mass transport problems, which is well described in Crank [1975]. The heat transport problem can be described in a similar way as the corresponding mass transport problem by means of the analogy between them. As one of the classical heat transport problems [Carslaw and Jaeger, 1959], for example, the temperature profile in a finite volume of a well-stirred fluid in contact with a solid (e.g., temperature rise in a calorimeter when a spherical solid is introduced) can be expressed by the same mathematical model as the model for the concentration profile of solute in the batch adsorption vessel.

Recently, core-shell materials have received much attention because such composite particles may be useful in many applications such as development of adsorbents, catalysts, calorimetric sensors, optoelectronic devices, and bioprocessing devices [Chanda and Rempel, 1997; Liu et al., 2006; Fu et al., 2005; Ding et al., 2004; Sakiyama et al., 2001; Yu and An, 2004; Wang and Harrison, 1999; Yu and Mulvaney, 2003; Marinakos et al., 2001]. The core-shell composite is prepared by the surface coating of nanoparticles with various materials. A large variety of properties (adsorptive, thermal, magnetic, optical, electrical, mechanical, etc.) can be assigned to the composite by using various kinds of nanoparticles and appropriate coatings. Core-shell particles have also been used as precursors to prepare hollow structures by the complete removal of core materials through chemical etching or combustion [Marinakos et al., 2001], and partial elimination of the core has enabled preparation of novel nanostructures inside the shell [Rodriguez-Gonzalez et al., 2002; Sun et al., 2002].

†To whom correspondence should be addressed.
E-mail: ispark@kyungnam.ac.kr

Numerous papers for the preparation of the core-shell composite have appeared; however, exact mathematical analysis is not abundant in composite research. Chanda and Rempel [1997, 1999] and Li et al. [2003] derived an exact solution for the solute concentration in the batch adsorption vessel loaded with the impermeable core-shell composite. Park [2005] derived an exact solution for the solute concentration in the constant molar flow semi-batch adsorption vessel loaded with the impermeable core-shell composite. The solution for the batch adsorption vessel is readily obtained by the differentiation of the solution of the semi-batch adsorption vessel with respect to time.

The aim of this work is to extend the analysis of Park [2005] to account for the permeability of the inner core. Solution for the impermeable core-shell composite can be recovered by taking the contact affinity at the core-shell interface to zero. Solution for the homogeneous particle can be also obtained by taking appropriate limits.

MATHEMATICAL MODEL

1. Mass Balance

Consider a well-stirred vessel in which core-shell composites are loaded. The vessel is initially evacuated. At time t=0, a pure gas is introduced into the vessel with a molar flow rate $\dot{N}X(t)$, where X(t) is the dimensionless unit forcing function, which specifies how to feed the pure gas into the vessel, and $\dot{N}$ is the intensity of the forcing function. The schematic sketch of the well-stirred vessel is shown in Fig. 1.

The simplifying assumptions are: (1) ideal mixing in the vessel; (2) local linear equilibrium at the particle surface; (3) homogeneous particle diffusion or heat conduction within the outer shell layer of particle; (4) local linear equilibrium at the core-shell interface, (5) homogeneous particle diffusion or heat conduction within the inner core of particle; (6) negligible swelling or shrinking of the core and the shell. Based on the above assumptions, the mathematical model is as follows:

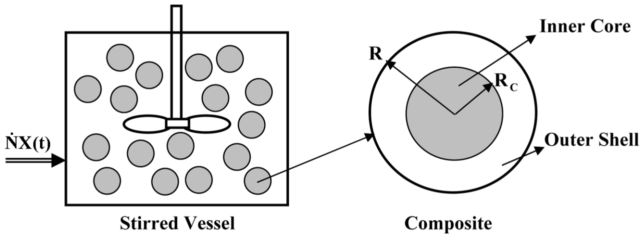

Fig. 1. Semi-batch well-stirred vessel and core-shell structured composite.

Intraparticle Mass or Heat Balance in Inner Permeable Core (Particle Phase 1, $0 \le r \le R_C$):

$$\text{Mass: } \frac{\partial C_{\mu 1}}{\partial t} = D_1 \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_{\mu 1}}{\partial r}\right) \tag{1a}$$

$$\text{at } t=0 \qquad C_{\mu 1}=0 \tag{1b}$$

$$\text{Heat: } \frac{\partial T_1}{\partial t} = k_1 \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial T_1}{\partial r}\right) \tag{2a}$$

$$\text{at } t=0 \qquad T_1=T_i \tag{2b}$$

Intraparticle Mass or Heat Balance in Outer Shell (Particle Phase 2, $R_C \le r \le R$):

$$\text{Mass: } \frac{\partial C_{\mu 2}}{\partial t} = D_2 \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_{\mu 2}}{\partial r}\right) \tag{3a}$$

$$\text{at } t=0 \qquad C_{\mu 2}=0 \tag{3b}$$

$$\text{Heat: } \frac{\partial T_2}{\partial t} = k_2 \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial T_2}{\partial r}\right) \tag{4a}$$

$$\text{at } t=0 \qquad T_2=T_i \tag{4b}$$

Mass or Heat Balance around the Well-Stirred Vessel:

$$\text{Mass: } V_b \frac{dC_b}{dt} + V\frac{d\langle C_\mu \rangle}{dt} = \dot{N}X(t) \tag{5a}$$

$$\langle C_\mu \rangle = \left(1 - \frac{R_C^3}{R^3}\right)\langle C_{\mu 2}\rangle + \frac{R_C^3}{R^3}\langle C_{\mu 1}\rangle \tag{5b}$$

$$\langle C_{\mu 2}\rangle = \frac{3}{R^3 - R_C^3}\int_{R_C}^{R} r^2 C_{\mu 2} dr; \quad \langle C_{\mu 1}\rangle = \frac{3}{R_C^3}\int_0^{R_C} r^2 C_{\mu 1} dr \tag{5c}$$

$$\text{at } t=0 \qquad C_b=0 \tag{5d}$$

$$\text{Heat: } V_b \frac{dT_b}{dt} + V\left(\frac{c_m \rho_m}{c_b \rho_b}\right)\frac{d\langle T \rangle}{dt} = \frac{\dot{N}}{c_b \rho_b}X(t) \tag{6a}$$

$$\langle T \rangle = \left(1 - \frac{R_C^3}{R^3}\right)\langle T_2\rangle + \frac{R_C^3}{R^3}\langle T_1\rangle \tag{6b}$$

$$\langle T_2\rangle = \frac{3}{R^3 - R_C^3}\int_{R_C}^{R} r^2 T_2 dr; \quad \langle T_1\rangle = \frac{3}{R_C^3}\int_0^{R_C} r^2 T_1 dr \tag{6c}$$

$$\text{at } t=0 \qquad T_b=T_i \tag{6d}$$

Three Boundary Conditions and Two Linear Equilibrium Relationships:

$$\text{Mass: } \left.\frac{\partial C_{\mu 1}}{\partial r}\right|_{r=0} = 0 \tag{7a}$$

$$\left[D_2 \frac{\partial C_{\mu 2}}{\partial r}\right]_{r=R} = k_f (C_b - C_s) \tag{7b}$$

$$D_1 \left.\frac{\partial C_{\mu 1}}{\partial r}\right|_{r=R_C} = D_2 \left.\frac{\partial C_{\mu 2}}{\partial r}\right|_{r=R_C} \tag{7c}$$

$$C_{\mu 2}|_{r=R} = K_2 C_s, \qquad (C_s = C_b|_{r=R}) \tag{7d}$$

$$C_{\mu 1}|_{r=R_C} = K_1 C_{\mu 2}|_{r=R_C} \tag{7e}$$

$$\text{Heat: } \left.\frac{\partial T_1}{\partial r}\right|_{r=0} = 0 \tag{8a}$$

$$\left[\kappa_s \frac{\partial T_2}{\partial r}\right]_{r=R} = h_f (T_b - T_s) \tag{8b}$$

$$k_1 \left.\frac{\partial T_1}{\partial r}\right|_{r=R_C} = k_2 \left.\frac{\partial T_2}{\partial r}\right|_{r=R_C} \tag{8c}$$

$$T_2|_{r=R} = K_2 T_s, \qquad (T_s = T_b|_{r=R}) \tag{8d}$$

$$T_1|_{r=R_C} = K_1 T_2|_{r=R_C} \tag{8e}$$

Unit Step Forcing Function:

For the constant molar flow semi-batch well-stirred vessel, the forcing function X(t) is

$$X(t)=U(t) \tag{9}$$

Eq. (7a) [or Eq. (8a) for heat transport] is the usual symmetric boundary conditions at the centre of the particle, Eq. (7b) [or Eq. (8b) for heat transport] represents the contact resistance at the bulk-particle interface, and Eq. (7c) [or Eq. (8c) for heat transport] is the continuity of flux at the shell-core interface within particles. Eqs. (7d) and (7e) [or Eqs. (8d) and (8e) for heat transport] represent the linear contact affinities at the bulk-particle interface and at shell-core interface within particle, respectively. In heat transport problems, it should be noted that temperatures of fluid and particle at the interface and temperatures of shell and core at the interface are usually assumed to be the same, respectively [Carslaw and Jaeger, 1959; Levine, 1999]. In mass transfer problems, however, the concentrations of two phases at the interface are usually different from each other as physical properties are different in the two phases. Nevertheless, Eqs. (7d) and (7e) will be accepted in mass transfer problems of a constant molar flow (CMF) semi-batch vessel since very low concentration is maintained in a CMF semi-batch adsorption vessel [Park and Do, 1996].

2. Non-Dimensionalization

With the dimensionless variables and parameters defined in Table 1, the model equations for both mass and heat transport problems

Table 1. Definition of dimensionless variables and parameters

Variables and parameters	Mass transfer $C_0 \equiv$ reference	Heat transfer $T_0 \equiv$ reference $T_i \equiv$ feed temperature
A_b	C_b/C_0	$(T_b - T_i)/(T_0 - T_i)$
A_s	C_s/C_0	$(T_s - T_i)/(T_0 - T_i)$
A_2	C_2/K_2C_0	$(T_2 - T_i)/K_2(T_0 - T_i)$
A_1	C_1/K_2C_0	$(T_1 - T_i)/K_2(T_0 - T_i)$
A	C/K_2C_0	$(T - T_i)/K_2(T_0 - T_i)$
τ	D_2t/R^2	k_2t/R^2
x	r/R	r/R
x_C	R_C/R	R_C/R
ξ	k_fR/K_2D_2	$h_fR/K_2\kappa_s$
β_0	VK_2/V_b	$(c_m\rho_m/c_b\rho_b)(VK_2/V_b)$
a	$\sqrt{D_1/D_2}$	$\sqrt{k_1/k_2}$
Ω	$\dfrac{R^2/D_2}{V_bC_0/\dot{N}}$	$\dfrac{R^2/k_2}{c_b\rho_bV_b(T_0 - T_i)/\dot{N}}$

given in the previous section are written in dimensionless forms as follows:

Intraparticle Mass or Heat Balance in Inner Permeable Core ($0\le x\le x_C$):

$$\frac{\partial A_1}{\partial \tau}=a^2\left(\frac{\partial^2 A_1}{\partial x^2}+\frac{2}{x}\frac{\partial A_1}{\partial x}\right) \tag{10a}$$

$$\text{at } \tau=0 \qquad A_1=0 \tag{10b}$$

Intraparticle Mass or Heat Balance in Outer Shell ($x_C\le x\le 1$):

$$\frac{\partial A_2}{\partial \tau}=\left(\frac{\partial^2 A_2}{\partial x^2}+\frac{2}{x}\frac{\partial A_2}{\partial x}\right) \tag{11a}$$

$$\text{at } \tau=0 \qquad A_2=0 \tag{11b}$$

Mass or Heat Balance around the Well-Stirred Vessel (Bulk Phase):

$$\frac{dA_b}{d\tau}+\beta_0\frac{d\langle A\rangle}{d\tau}=\Omega X(\tau) \tag{12a}$$

$$\langle A\rangle=(1-x_C^3)\langle A_2\rangle+x_C^3\langle A_1\rangle \tag{12b}$$

$$\langle A_2\rangle=\frac{3}{1-x_C^3}\int_{x_C}^1 x^2A_2dx; \qquad \langle A_2\rangle=\frac{3}{1-x_C^3}\int_{x_C}^1 x^2A_2dx \tag{12c}$$

$$\text{at } \tau=0 \qquad A_b=0 \tag{12d}$$

Three Boundary Conditions and Two Linear Equilibrium Relationships:

$$\left.\frac{\partial A_1}{\partial x}\right|_{x=0}=0 \tag{13a}$$

$$\left[\frac{\partial A_2}{\partial x}\right]_{x=1}=\xi(A_b-A_s) \tag{13b}$$

$$a^2\left.\frac{\partial A_1}{\partial x}\right|_{x=x_C}=\left.\frac{\partial A_2}{\partial x}\right|_{x=x_C} \tag{13c}$$

$$A_2|_{x=1}=A_s(=A_b|_{x=1}) \tag{13d}$$

$$A_1|_{x=x_C}=K_1A_2|_{x=x_C} \tag{13e}$$

Unit Step Forcing Function:

$$X(\tau)=U(\tau) \tag{14}$$

ANALYTICAL SOLUTION

1. Solution in Laplace Domain

1-1. Solution in Terms of Overall Transfer Function G(s)

From Eq. (12), the overall transfer function which relates the forcing function to the response in Laplace domain are given by

$$G(s)\equiv\frac{\bar{A}_b}{\Omega\bar{X}}=\frac{1}{s(1+\beta_0F(s))} \tag{15}$$

in terms of the vessel transfer function F(s). Substituting the forcing function $\bar{X}=1/s$ into Eq. (15), we obtain the solution for the step response in Laplace domain:

$$\left(\frac{\bar{A}_b}{\Omega}\right)_{step}=\frac{1}{s^2(1+\beta_0F(s))} \tag{16}$$

The vessel transfer function F(s) in Eqs. (15) and (16) is defined by

$$F(s)\equiv\frac{\langle\bar{A}_\mu\rangle}{\bar{A}_b}=(1-x_C^3)F_2(s)+x_C^3F_1(s); \tag{17}$$

where $F_1(s)$ is the vessel transfer function for the inner core and $F_2(s)$ is the vessel transfer function for the outer shell, which are defined, respectively, by

$$F_1(s)\equiv\frac{\langle\bar{A}_1\rangle}{\bar{A}_b}=\frac{f_{21}(s)/x_C^3}{f_1(s)}; \quad F_2(s)\equiv\frac{\langle\bar{A}_2\rangle}{\bar{A}_b}=\frac{f_{22}(s)/(1-x_C^3)}{f_1(s)} \tag{18}$$

1-2. Vessel Transfer Function F(s)

General solution of (10) in Laplace domain is:

$$\bar{A}_1=b_{11}\frac{\cosh(x\sqrt{s}/a)}{x}+b_{12}\frac{\sinh(x\sqrt{s}/a)}{x} \tag{19}$$

General solution of (11) in Laplace domain is:

$$\bar{A}_2=b_{21}\frac{\cosh(x\sqrt{s})}{x}+b_{22}\frac{\sinh(x\sqrt{s})}{x} \tag{20}$$

Applying boundary conditions and linear adsorption affinities (13a)-(13e) to Eqs. (19) and (20), we have

$$b_{11}=0 \tag{21a}$$

$$b_{12}=\frac{b_{22}K_1[1-Q(s)\coth(x_C\sqrt{s})]\sinh(x_C\sqrt{s})}{\sinh\left(\frac{x_C\sqrt{s}}{a}\right)} \tag{21b}$$

$$b_{21}=-b_{22}Q(s) \tag{21c}$$

$$b_{22}=\frac{\bar{A}_b}{\left(\begin{array}{l}\left[\left(1-\frac{1}{\xi}\right)\sinh(\sqrt{s})+\frac{\sqrt{s}}{\xi}\cosh(\sqrt{s})\right]\\-\left[\left(1-\frac{1}{\xi}\right)\cosh(\sqrt{s})+\frac{\sqrt{s}}{\xi}\sinh(\sqrt{s})\right]Q(s)\end{array}\right)} \tag{21d}$$

$$Q(s)=\tanh(x_C\sqrt{s})\left(\frac{\left(\begin{array}{l}a^2K_1\left[1-\frac{x_C\sqrt{s}}{a}\coth\left(\frac{x_C\sqrt{s}}{a}\right)\right]\\-[1-x_C\sqrt{s}\coth(x_C\sqrt{s})]\end{array}\right)}{\left(\begin{array}{l}a^2K_1\left[1-\frac{x_C\sqrt{s}}{a}\coth\left(\frac{x_C\sqrt{s}}{a}\right)\right]\\-[1-x_C\sqrt{s}\tanh(x_C\sqrt{s})]\end{array}\right)}\right) \tag{21e}$$

Subsequently, by substitutions of Eq. (19) for $\bar{A}_1$ and Eq. (20) for $\bar{A}_2$ into Eqs. (17) and (18), functions $f_1(s)$, $f_{21}(s)$ and $f_{22}(s)$ in Eq. (18) can be obtained as:

$$\begin{aligned}f_1(s)=&\left[\left(1-\frac{1}{\xi}\right)\sinh(\sqrt{s})+\frac{\sqrt{s}}{\xi}\cosh(\sqrt{s})\right]\\&-\left[\left(1-\frac{1}{\xi}\right)\cosh(\sqrt{s})+\frac{\sqrt{s}}{\xi}\sinh(\sqrt{s})\right]Q(s)\end{aligned} \tag{22a}$$

$$\begin{aligned}f_{21}(s)=&\frac{3}{s}(a^2K_1)\left[\frac{x_C\sqrt{s}}{a}\coth\left(\frac{x_C\sqrt{s}}{a}\right)-1\right]\times\\&[\sinh(x_C\sqrt{s})-Q(s)\cosh(x_C\sqrt{s})]\end{aligned} \tag{22b}$$

$$f_{22}(s)=\frac{3}{s}\left\{\begin{array}{l}\left[\begin{array}{l}(\sqrt{s}\cosh(\sqrt{s})-\sinh(\sqrt{s}))\\-(x_C\sqrt{s}\cosh(x_C\sqrt{s})-\sinh(x_C\sqrt{s}))\end{array}\right]\\+\left[\begin{array}{l}(\cosh(\sqrt{s})-\sqrt{s}\sinh(\sqrt{s}))\\-(\cosh(x_C\sqrt{s})-x_C\sqrt{s}\sinh(x_C\sqrt{s}))\end{array}\right]Q(s)\end{array}\right\} \tag{22c}$$

Thus, vessel transfer function F(s) is defined completely by Eqs. (17) and (18) by substitution of Eq. (22) for $f_1(s)$, $f_{21}(s)$ and $f_{22}(s)$.

2. Solution in Time Domain

The analytical solution of the model can be obtained by the inverse transformation using the method of residue.

Using the power series expansion of F(s), we can rewrite the solution in Laplace domain as

$$\left(\frac{\mathrm{A}_b}{\Omega}\right)_{step}=\frac{1}{\mathrm{s}^2[1+\beta_0\mathrm{F(s)}]}=\frac{1}{\mathrm{s}^2}\left[\frac{1}{1+\beta_0(\mathrm{a}_0+\mathrm{a}_1\mathrm{s}+\mathrm{a}_2\mathrm{s}^2+\mathrm{a}_3\mathrm{s}^3+\cdots)}\right]$$

$$=\frac{1}{\mathrm{s}^2}\left[\frac{1}{1+\beta_0\mathrm{a}_0}-\frac{\beta_0(\mathrm{a}_1)}{(1+\beta_0\mathrm{a}_0)^2}\mathrm{s}\right]+\mathrm{P}_n(\mathrm{s}) \tag{23a}$$

where $\mathrm{P}_n(\mathrm{s})$ is the n-th order polynomial of s, and a_0 and a_1 are given by

$$\mathrm{a}_0=(1-\mathrm{x}_C^3)+\mathrm{K}_1\mathrm{x}_C^3 \tag{23b}$$

$$\mathrm{a}_1=-\frac{1}{3\xi}[(1-\mathrm{x}_C^3)+\mathrm{K}_1\mathrm{x}_C^3]^2-\frac{1}{15}\left[\begin{array}{l}[(1-\mathrm{x}_C^3)+\mathrm{K}_1\mathrm{x}_C^3]\\ +4(\mathrm{K}_1-1)(\mathrm{x}_C^3-\mathrm{x}_C^5)+5(\mathrm{K}_1-1)^2(\mathrm{x}_C^5-\mathrm{x}_C^6)+\dfrac{1-\mathrm{a}^2}{\mathrm{a}^2}\mathrm{K}_1\mathrm{x}_C^5\end{array}\right] \tag{23c}$$

As we can see in Eq. (23a), there are two kinds of poles in Laplace domain solution: One is the double pole at s=0; the other is the infinite number of poles at $1+\beta_0\mathrm{F(s)}=0$. Hence, the solution in time domain consists of two parts: One part comes from the double pole at s=0, which corresponds to the long time solution after the transient part dissipates at $\tau\to\infty$; the other part comes from the infinite number of poles at $1+\beta_0\mathrm{F(s)}=0$, which corresponds to the transient part of the solution. That is,

$$\left(\frac{\mathrm{A}_b}{\Omega}\right)_{step}=\left(\frac{\mathrm{A}_b}{\Omega}\right)_{step,1}+\left(\frac{\mathrm{A}_b}{\Omega}\right)_{step,2} \tag{24}$$

where $(\mathrm{A}_b/\Omega)_{step,1}$ is the long time solution and $(\mathrm{A}_b/\Omega)_{step,2}$ is the transient part.

Using Eq. (23), we can readily obtain the residue at the double pole at s=0 as

$$\left(\frac{\mathrm{A}_b}{\Omega}\right)_{step,1}=\frac{1}{1+\beta_0\mathrm{a}_0}\tau-\frac{\beta_0(\mathrm{a}_1)}{(1+\beta_0\mathrm{a}_0)^2}$$

That is,

$$\left(\frac{\mathrm{A}_b}{\Omega}\right)_{step,1}=\delta_0\tau+\beta_0[(1-\mathrm{x}_C^3)+\mathrm{K}_1\mathrm{x}_C^3]\delta_0^2(\delta_f+\delta_a) \tag{25a}$$

where

$$\delta_0=\frac{1}{1+\beta_0[(1-\mathrm{x}_C^3)+\mathrm{K}_1\mathrm{x}_C^3]} \tag{25b}$$

$$\delta_f=\frac{1}{3\xi}[(1-\mathrm{x}_C^3)+\mathrm{K}_1\mathrm{x}_C^3] \tag{25c}$$

$$\delta_a=\frac{1}{15}\left[1+\frac{4(\mathrm{K}_1-1)(\mathrm{x}_C^3-\mathrm{x}_C^5)+5(\mathrm{K}_1-1)^2(\mathrm{x}_C^5-\mathrm{x}_C^6)+\left(\dfrac{1-\mathrm{a}^2}{\mathrm{a}^2}\right)\mathrm{K}_1\mathrm{x}_C^5}{(1-\mathrm{x}_C^3)+\mathrm{K}_1\mathrm{x}_C^3}\right] \tag{25d}$$

The sum of residues at the infinite number of poles at $1+\beta_0\mathrm{F(s)}=0$ can be obtained by a somewhat tedious procedure of inverse transform as

$$\left(\frac{\mathrm{A}_b}{\Omega}\right)_{step,2}=\sum_{n=1}^{\infty}\frac{-\beta_0(\Psi_{21}(\lambda_n)+\Psi_{22}(\lambda_n))\exp(-\lambda_n^2\tau)}{\lambda_n^4[\Phi_1(\lambda_n)+\beta_0(\Phi_{21}(\lambda_n)+\Phi_{22})(\lambda_n)]} \tag{26}$$

Eigenvalues λ_n (for n=1, 2, $\cdots$, ∞) in the above equation are given by the positive roots of the following transcendental equation:

$$\Psi_1(\lambda)+\beta_0[\Psi_{22}(\lambda)+\Psi_{21}(\lambda)]=0 \tag{27}$$

The six functions in Eqs. (26) and (27) are defined by

$$\Psi_1(\lambda)=(-\mathrm{i})\lim_{s\to-\lambda^2}\mathrm{f}_1(\mathrm{s}) \tag{28a}$$

$$\Psi_{21}(\lambda)=(-\mathrm{i})\lim_{s\to-\lambda^2}\mathrm{f}_{21}(\mathrm{s}) \tag{28b}$$

$$\Psi_{22}(\lambda)=(-\mathrm{i})\lim_{s\to-\lambda^2}\mathrm{f}_{22}(\mathrm{s}) \tag{28c}$$

Table 2. Definition of functions contained in transient part of response

$$\alpha_1=1-\mathrm{a}^2\mathrm{K}_1+\mathrm{a}^2\mathrm{K}_1\frac{\lambda\mathrm{x}_C}{\mathrm{a}}\cot\left(\frac{\lambda\mathrm{x}_C}{\mathrm{a}}\right)+\lambda\mathrm{x}_C\tan(\lambda\mathrm{x}_C) \tag{30a}$$

$$\alpha_2=\cos(\lambda)-\frac{\lambda}{\xi}\sin(\lambda) \tag{30b}$$

$$\alpha_3=1-\mathrm{a}^2\mathrm{K}_1-\lambda\mathrm{x}_C\cot(\lambda\mathrm{x}_C)+\mathrm{a}^2\mathrm{K}_1\frac{\lambda\mathrm{x}_C}{\mathrm{a}}\cot\left(\frac{\lambda\mathrm{x}_C}{\mathrm{a}}\right) \tag{30c}$$

$$\alpha_4=\left(\frac{1}{\xi}-1\right)\cos(\lambda)+\frac{\lambda}{\xi}\sin(\lambda) \tag{30d}$$

$$\alpha_5=\left[\begin{array}{l}-\mathrm{aK}_1\cot\left(\dfrac{\lambda\mathrm{x}_C}{\mathrm{a}}\right)+\mathrm{aK}_1\dfrac{\lambda\mathrm{x}_C}{\mathrm{a}}\csc^2\left(\dfrac{\lambda\mathrm{x}_C}{\mathrm{a}}\right)\\ -\lambda\mathrm{x}_C\sec^2(\lambda\mathrm{x}_C)-\tan(\lambda\mathrm{x}_C)\end{array}\right]\tan(\lambda\mathrm{x}_C) \tag{30e}$$

$$\alpha_6=\alpha_3\alpha_4\sec^2(\lambda\mathrm{x}_C) \tag{30f}$$

$$\alpha_7=\alpha_4\left[\begin{array}{l}-\cot(\lambda\mathrm{x}_C)+\mathrm{aK}_1\cot\left(\dfrac{\lambda\mathrm{x}_C}{\mathrm{a}}\right)\\ +\lambda\mathrm{x}_C\left[\csc^2(\lambda\mathrm{x}_C)-\mathrm{K}_1\csc^2\left(\dfrac{\lambda\mathrm{x}_C}{\mathrm{a}}\right)\right]\end{array}\right]\tan(\lambda\mathrm{x}_C) \tag{30g}$$

$$\alpha_8=\alpha_3\left[\frac{\lambda}{\xi}\cos(\lambda)+\sin(\lambda)\right]\tan(\lambda\mathrm{x}_C) \tag{30h}$$

$$\alpha_9=\frac{\lambda}{\xi}\cos(\lambda)+\left(1-\frac{1}{\xi}\right)\sin(\lambda) \tag{30i}$$

$$\beta_1=\mathrm{a}^4\mathrm{K}_1\left[\left(\frac{\lambda\mathrm{x}_C}{\mathrm{a}}\right)\cot\left(\frac{\lambda\mathrm{x}_C}{\mathrm{a}}\right)\right]^2[1-\lambda\mathrm{x}_C\tan(\lambda\mathrm{x}_C)] \tag{30j}$$

$$\beta_2=\mathrm{a}^2\left[\frac{\lambda\mathrm{x}_C}{\mathrm{a}}\csc\left(\frac{\lambda\mathrm{x}_C}{\mathrm{a}}\right)\right]^2[1+\lambda\mathrm{x}_C\tan(\lambda\mathrm{x}_C)] \tag{30k}$$

$$\beta_3=\mathrm{a}^2\left[\left(\frac{\lambda\mathrm{x}_C}{\mathrm{a}}\right)\cot\left(\frac{\lambda\mathrm{x}_C}{\mathrm{a}}\right)\right][-2\mathrm{a}^2\mathrm{K}_1+\lambda^2\mathrm{x}_C^2+2\mathrm{a}^2\mathrm{K}_1\lambda\mathrm{x}_C\tan(\lambda\mathrm{x}_C)] \tag{30l}$$

$$\beta_4=\mathrm{a}^2[-1+\mathrm{a}^2\mathrm{K}_1-\lambda^2\mathrm{x}_C^2-(1+\mathrm{a}^2\mathrm{K}_1)\lambda\mathrm{x}_C\tan(\lambda\mathrm{x}_C)] \tag{30m}$$

$$\beta_5=\mathrm{a}^2\mathrm{K}_1\left[1-\frac{\lambda\mathrm{x}_C}{\mathrm{a}}\cot\left(\frac{\lambda\mathrm{x}_C}{\mathrm{a}}\right)\right][\lambda\mathrm{x}_C\sec(\lambda\mathrm{x}_C)] \tag{30n}$$

$$\gamma_1=-2\alpha_1[\lambda\cos(\lambda)-\lambda\mathrm{x}_C\cos(\lambda\mathrm{x}_C)-\sin(\lambda)+\sin(\lambda\mathrm{x}_C)] \tag{30o}$$

$$\gamma_2=2\alpha_3\gamma_8\tan(\lambda\mathrm{x}_C) \tag{30p}$$

$$\gamma_3=\alpha_1[-\sin(\lambda)+\mathrm{x}_C^2\sin(\lambda\mathrm{x}_C)] \tag{30q}$$

$$\gamma_4=\frac{-\alpha_3\alpha_5\gamma_8}{\lambda\alpha_1} \tag{30r}$$

$$\gamma_5=\frac{-\alpha_3\gamma_8}{\lambda}\sec^2(\lambda\mathrm{x}_C) \tag{30s}$$

$$\gamma_6=\frac{-\alpha_7\gamma_8}{\lambda\alpha_4} \tag{30t}$$

$$\gamma_7=\alpha_3[\cos(\lambda)-\mathrm{x}_C^2\cos(\lambda\mathrm{x}_C)]\tan(\lambda\mathrm{x}_C) \tag{30u}$$

$$\gamma_8=-\cos(\lambda)+\cos(\lambda\mathrm{x}_C)-\lambda\sin(\lambda)+\lambda\mathrm{x}_C\sin(\lambda\mathrm{x}_C) \tag{30v}$$

$$\Phi_1(\lambda)=(-\mathrm{i})\lim_{s\to-\lambda^2}\frac{\mathrm{df}_1(\mathrm{s})}{\mathrm{ds}} \tag{28d}$$

$$\Phi_{21}(\lambda)=(-\mathrm{i})\lim_{s\to-\lambda^2}\frac{\mathrm{df}_{21}(\mathrm{s})}{\mathrm{ds}} \tag{28e}$$

$$\Phi_{22}(\lambda)=(-\mathrm{i})\lim_{s\to-\lambda^2}\frac{\mathrm{df}_{22}(\mathrm{s})}{\mathrm{ds}} \tag{28f}$$

which can be obtained as

$$\Psi_1(\lambda)=\alpha_9+\left(\frac{\alpha_3\alpha_4}{\alpha_1}\right)\tan(\lambda \mathrm{x}_C) \tag{29a}$$

$$\Psi_{21}(\lambda)=\frac{3}{\lambda^2}\left(\frac{\beta_5}{\alpha_1}\right) \tag{29b}$$

$$\Psi_{22}(\lambda)=\frac{3}{2\lambda^2}\left(\frac{\gamma_1+\gamma_2}{\alpha_1}\right) \tag{29c}$$

$$\Phi_1(\lambda)=\frac{-1}{2\lambda}\left(\frac{\alpha_1\alpha_2+[\alpha_3\alpha_4\alpha_5/\alpha_1+\alpha_6+\alpha_7]\mathrm{x}_C+\alpha_8}{\alpha_1}\right) \tag{29d}$$

$$\Phi_{21}(\lambda)=\frac{-3\mathrm{K}_1}{2\lambda^4}\left(\frac{\beta_1+\beta_2+\beta_3+\beta_4}{\alpha_1^2}\right)[\lambda \mathrm{x}_C\sec(\lambda \mathrm{x}_C)] \tag{29e}$$

$$\Phi_{22}(\lambda)=\frac{3}{2\lambda^4}\left(\frac{\gamma_1+\gamma_2+\lambda^2[\gamma_3+(\gamma_4+\gamma_5+\gamma_6)\mathrm{x}_C+\gamma_7]}{\alpha_1}\right) \tag{29f}$$

Functions of λ in Eq. (29) (i.e., α's, β's, γ's) are given in Table 2.

This completes the derivation of the step response of a CMF semi-batch vessel in contact with permeable core-shell composites.

DISCUSSION

By differentiation of the step response with respect to time, the impulse response can be obtained [Park, 2005]. Hence, by differentiation of Eq. (24), we obtain the solution for the batch vessel in contact with permeable core-shell composites:

$$\left(\frac{\mathrm{A}_b}{\Omega}\right)_{batch}=\delta_0+\sum_{n=1}^{\infty}\frac{\beta_0(\Psi_{21}(\lambda_n)+\Psi_{22}(\lambda_n))\exp(-\lambda_n^2\tau)}{\lambda_n^2[\Phi_1(\lambda_n)+\beta_0(\Phi_{21}(\lambda_n)+\Phi_{22})(\lambda_n)]} \tag{31}$$

As we can see in comparison of Eqs. (25) and (31), only the equilibrium information is obtained from the long time solution of the batch vessel while both the equilibrium and the kinetic information is obtained from the long time solution of the CMF semi-batch vessel. Using the definition of variables and parameters in Table 1, Eq. (31) represents the concentration of solute in the well-stirred batch adsorption vessel loaded with permeable core-shell adsorbents in mass transport problem. In a heat transport problem, Eq. (31) represents the fluid temperature in a well-stirred batch vessel in contact with core-shell particles.

Taking limits of Eqs. (24) and (27) at $\mathrm{K}_1\to0$, we can obtain the step response and the transcendental equation for the eigenvalues in case of impermeable core-shell composites (derivation is given in Appendix):

$$\left(\frac{\mathrm{A}_b}{\Omega}\right)_{step,1}=\delta_0\tau+\beta_0(1-\mathrm{x}_C^3)\delta_0^2(\delta_f+\delta_a) \tag{32a}$$

$$\left(\frac{\mathrm{y}_b}{\Omega}\right)_{step,2}=6\beta_0\sum_{n=1}^{\infty}\frac{\begin{Bmatrix}(1+\lambda_n^2\mathrm{x}_C)\sin[\lambda_n(1-\mathrm{x}_C)]\\-\lambda_n(1-\mathrm{x}_C)\cos[\lambda_n(1-\mathrm{x}_C)]\end{Bmatrix}}{\lambda_n^4\begin{Bmatrix}\mathrm{A}_n\sin[\lambda_n(1-\mathrm{x}_C)]\\+\mathrm{B}_n\cos[\lambda_n(1-\mathrm{x}_C)]\end{Bmatrix}}\exp(-\lambda_n^2\tau) \tag{32b}$$

$$\tan[\lambda(1-\mathrm{x}_C)]=\lambda\frac{\lambda^2\mathrm{x}_C+(\lambda^2/\xi-3\beta_0)(1-\mathrm{x}_C)}{(\lambda^2/\xi-3\beta_0)(1+\lambda_n^2\mathrm{x}_C)-\lambda^2};$$

$$\lambda=\lambda_n,\ (\mathrm{n}=1, 2, \cdots, \infty) \tag{32c}$$

$$\delta_0=\frac{1}{1+\beta_0(1-\mathrm{x}_C^3)} \tag{32d}$$

$$\delta_f=\frac{1-\mathrm{x}_C^3}{3\xi} \tag{32e}$$

$$\delta_a=\frac{1}{15}\left(1-\frac{4(1-\mathrm{x}_C^2)\mathrm{x}_C^3}{1-\mathrm{x}_C^3}+\frac{5(1-\mathrm{x}_C)\mathrm{x}_C^5}{1-\mathrm{x}_C^3}\right) \tag{32f}$$

$$\mathrm{A}_n=2\left(1-\frac{1}{\xi}\right)+\left(3\beta_0-\frac{\lambda_n^2}{\xi}\right)-\left(1+\frac{2}{\xi}\right)\lambda_n^2\mathrm{x}_C+\left(\lambda_n^2+3\beta_0-\frac{\lambda_n^2}{\xi}\right)\mathrm{x}_C^2 \tag{32g}$$

$$\mathrm{B}_n=\lambda_n\left[\left(1+\frac{2}{\xi}\right)+\left\{3\beta_0-\frac{\lambda_n^2}{\xi}+2\left(1-\frac{1}{\xi}\right)\right\}\mathrm{x}_C-\left(3\beta_0-\frac{\lambda_n^2}{\xi}\right)\mathrm{x}_C^2\right] \tag{32h}$$

These are the same equations as those equations for the impermeable core-shell composites reported by Park [2005].

Taking limits of Eqs. (24) and (27) at $\mathrm{K}_1\to1$ and $\mathrm{a}\to1$, we can obtain the step response and the transcendental equation for the eigenvalues in the case of homogeneous particles:

$$\left(\frac{\mathrm{A}_b}{\Omega}\right)_{step,1}=\delta_0\tau+\beta_0\delta_0^2(\delta_f+\delta_a) \tag{33a}$$

$$\left(\frac{\mathrm{y}_b}{\Omega}\right)_{step,2}=6\beta_0\sum_{n=1}^{\infty}\frac{\sin(\lambda_n)-\lambda_n\cos(\lambda_n)}{\lambda_n^4[\mathrm{A}_n\sin(\lambda_n)+\mathrm{B}_n\cos(\lambda_n)]}\exp(-\lambda_n^2\tau) \tag{33b}$$

$$\tan(\lambda)=\lambda\frac{(\lambda^2/\xi-3\beta_0)}{(\lambda^2/\xi-3\beta_0)-\lambda^2};\ \lambda=\lambda_n,\ (\mathrm{n}=1, 2, \cdots, \infty) \tag{33c}$$

$$\delta_0=\frac{1}{1+\beta_0} \tag{33d}$$

$$\delta_f=\frac{1}{3\xi} \tag{33e}$$

$$\delta_a=\frac{1}{15} \tag{33f}$$

$$\mathrm{A}_n=2\left(1-\frac{1}{\xi}\right)+\left(3\beta_0-\frac{\lambda_n^2}{\xi}\right) \tag{33g}$$

$$\mathrm{B}_n=\lambda_n\left[\left(1+\frac{2}{\xi}\right)\right] \tag{33h}$$

Note that Eqs. (33a)-(33h) are simply the limits of Eqs. (32a)-(32h) at $\mathrm{x}_C\to0$. It is not surprising that the impermeable core-shell composite becomes homogeneous in both limits at $\mathrm{K}_1\to1$ & $\mathrm{a}\to1$ and $\mathrm{x}_C\to0$. Park [2002] reported different forms of the response and the transcendental equation in case of homogeneous particles, which can be readily converted to Eq. (33).

CONCLUSION

We have derived an exact analytical solution of a mathematical model describing the concentration of solute or the temperature of the fluid in a constant molar flow semi-batch well-stirred vessel in contact with permeable core-shell composites. In both limits at $\mathrm{K}_1\to1$ & $\mathrm{a}\to1$ and $\mathrm{x}_C\to0$, the solution in this work reduces to the solution in case of homogeneous particles reported in the reference. Moreover, in the limit at $\mathrm{K}_1\to0$, the solution reduces to the solution in the case of impermeable core-shell composites reported in the reference. Finally, we should remark that the analytical solution is for spherical shell and spherical core only. For non-spherical core-shell composites, the results in this work may only be approximate.

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APPENDIX: Derivation of Eq. (32) from Eq. (26) by Taking the Limit as $K_1 \to 0$

In the limit as $K_1 \to 0$, we can have easily the following from Eq. (30):

$$\alpha_1 = 1 + \lambda x_C \tan(\lambda x_C) \tag{A.1a}$$

$$\alpha_2 = \cos(\lambda) - \frac{\lambda}{\xi}\sin(\lambda) \tag{A.1b}$$

$$\alpha_3 = 1 - \lambda x_C \cot(\lambda x_C) \tag{A.1c}$$

$$\alpha_4 = \left(\frac{1}{\xi} - 1\right)\cos(\lambda) + \frac{\lambda}{\xi}\sin(\lambda) \tag{A.1d}$$

$$\alpha_5 = [-\lambda x_C \sec^2(\lambda x_C) - \tan(\lambda x_C)]\tan(\lambda x_C) \tag{A.1e}$$

$$\alpha_6 = \alpha_3 \alpha_4 \sec^2(\lambda x_C) \tag{A.1f}$$

$$\alpha_7 = \alpha_4[-\cot(\lambda x_C) + \lambda x_C \csc^2(\lambda x_C)]\tan(\lambda x_C) \tag{A.1g}$$

$$\alpha_8 = \alpha_3\left[\frac{\lambda}{\xi}\cos(\lambda) + \sin(\lambda)\right]\tan(\lambda x_C) \tag{A.1h}$$

$$\alpha_9 = \frac{\lambda}{\xi}\cos(\lambda) + \left(1 - \frac{1}{\xi}\right)\sin(\lambda) \tag{A.1i}$$

$$\beta_1 = 0 \tag{A.1j}$$

$$\beta_2 = a^2\left[\frac{\lambda x_C}{a}\csc\left(\frac{\lambda x_C}{a}\right)\right]^2[1 + \lambda x_C \tan(\lambda x_C)] \tag{A.1k}$$

$$\beta_3 = a^2\left[\left(\frac{\lambda x_C}{a}\right)\cot\left(\frac{\lambda x_C}{a}\right)\right](\lambda x_C)^2 \tag{A.1l}$$

$$\beta_4 = a^2[-1 - \lambda^2 x_C^2 - \lambda x_C \tan(\lambda x_C)] \tag{A.1m}$$

$$\beta_5 = 0 \tag{A.1n}$$

$$\gamma_1 = -2\alpha_1[\lambda\cos(\lambda) - \lambda x_C \cos(\lambda x_C) - \sin(\lambda) + \sin(\lambda x_C)] \tag{A.1o}$$

$$\gamma_2 = 2\alpha_3 \gamma_8 \tan(\lambda x_C) \tag{A.1p}$$

$$\gamma_3 = \alpha_1[-\sin(\lambda) + x_C^2 \sin(\lambda x_C)] \tag{A.1q}$$

$$\gamma_4 = \frac{-\alpha_3 \alpha_5 \gamma_8}{\lambda \alpha_1} \tag{A.1r}$$

$$\gamma_5 = \frac{-\alpha_3 \gamma_8}{\lambda}\sec^2(\lambda x_C) \tag{A.1s}$$

$$\gamma_6 = \frac{-\alpha_7 \gamma_8}{\lambda \alpha_4} \tag{A.1t}$$

$$\gamma_7 = \alpha_3[\cos(\lambda) - x_C^2 \cos(\lambda x_C)]\tan(\lambda x_C) \tag{A.1u}$$

$$\gamma_8 = -\cos(\lambda) + \cos(\lambda x_C) - \lambda\sin(\lambda) + \lambda x_C \sin(\lambda x_C) \tag{A.1v}$$

By substitution of above equations into Eq. (29), we can obtain the following using a standard software package such as MATHEMATICA®:

$$\Phi_1(\lambda) = \frac{\left\{\begin{array}{l} [-2\lambda^2 x_C^3 + \xi\{-1 + (-1 + 2x_C)(\lambda x_C)^2\}]\cos(\lambda) \\ \quad + [2\lambda^2 x_C + \xi(-1 + (\lambda x_C)^2)]\cos[\lambda(1 - 2x_C)] \\ \quad + \lambda\left\{\begin{array}{l} [1 + \lambda^2(x_C^2 - 2x_C^3)]\sin(\lambda) \\ \quad + (1 + 2\xi x_C - (\lambda x_C)^2)\sin[\lambda(1 - 2x_C)] \end{array}\right\} \end{array}\right\}}{4\lambda\xi[\cos(\lambda x_C) + \lambda x_C \sin(\lambda x_C)]^2} \tag{A.2a}$$

$$\Phi_{21}(\lambda) = 0 \tag{A.2b}$$

$$\Phi_{22}(\lambda) = \frac{3\left[\begin{array}{l} 2\lambda[-1 + \lambda^2(-1 + x_C)x_C^2]\cos(\lambda) \\ \quad + 2\lambda\{-1 + [2 + \lambda^2(-1 + x_C)]x_C\}\cos[\lambda(1 - 2x_C)] \\ \quad + \{2 + \lambda^2[-1 + x_C^2(2 + \lambda^2(-1 + 2x_C))]\}\sin(\lambda) \\ \quad + \{2 + \lambda^2[-1 + x_C(4 + (\lambda^2 - 2)x_C)]\}\sin[\lambda(1 - 2x_C)] \end{array}\right]}{4\lambda^4[\cos(\lambda x_C) + \lambda x_C \sin(\lambda x_C)]^2} \tag{A.2c}$$

$$\Psi_1(\lambda) = \frac{\left\{\begin{array}{l} \lambda[1 + (-1 + \xi)x_C]\cos[\lambda(1 - x_C)] \\ \quad + (-1 + \xi - \lambda^2 x_C)\sin[\lambda(1 - x_C)] \end{array}\right\}}{\xi[\cos(\lambda x_C) + \lambda x_C \sin(\lambda x_C)]} \tag{A.2d}$$

$$\Psi_{21}(\lambda) = 0 \tag{A.2e}$$

$$\Psi_{22}(\lambda) = \frac{3\{\lambda(-1 + x_C)\cos[\lambda(1 - x_C)] + (1 + \lambda^2 x_C)\sin[\lambda(1 - x_C)]\}}{\lambda^2[\cos(\lambda x_C) + \lambda x_C \sin(\lambda x_C)]} \tag{A.2f}$$

Thus, we have the following:

$$-\beta_0[\Psi_{22}(\lambda) + \Psi_{21}(\lambda)] = -\beta_0 \Psi_{22}(\lambda) = \frac{3\beta_0\{\lambda(1 - x_C)\cos[\lambda(1 - x_C)] - (1 + \lambda^2 x_C)\sin[\lambda(1 - x_C)]\}}{\lambda^2[\cos(\lambda x_C) + \lambda x_C \sin(\lambda x_C)]} \tag{A.3}$$

$$\Psi_1(\lambda) + \beta_0[\Psi_{22}(\lambda) + \Psi_{21}(\lambda)] = \frac{\left\{\begin{array}{l} \lambda[3\beta_0\xi(-1 + x_C) + \lambda^2(1 + (-1 + \xi)x_C)]\cos[\lambda(1 - x_C)] \\ + [3\beta_0\xi - \lambda^4 x_C + \lambda^2(-1 + \xi + 3\beta_0 x_C)]\sin[\lambda(1 - x_C)] \end{array}\right\}}{\lambda^2[\cos(\lambda x_C) + \lambda x_C \sin(\lambda x_C)]} \tag{A.4}$$

$$\begin{aligned} &\lambda^4[\Phi_1(\lambda) + \beta_0(\Phi_{21}(\lambda) + \Phi_{22})(\lambda)] \\ &-\left(\lambda^2 + \frac{\lambda^4 x_C^2}{2\alpha_1}\right)[\Psi_1(\lambda_n) + \beta_0(\Psi_{21}(\lambda) + \Psi_{22})(\lambda)] \\ &= \frac{-\lambda^2\left\{\begin{array}{l} \lambda\left[\begin{array}{l} (1 - x_C)(2 - \lambda^2 x_C)/\xi \\ + (1 + (2 + 3\beta_0)x_C - 3\beta_0 x_C^2) \end{array}\right]\cos[\lambda(1 - x_C)] \\ + \left[\begin{array}{l} -2/\xi + \lambda^2(-1/\xi - (1 + 2/\xi)x_C \\ + (1 - 1/\xi)x_C^2) + (2 + 3\beta_0(1 + x_C^2)) \end{array}\right]\sin[\lambda(1 - x_C)] \end{array}\right\}}{2[\cos(\lambda x_C) + \lambda x_C \sin(\lambda x_C)]} \end{aligned} \tag{A.5}$$

Thus, the transcendental equation for λ is:

$$\Psi_1(\lambda) + \beta_0[\Psi_{22}(\lambda) + \Psi_{21}(\lambda)] = 0 \tag{A.6a}$$

That is (from Eqs. (A.4) and (A.6a)),

$$\begin{aligned} \tan[\lambda(1 - x_C)] &= \frac{\lambda[3\beta_0\xi(-1 + x_C) + \lambda^2(1 + (-1 + \xi)x_C)]}{-[3\beta_0\xi - \lambda^4 x_C + \lambda^2(-1 + \xi + 3\beta_0 x_C)]} \\ &= \lambda\frac{\lambda^2 x_C + (\lambda^2/\xi - 3\beta_0)(1 - x_C)}{(\lambda^2/\xi - 3\beta_0)(1 + \lambda^2 x_C) - \lambda^2} \end{aligned} \tag{A.6b}$$

Next, we have the following since $\Psi_1(\lambda) + \beta_0[\Psi_{22}(\lambda) + \Psi_{21}(\lambda)] = 0$:

$$\frac{-\beta_0(\Psi_{21}(\lambda) + \Psi_{22}(\lambda))}{\lambda^4[\Phi_1(\lambda) + \beta_0(\Phi_{21}(\lambda) + \Phi_{22}(\lambda))]} = \frac{-\beta_0(\Psi_{21}(\lambda) + \Psi_{22}(\lambda))}{\left\{\begin{array}{l} \lambda^4[\Phi_1(\lambda) + \beta_0(\Phi_{21}(\lambda) + \Phi_{22}(\lambda))] \\ -\left(\lambda^2 + \frac{\lambda^4 x_C^2}{2\alpha_1}\right)\{\Psi_1(\lambda) + \beta_0[\Psi_{22}(\lambda) + \Psi_{21}(\lambda)]\} \end{array}\right\}} \tag{A.7}$$

Finally, substituting Eqs. (A.3) and (A.5) into Eq. (A.7), we have

$$\frac{-\beta_0(\Psi_{21}(\lambda) + \Psi_{22}(\lambda))}{\lambda^4[\Phi_1(\lambda) + \beta_0(\Phi_{21}(\lambda) + \Phi_{22}(\lambda))]}$$

$$= \frac{6\beta_0\{(1+\lambda^2 x_C)\sin[\lambda(1-x_C)] - \lambda(1-x_C)\cos[\lambda(1-x_C)]\}}{\lambda^4\{A_n(\lambda)\sin[\lambda(1-x_C)] + B_n(\lambda)\cos[\lambda(1-x_C)]\}} \quad \text{(A.8a)}$$

$$A_n(\lambda) = 2\left(1-\frac{1}{\xi}\right) + \left(3\beta_0 - \frac{\lambda^2}{\xi}\right) - \left(1+\frac{2}{\xi}\right)\lambda^2 x_C + \left(\lambda^2 + 3\beta_0 - \frac{\lambda^2}{\xi}\right)x_C^2 \quad \text{(A.8b)}$$

$$B_n(\lambda) = \lambda\left[\left(1+\frac{2}{\xi}\right) + \left\{3\beta_0 - \frac{\lambda^2}{\xi} + 2\left(1-\frac{1}{\xi}\right)\right\}x_C - \left(3\beta_0 - \frac{\lambda^2}{\xi}\right)x_C^2\right] \quad \text{(A.8c)}$$

This completes the derivation of Eq. (32) from Eq. (26) by taking the limit as $K_1 \rightarrow 0$.

NOMENCLATURE

- C : concentration in particle phase [mol/m^3]
- C_0 : reference concentration, on which dimensionless concentration is based [mol/m^3]
- C_b : concentration in fluid phase [mol/m^3]
- C_s : concentration in fluid phase at particle surface [mol/m^3]
- C_1, C_2: concentration in the core and the shell within particle, respectively [mol/m^3]
- c_b, c_m : molar heat capacity of fluid phase and mean molar heat capacity of particle phase, respectively [J/mol·K]
- D_1, D_2 : effective diffusivity in the core and shell, respectively [m^2/s]
- h_f : external film heat transfer coefficient [J/m^2·s·K]
- K_1, K_2 : dimensionless contact affinity at core-shell interface and fluid-particle interface, respectively
- k_f : external film mass transfer coefficient [m/s]
- k_1, k_2 : effective thermal diffusivity in the core and shell, respectively [m^2/s]
- $\dot{N}$: molar flow rate of adsorbate into vessel [mol/sec]
- R : radius of adsorbent particle [m]
- R_C : radius of inert core [m]
- r : radius variable of adsorbent particle [m]
- T : temperature in particle phase [K]
- T_0 : reference temperature, on which dimensionless temperature is based [K]
- T_b : temperature in fluid phase [K]
- T_i : feed temperature, or temperature within vessel at t=0 [K]
- T_s : temperature in fluid phase at particle surface [K]
- T_1, T_2 : temperature in the core and the shell within particle, respectively [K]
- t : time variable [s]
- V_b, V: volume of fluid phase and total particles including cores and shells within vessel, respectively [m^3]
- κ_s : thermal conductivity of the outer shell of the core-shell composite [J/m·s·K]
- ρ_b, ρ_m: molar density of fluid phase and mean molar density of particle phase, respectively [mol/m^3]

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