THE UNSTEADY-STATE SOLUTION FOR A FINITE DISPERSION-TYPE CATALYTIC PACKED-BED TUBULAR REACTOR

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(Received 3 September 1984 • accepted 25 March 1985)

Abstract—The unsteady-state solution is obtained by an operator theory in functional analysis setting for a general finite catalytic packed-bed tubular reactor model with axial dispersion in the bed, mass transfer between the catalyst particles and the flowing phase, and intraparticle diffusion and surface reaction in the catalyst particles.

INTRODUCTION

Catalytic packed-bed reactors are most often used in chemical processes and diverse models with varying degrees of complexity have been proposed in the past to analyze and predict process behavior and reactor performances. The physicochemical phenomena taking place inside the reactors are quite complex. From the macroscopic point of view, however, they can be classified into the following main events: dispersion of reacting mass by the complex flow through the packed bed, mass transfer between the flowing phase and the exterior surface of the catalysts, intraparticle diffusion through porous structures of the catalyst, and adsorption and reaction on the surface within the pores. All or part of these phenomena are usually taken into account in the model depending upon the relative significance of each phenomenon on the overall behavior of the reactor and upon the intended objective of the study.

A quite comprehensive model incorporating the above phenomena except the reaction on the surface was first proposed by Kubin [1,2] and Kucera [3]. The model equations were then solved in the Laplace-transformed domain. They derived moment expressions as well from the solution, relating model parameters to the moments. The moment method was further elaborated and extensively used by many other workers in the estimation of rate parameters of the model (for example [4-7]). The moment method, however, is known to suffer from an unequal weighting in the range of experimental responses [8,9]. Higher moments beyond the second, therefore, cannot be satisfied and have to be ignored in parameter estimations. An apparent alternative approach is a frequency-domain analysis which provides a uniform weighting in the time-domain by Parseval's theorem. Indeed, a considerable number of workers pursued this approach [10-12]. On the other hand, the direct time-domain analysis seems more attractive. Wakao and coworkers [9,13,14] have shown that the parameter estimation is most satisfactory when the time-domain solution is used. However, the analytical time-domain solution is not easily obtainable. Therefore, one most likely has to resort to numerical methods, perhaps combined with inverse Laplace transforms and Fourier series. In view of this, an analytical solution, if available, is very useful particularly when one wants to investigate the effects of process parameters on the behavior of the reactor. In this direction, Rasmuson and Neretnieks [15,16] obtained an analytical solution in the form of an indefinite integral by a Laplace inversion formula for the Kubin's model [2]. Their model assumed an infinitely long tubular reactor (thus the exit boundary condition was at infinity) with zero initial and constant feed conditions.

In this paper, we present the analytical solution for a finite-length catalytic packed-bed reactor model in which the surface reaction is included. In addition, arbitrary initial and general boundary conditions are considered. The method of solution is by an operator theory

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in functional analysis setting as applied in our previous paper [17]. The method is useful and elegant in the sense that it easily lends itself to overcoming seemingly insurmountable algebraic manipulations that might otherwise be encountered and yet reveals certain structural properties of the solution. We add that the method was first used by Ramkrishna and Amundson [18] to solve chemical engineering problems and that further references can be found in the paper [17].

A PACKED-BED REACTOR MODEL

We consider a tubular reactor packed with spherical catalyst particles of uniform size in which a diffusion and a first-order surface reaction take place. Axial dispersion also takes place in the flowing phase within the reactor. We assume that the catalyst particle-diameter is small compared with the overall bed length and that the rate of surface reaction and the diffusion are slow compared with the adsorption rate on the pore surfaces. Thus the adsorbed phase is assumed to be in local equilibrium.

The mass balance in the flowing phase of the reactor leads to

$$D_z\frac{\partial^2 C}{\partial \bar{z}^2}-v\frac{\partial C}{\partial \bar{z}}-\frac{3D_e}{R}\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\left(\frac{\partial C_p}{\partial \bar{r}}\right)\Big|_{\bar{r}=R}=\frac{\partial C}{\partial \bar{t}} \quad (1)$$

and that in the spherical catalyst particles give

$$D_e\left(\frac{\partial^2 C_p}{\partial \bar{r}^2}+\frac{2}{\bar{r}}\frac{\partial C_p}{\partial \bar{r}}\right)-kC_a=\varepsilon_p\frac{\partial C_p}{\partial \bar{t}}+\frac{\partial C_a}{\partial \bar{t}} \quad (2)$$

The local adsorption equilibrium relationship is given by

$$C_a=K_A C_p \quad (3)$$

The initial conditions (I.C.) and the boundary conditions (B.C.) are

I. C.

$$C(\bar{z},\,0)=G(\bar{z}) \quad (4)$$

$$C_p(\bar{r},\,\bar{z},\,0)=H(\bar{r},\,\bar{z}) \quad (5)$$

B.C.

$$D_e\frac{\partial C_p}{\partial \bar{r}}\Big|_{\bar{r}=R}=\varepsilon_p k_f(C-C_p|_{\bar{r}=R}) \quad (6)$$

$$C(0^+,\bar{t})-\frac{D_z}{v}\frac{\partial C}{\partial \bar{z}}\Big|_{\bar{z}=0^+}=F(\bar{t}) \quad (7)$$

$$D_z\frac{\partial C}{\partial \bar{z}}\Big|_{\bar{z}=l^-}=0 \quad (8)$$

where G(z), H(r,z) and F(t) are arbitrary functions describing the initial concentration distribution in the flowing phase, that in the particle, and the feed condition at the reactor inlet, respectively. Here $\bar{z}$, $\bar{r}$ and $\bar{t}$ are the actual coordinates and time which will be made dimensionless shortly. The boundary conditions in Eqs. (7) and (8) are the most commonly used ones at the inlet and the exit of the reactor for finite reactor models. Our objective is to find $C(\bar{z},\bar{t})$ and $C_p(\bar{r},\bar{z},\bar{t})$ at position $(\bar{r},\bar{z})$ at time $\bar{t}$, or equivalently the dimensionless concentrations c(z,t) and $c_p(r,z,t)$ defined below.

We define the following dimensionless quantities and coordinates:

$$Pe=\frac{vl}{D_z},\quad r=\frac{\bar{r}}{R},\quad t=\frac{v\bar{t}}{l},\quad z=\frac{\bar{z}}{l},\quad \alpha=\frac{l\,D_e}{vR^2},\quad \beta=\frac{Rk_f\varepsilon_p}{D_e},$$

$$\Phi=R\sqrt{\frac{kK_A}{D_e}},\quad f(t)=\frac{F(\bar{t})}{C_0},\quad g(z)=\frac{G(\bar{z})}{C_0},\quad h(r,z)=\frac{H(\bar{r},\bar{z})}{C_0} \quad (9)$$

$$c(z,t)=\frac{C(\bar{z},\bar{t})}{C_0},\quad c_p(r,z,t)=\frac{C_p(\bar{r},\bar{z},\bar{t})}{C_0} \quad (10)$$

In addition, if we introduce the following transformations

$$u_1(z,t)=e^{-\frac{Pe}{2}z}c(z,t) \quad (11)$$

$$u_2(r,z,t)=r\,c_p(r,z,t) \quad (12)$$

Eqs. (1) - (3) become

$$\frac{\partial u_1}{\partial t}=\frac{1}{Pe}\frac{\partial^2 u_1}{\partial z^2}-\left\{3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)+\frac{Pe}{4}\right\}u_1+3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)e^{-\frac{Pe}{2}z}(u_2|_{r=1}) \quad (13)$$

$$\frac{\partial u_2}{\partial t}=\frac{\alpha}{\varepsilon_p+K_A}\left(\frac{\partial^2 u_2}{\partial r^2}-\Phi^2 u_2\right) \quad (14)$$

where the convective term in the first equation has now been eliminated and the second equation is of the flat-plate geometry type. Thus the transformed equations, as will be seen in the analysis to follow, will turn out to be more convenient and easily tractable in the self-adjoint formalism. The transformations also induce the change in the initial and boundary conditions:

I.C.

$$u_1(z,\,0)=e^{-\frac{Pe}{2}z}g(z) \quad (15)$$

$$u_2(r,z,\,0)=rh(r,z) \quad (16)$$

B.C.

$$u_1(0^+,t)-\frac{2}{Pe}\left(\frac{\partial u_1}{\partial z}\right)\Big|_{z=0^+}=2f(t) \quad (17)$$

$$u_1(1^-,t)+\frac{2}{Pe}\left(\frac{\partial u_1}{\partial z}\right)\Big|_{z=1^-}=0 \quad (18)$$

$$u_2|_{r=0}=0 \quad (19)$$

$$\frac{\partial u_2}{\partial r}\Big|_{r=1}=\beta e^{\frac{Pe}{2}z}u_1(z,t)+(1-\beta)u_2|_{r=1} \quad (20)$$

THE MODEL IN AN OPERATOR FORM

In order to shape the problem in the framework of

operator theory approach, we recast the problem in an operator form. First we define an operator $\underset{\sim}{L}$ by

$$\underset{\sim}{L}=\begin{pmatrix} -\frac{1}{Pe}\frac{\partial^2}{\partial z^2}+\left[3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)+\frac{Pe}{4}\right], & -\lim_{r\to 1}3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)e^{-\frac{Pe}{2}z} \\ 0 & , \quad -\frac{\alpha}{\varepsilon_p+K_A}\left(\frac{\partial^2}{\partial r^2}-\Phi^2\right) \end{pmatrix} \tag{21}$$

The boundary operators $\underset{\sim}{Z}_1$, $\underset{\sim}{Z}_2$, $\underset{\sim}{R}_1$ and $\underset{\sim}{R}_2$ are likewise defined by

$$\underset{\sim}{Z}_1=\lim_{z\to 0^+}\begin{bmatrix} 1-\frac{2}{Pe}\frac{\partial}{\partial z} & 0 \\ 0 & 0 \end{bmatrix} \tag{22}$$

$$\underset{\sim}{Z}_2=\lim_{z\to 1^-}\begin{bmatrix} 1+\frac{2}{Pe}\frac{\partial}{\partial z} & 0 \\ 0 & 0 \end{bmatrix} \tag{23}$$

$$\underset{\sim}{R}_1=\lim_{r\to 0}\begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \tag{24}$$

$$\underset{\sim}{R}_2=\lim_{r\to 1}\begin{bmatrix} 0 & 0 \\ \beta e^{\frac{Pe}{2}z} & -\frac{\partial}{\partial r}+(1-\beta) \end{bmatrix} \tag{25}$$

We also let

$$\underset{\sim}{u}=\begin{bmatrix} u_1(z,t) \\ u_2(r,z,t) \end{bmatrix} \quad \underset{\sim}{a}(r,z)=\begin{bmatrix} e^{-\frac{Pe}{2}z}g(z) \\ r\,h(r,z) \end{bmatrix}$$

$$\underset{\sim}{b}(t)=\begin{bmatrix} 2f(t) \\ 0 \end{bmatrix} \tag{26}$$

Then Eqs. (13) - (20) can be stated as

$$\underset{\sim}{L}\,\underset{\sim}{u}=-\frac{\partial \underset{\sim}{u}}{\partial t} \tag{27}$$

I. C.

$$\underset{\sim}{u}|_{t=0}=\underset{\sim}{a}(r,z) \tag{28}$$

B. C.

$$\underset{\sim}{Z}_1\underset{\sim}{u}=\underset{\sim}{b}(t) \tag{29}$$

$$\underset{\sim}{Z}_2\underset{\sim}{u}=\underset{\sim}{0} \tag{30}$$

$$\underset{\sim}{R}_1\underset{\sim}{u}=\underset{\sim}{0} \tag{31}$$

$$\underset{\sim}{R}_2\underset{\sim}{u}=\underset{\sim}{0} \tag{32}$$

At this stage, the gain is not obvious except the notational simplicity.

A HILBERT SPACE METHOD

Since the model has been recast into an operator form, we can use the Hilbert space approach of our previous paper [17]. The same abstract reasoning and argument can be applied, but the actual calculations and operations are quite different. The gist of the approach is that we first seek an appropriate Hilbert space on which the operator $\underset{\sim}{L}$ is self-adjoint. Then we show that the operator $\underset{\sim}{L}$ satisfies Garding's inequality. The last condition is necessary to ensure that the eigenvalues of $\underset{\sim}{L}$ are all positive and $\underset{\sim}{L}$ possesses a compact normal resolvent. Such a structural analysis not only directly leads to a neat analytical solution, but also reduces the amount of algebraic manipulations.

We define a space H_t as the Cartesian product space of two spaces H_1 and H_2:

$$H_t=H_1\times H_2 \tag{33}$$

with an inner product defined for any two vectors $\underset{\sim}{w}=(w_1\ w_2)^T$ and $\underset{\sim}{v}=(v_1\ v_2)^T$ in H_t by

$$\begin{aligned}(\underset{\sim}{w},\underset{\sim}{v})&=(w_1,v_1)_1+(w_2,v_2)_2\\&=\int_0^1 w_1(z,t)v_1(z,t)\,dz+3(\varepsilon_p+K_A)\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\times\\&\quad\int_0^1\int_0^1 e^{-Pez}w_2(r,z,t)v_2(r,z,t)\,dr\,dz\end{aligned} \tag{34}$$

where $(\ ,\ )_1$ and $(\ ,\ )_2$ are the inner products in H_1 and H_2, respectively. Here we treat t as a parameter. The space H_1 is $L_2[0,1]$, the space of square integrable functions in z for all t $(0<t<\infty)$, and the space H_2 is essentially $L_2[[0,1]\times[0,1]]$, the space of square integrable functions in z and r for all t $(0<t<\infty)$ except the weighting factor $3(\varepsilon_p+K_A)\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)e^{Pez}$. It is easy to show that H_t is complete and therefore is a Hilbert space. When the elements in H_t do not depend on t, we denote H_t simply by H.

We define the domain of the operator $\underset{\sim}{L}$ as

$$\begin{aligned}D=\{\underset{\sim}{w}\,|\,\underset{\sim}{w}=(w_1\ w_2)^T\in H,\ w_1\in C^2[0,1]\ \text{for z},\\ w_2\in C^2[0,1]\ \text{for r},\\ \underset{\sim}{Z}_1\underset{\sim}{w}=\underset{\sim}{Z}_2\underset{\sim}{w}=\underset{\sim}{R}_1\underset{\sim}{w}=\underset{\sim}{R}_2\underset{\sim}{w}=0\}\end{aligned} \tag{35}$$

Since D is a dense subspace of H, the operator $\underset{\sim}{L}$ is densely defined on H. We denote the adjoint operator of $\underset{\sim}{L}$ as $\underset{\sim}{L}^*$ and the domain of $\underset{\sim}{L}^*$ as D^*, then for two vectors $\underset{\sim}{w}=(w_1\ w_2)^T\in D$ and $\underset{\sim}{v}=(v_1\ v_2)^T\in D^*$ we have

$$(\underset{\sim}{L}\,\underset{\sim}{w},\ \underset{\sim}{v})=\int_0^1\left\{-\frac{1}{Pe}\frac{\partial^2 w_1}{\partial z^2}+\left[3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)+\frac{Pe}{4}\right]w_1-3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)e^{-\frac{Pe}{2}z}w_2|_{r=1}\right\}v_1\,dz$$

$$+3(\varepsilon_p+K_A)\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\int_0^1\int_0^1-\frac{\alpha}{\varepsilon_p+K_A}\left(\frac{\partial^2 w_2}{\partial r^2}-\Phi^2 w_2\right)v_2 e^{-Pez}drdz=-\frac{1}{Pe}\times$$

$$\left(\frac{\partial w_1}{\partial z}v_1-w_1\frac{\partial v_1}{\partial z}\right)\Big|_{z=0}^{1}+\int_0^1\left\{-\frac{1}{Pe}\frac{\partial^2 v_1}{\partial z^2}+\left[3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)+\frac{Pe}{4}\right)v_1\right\}w_1dz-$$

$$3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\int_0^1 e^{-\frac{Pe}{2}z}w_2|_{r=1}v_1dz-3\alpha\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\times\int_0^1\left(\frac{\partial w_2}{\partial r}v_2-w_2\frac{\partial v_2}{\partial r}\right)\Big|_{r=0}^{1}e^{-Pez}dz$$

$$-3\alpha\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\int_0^1\int_0^1\left(\frac{\partial^2 v_2}{\partial r^2}-\Phi^2 v_2\right)w_2 e^{-Pez}drdz=(\underset{\sim}{w},\underset{\sim}{L}\underset{\sim}{v}) \tag{36}$$

showing that $\underset{\sim}{L}=\underset{\sim}{L}^*$ and $D=D^*$. Therefore $\underset{\sim}{L}$ is a self-adjoint operator. Thus the eigenvalues of $\underset{\sim}{L}$ are all real and the eigenvectors for distinct eigenvalues are mutually orthogonal. We further calculate to obtain

$$(\underset{\sim}{L}\underset{\sim}{w},\underset{\sim}{w})=\int_0^1\left\{-\frac{1}{Pe}\frac{\partial^2 w_1}{\partial z^2}+\left[3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)+\frac{Pe}{4}\right]w_1-3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)e^{-\frac{Pe}{2}z}w_2|_{r=1}\right\}w_1dz$$

$$+3(\varepsilon_p+K_A)\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\int_0^1\int_0^1-\frac{\alpha}{\varepsilon_p+K_A}\left(\frac{\partial^2 w_2}{\partial r^2}-\Phi^2 w_2\right)w_2 e^{-Pez}\,drdz=$$

$$\frac{1}{2}\left[(w_1|_{z=1})^2+(w_1|_{z=0})^2\right]+\frac{1}{Pe}\int_0^1\left(\frac{\partial w_1}{\partial z}\right)^2dz+\left[3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)+\frac{Pe}{4}\right]\int_0^1 w_1^2dz$$

$$-6\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\int_0^1 e^{-\frac{Pe}{2}z}w_2|_{r=1}w_1dz-3\alpha(1-\beta)\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\int_0^1(w_2|_{r=1})^2e^{-\frac{Pe}{2}z}dz+$$

$$3\alpha\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\int_0^1\int_0^1\left[\left(\frac{\partial w_2}{\partial r}\right)^2+\Phi^2 w_2^2\right]e^{-Pez}\,drdz\geq\frac{Pe}{4}\int_0^1 w_1^2dz+3\alpha\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\Phi^2$$

$$\int_0^1\int_0^1 w_2^2\,e^{-Pez}drdz\geq\theta(\underset{\sim}{w},\underset{\sim}{w}) \tag{37}$$

where $\theta=\min\left\{\frac{Pe}{4},\frac{\alpha\Phi^2}{\varepsilon_p+K_A}\right\}$ is positive. In converting the equality to inequality we used the obvious relationships

$$-2\int_0^1 e^{-\frac{Pe}{2}z}w_2|_{r=1}w_1dz\geq-\int_0^1 e^{-Pez}(w_2|_{r=1})^2dz-\int_0^1(w_1)^2dz \tag{38}$$

$$\int_0^1\left(\frac{\partial w_2}{\partial r}\right)^2dr\geq\left[\int_0^1\frac{\partial w_2}{\partial r}dr\right]^2=(w_2|_{r=1})^2 \tag{39}$$

Equation (37) shows that operator $\underset{\sim}{L}$ is strictly positive on D which is a dense subspace of H. Thus the eigenvalues of $\underset{\sim}{L}$ are all positive.

AN ORTHONORMAL BASIS AND THE SOLUTION

We now try to find an orthonormal basis in the Hilbert space. H. Since Eq. (37) is also a Garding's inequality, the inverse opertor $\underset{\sim}{L}^{-1}$ not only exists but also is compact, i.e., $\underset{\sim}{L}$ has a compact normal resolvent. Thus $\underset{\sim}{L}$ can be expressed as a weighted sum of projections. This implies that $\underset{\sim}{L}$ has a countable number positive eigenvalues and that the set of corresponding eigenvectors is complete and forms an orthonormal basis of D. Because D is dense in H, the set of eigenvectors of $\underset{\sim}{L}$ is also an orthonormal basis of H.

With this structural insight, we now determine the eigenvalues $\{\lambda\}$ and the eigenvectors $\{\underset{\sim}{\psi}\}$ of $\underset{\sim}{L}$ from

$$\underset{\sim}{L}\,\underset{\sim}{\psi}=\lambda\,\underset{\sim}{\psi} \tag{40}$$

where $\underset{\sim}{\psi}=(\psi_1\ \psi_2)^T$ in D. Rewriting Eq. (40), we have

$$-\frac{1}{Pe}\frac{\partial^2\psi_1}{\partial Z^2}+\left[3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)+\frac{Pe}{4}\right]\psi_1-$$

$$3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)e^{-\frac{Pe}{2}z}(\psi_2|_{r=1})=\lambda\psi_1 \tag{41}$$

$$-\frac{\alpha}{\varepsilon_p+K_A}\left(\frac{\partial^2\psi_2}{\partial r^2}-\Phi^2\psi_2\right)=\lambda\psi_2 \tag{42}$$

Since $\underset{\sim}{\psi}$ is in D, we have $\underset{\sim}{R}_1\underset{\sim}{\psi}=\underset{\sim}{R}_2\underset{\sim}{\psi}=0$, i.e., for ψ_2,

$$\psi_2|_{r=0}=0 \tag{43}$$

$$\beta\,e^{\frac{Pe}{2}z}\psi_1-\frac{\partial\psi_2}{\partial r}\Big|_{r=1}+(1-\beta)\psi_2|_{r=1}=0 \tag{44}$$

Solving Eq. (42) with Eqs. (43) and (44), we readily obtain

$$\psi_2=\frac{\beta\,e^{\frac{Pe}{2}z}\sin(\sqrt{\nu}\,r)}{\sqrt{\nu}\,\cos\sqrt{\nu}+(\beta-1)\,\sin\sqrt{\nu}}\psi_1 \tag{45}$$

where

$$\nu=\left(\frac{\varepsilon_p+K_A}{\alpha}\right)\lambda-\Phi^2$$

Substituting Eq. (46) into Eq. (41), we get

$$\frac{\partial^2 \psi_1}{\partial z^2} + \sigma \psi_1 = 0 \tag{47}$$

where

$$\sigma = \mathrm{Pe}\left[\lambda - 3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right) - \frac{\mathrm{Pe}}{4} + 3\alpha\beta^2\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\times \frac{\sin\sqrt{\nu}}{\sqrt{\nu}\cos\sqrt{\nu} + (\beta-1)\sin\sqrt{\nu}}\right] \tag{48}$$

subject to $\underset{\sim}{Z}_1 \underset{\sim}{\psi} = \underset{\sim}{Z}_2 \underset{\sim}{\psi} = 0$, i.e., for ψ_1,

$$\psi_1|_{z=0^+} - \frac{2}{\mathrm{Pe}}\frac{\partial \psi_1}{\partial z}|_{z=0^+} = 0 \tag{49}$$

$$\psi_1|_{z=1^-} + \frac{2}{\mathrm{Pe}}\frac{\partial \psi_1}{\partial z}|_{z=1^-} = 0 \tag{50}$$

Equation (47) with Eqs. (49) and (50) is a classical Sturm-Liouville problem for the operator $-\frac{\partial^2}{\partial z^2}$ with σ representing its eigenvalues. Therefore, the eigenvalues $\{\sigma\}$ of Eq. (47) are again all positive and the eigenvectors $\{\psi_{1i}\}$ for distinct eigenvalues are orthogonal. If we donate σ by μ^2, then μ_i is the ith positive root of the transcendental equation

$$\tan\mu = \frac{\mathrm{Pe}\,\mu}{\mu^2 - \frac{\mathrm{Pe}^2}{4}} \tag{51}$$

and the corresponding eigenvectors of Eq. (47) are

$$\psi_{in} = \mu_i \cos(\mu_i z) + \frac{\mathrm{Pe}}{2}\sin(\mu_i z) \quad i = 1, 2, 3\cdots \tag{52}$$

Rearranging Eq. (48), we have

$$\sqrt{\left(\frac{\varepsilon_p + K_A}{\alpha}\right)\lambda - \Phi^2}\cot\sqrt{\left(\frac{\varepsilon_p + K_A}{\alpha}\right)\lambda - \Phi^2} = \frac{3\alpha\beta^2\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)}{\frac{\mu_i^2}{\mathrm{Pe}} - \lambda - 3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right) + \frac{\mathrm{Pe}}{4}} + 1 - \beta \tag{53}$$

Each μ_i value of Eq. (51) gives rise to an infinite mumber of positive eigenvalues. We denote them by $\{\lambda_i^{(k)}\}$ (k=1,2,3...), which can be determined from Eq. (53). The corresponding eigenvectors are

$$\underset{\sim}{\psi}_i^{(k)} = \begin{pmatrix} \psi_{i1}^{(k)} \\ \psi_{i2}^{(k)} \end{pmatrix} = \begin{pmatrix} \mu_i\cos(\mu_i z) + \frac{\mathrm{Pe}}{2}\sin(\mu_i z) \\ \frac{\beta\, e^{\frac{\mathrm{Pe}}{2}z}\sin(\sqrt{\nu_i^{(k)}}\, r)}{\sqrt{\nu_i^{(k)}}\cos\sqrt{\nu_i^{(k)}} + (\beta-1)\sin\sqrt{\nu_i^{(k)}}}\psi_{i1}^{(k)} \end{pmatrix} \quad i, k = 1, 2, 3, \cdots \tag{54}$$

where

$$\nu_i^{(k)} = \left(\frac{\varepsilon_p + K_A}{\alpha}\right)\lambda_i^{(k)} - \Phi^2 \tag{55}$$

As was already shown from the self-adjointness of $\underset{\sim}{L}$, these eigenvectors are mutually orthogonal, i.e., for $i \neq j$ or $k \neq l$ we have.

$$(\underset{\sim}{\psi}_i^{(k)}, \underset{\sim}{\psi}_j^{(l)}) = 0 \quad i, j, k, l = 1, 2, 3, \cdots \tag{56}$$

and for $k = l$ and i = j, we have

$$\| \underset{\sim}{\psi}_i^{(k)} \| = \sqrt{(\underset{\sim}{\psi}_i^{(k)}, \underset{\sim}{\psi}_i^{(k)})} = \frac{1}{2}\sqrt{(\mu_i^2 + \mathrm{Pe} + \frac{\mathrm{Pe}^2}{4})\{2 + \frac{(\varepsilon_p + K_A)\left[\frac{\mu_i^2}{\mathrm{Pe}} - \lambda_i^{(k)} - 3\alpha\beta\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right) + \frac{\mathrm{Pe}}{4}\right]^2}{3\alpha^2\beta^2\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\sin^2\sqrt{\nu_i^{(k)}}}\left(1 - \frac{\sin 2\sqrt{\nu_i^{(k)}}}{2\sqrt{\nu_i^{(k)}}}\right)\}} \tag{57}$$

Normalizing the eigenvectors $\{\psi_i^{(k)}\}$ with this norm we obtain

$$\underset{\sim}{\phi}_i^{(k)} = \frac{1}{\| \underset{\sim}{\psi}_i^{(k)} \|}\underset{\sim}{\psi}_i^{(k)} = \begin{pmatrix} \phi_{i1}^{(k)} \\ \phi_{i2}^{(k)} \end{pmatrix}$$

$$= \frac{1}{\| \underset{\sim}{\psi}_i^{(k)} \|}\begin{pmatrix} \mu_i\cos(\mu_i z) + \frac{\mathrm{Pe}}{2}\sin(\mu_i z) \\ \frac{\beta}{\sqrt{\nu_i^{(k)}}\cos\sqrt{\nu_i^{(k)}} + (\beta-1)\sin\sqrt{\nu_i^{(k)}}}\, e^{\frac{\mathrm{Pe}}{2}z}\sin(\sqrt{\nu_i^{(k)}}\, r)\left[\mu_i\cos(\mu_i z) + \frac{\mathrm{Pe}}{2}\sin(\mu_i z)\right] \end{pmatrix} \quad i, k = 1, 2, 3, \cdots \tag{58}$$

Thus we have a countable number of eigenvalues $\{\lambda_i^{(k)}\}$ (i,k=1,2,3...) and the corresponding orthonormal eigenvectors $\{\underset{\sim}{\phi}_i^{(k)}\}$, which form an orthonormal basis of H.

We now return to Eqs. (13)-(20), or Eqs. (27)-(32). We difine a subspace D_t of H_t:

$$D_t = \{\underset{\sim}{u} = \begin{pmatrix} u_1(z,t) \\ u_2(r,z,t) \end{pmatrix} \mid \underset{\sim}{u} \in H_t,\ u_1 \in C^2[0,1] \text{ for } z,\ u_2 \in C^2[0,1] \text{ for } r,\ \frac{\partial u_1}{\partial t} \in C^0([0,1]\times[0,\infty)),\ \frac{\partial u_2}{\partial t} \in C^0([0,1]\times[0,1]\times[0,\infty)),\ Z_1\underset{\sim}{u} = b(t),\ Z_2\underset{\sim}{u} = R_1\underset{\sim}{u} = R_2\underset{\sim}{u} = 0\} \tag{59}$$

Since for any $t>0$, $\{\underset{\sim}{\phi}_i^{(k)}\}$ is an orthonormal basis in H_t and for any $t>0$ and $\underset{\sim}{b}(t) \in H_t$, subspace D_t is dense in H_t we can expand $\underset{\sim}{u}$ in the orthonormal basis $\{\underset{\sim}{\phi}_i^{k}\}$ as

$$\underset{\sim}{u} = \sum_{i=1}^{\infty}\sum_{k=1}^{\infty} (\underset{\sim}{u}, \underset{\sim}{\phi}_i^{(k)})\underset{\sim}{\phi}_i^{(k)} \tag{60}$$

for $\underset{\sim}{a}(r,z) \in H_t$ and $\underset{\sim}{u} \in Dt$. The coefficients $(\underset{\sim}{u}, \underset{\sim}{\phi}_i^{(k)})$ can be determined from the inner product of Eq. (27) with $\underset{\sim}{\phi}_i^{(k)}$:

$$(L\underset{\sim}{u}, \underset{\sim}{\phi}_i^{(k)}) = -\frac{\partial}{\partial t}(\underset{\sim}{u}, \underset{\sim}{\phi}_i^{(k)}) \tag{61}$$

Since $\underset{\sim}{\phi}_i^{k} \in D$, $\underset{\sim}{u} \in D_t$, the left-hand side gives

$$(L\underset{\sim}{u}, \underset{\sim}{\phi}_i^{(k)}) = -f(t)\,\phi_{i1}^{(k)}|_{z=0} + (\underset{\sim}{u}, L\underset{\sim}{\phi}_i^{(k)}) = \lambda_i^{(k)}(\underset{\sim}{u}, \underset{\sim}{\phi}_i^{(k)}) - \frac{\mu_i}{\|\underset{\sim}{\psi}_i^{(k)}\|} f(t) \tag{62}$$

Combining Eq. (61) with Eq. (62), we have

$$\frac{d}{dt}(\underset{\sim}{u}, \underset{\sim}{\phi}_i^{(k)}) + \lambda_i^{(k)}(\underset{\sim}{u}, \underset{\sim}{\phi}_i^{(k)}) = \frac{\mu_i}{\|\underset{\sim}{\psi}_i^{(k)}\|} f(t) \tag{63}$$

The initial condition is obtained from Eq.(28) as

$$(\underset{\sim}{u}|_{t=0}, \underset{\sim}{\phi}_i^{(k)}) = (\underset{\sim}{a}(r,z), \underset{\sim}{\phi}_i^{(k)}) = \int_0^1 e^{-\frac{Pe}{2}z} g(z)\,\phi_{i1}^{(k)}(z)\,dz + 3(\varepsilon_p + K_A)\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\times \int_0^1\int_0^1 e^{-Pez} rh(r,z)\,\phi_{i2}^{(k)}(r,z)\,drdz$$

The solution of Eq. (63) subject to initial condition Eq. (64) is given by

$$(\underset{\sim}{u}, \underset{\sim}{\phi}_i^{(k)}) = e^{-\lambda_i^{(k)}t}\left[(\underset{\sim}{a}(r,z), \underset{\sim}{\phi}_i^{(k)}) + \frac{\mu_i}{\|\underset{\sim}{\psi}_i^{(k)}\|}\times \int_0^t e^{\lambda_i^{(k)}\tau} f(\tau)\,d\tau\right] \tag{65}$$

Substituting Eq. (65) into Eq. (60), we get

$$\underset{\sim}{u} = \sum_{i=1}^{\infty}\sum_{k=1}^{\infty}\left\{(\underset{\sim}{a}(r,z), \underset{\sim}{\phi}_i^{(k)}) + \frac{\mu_i}{\|\underset{\sim}{\psi}_i^{(k)}\|}\int_0^t e^{\lambda_i^{(k)}\tau} \times f(\tau)\,d\tau\right\} e^{-\lambda_i^{(k)}t}\underset{\sim}{\phi}_i^{(k)} \tag{66}$$

This is the solution sought for Eqs. (13)- (20).

We now revert to the original dimensionless concentrations c(z,t) and c_p(r,z,t). Then in view of Eqs.(11), (12) and (66) we have the final solution:

$$c(z,t) = e^{\frac{Pe}{2}z}\sum_{i=1}^{\infty}\sum_{k=1}^{\infty}\left\{\int_0^1 e^{-\frac{Pe}{2}z} g(z)\,\phi_{i1}^{(k)}(z)\,dz + 3(\varepsilon_p+K_A)\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\int_0^1\int_0^1 e^{-Pez} rh(r,z)\times \phi_{i2}^{(k)}(r,z)\,drdz + \frac{\mu_i}{\|\underset{\sim}{\psi}_i^{(k)}\|}\int_0^t e^{\lambda_i^{(k)}\tau} f(\tau)\,d\tau\right\}\times e^{-\lambda_i^{(k)}t}\phi_{i1}^{(k)}(z) \tag{67}$$

$$c_p(r,z,t) = \frac{1}{r}\sum_{i=1}^{\infty}\sum_{k=1}^{\infty}\left\{\int_0^1 e^{-\frac{Pe}{2}z} g(z)\,\phi_{i1}^{(k)}(z)\,dz + 3(\varepsilon_p+K_A)\left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\int_0^1\int_0^1 e^{-Pez} rh(r,z)\times \phi_{i2}^{(k)}(r,z)\,drdz + \frac{\mu_i}{\|\underset{\sim}{\psi}_i^{(k)}\|}\int_0^t e^{\lambda_i^{(k)}\tau}\times f(\tau)\,d\tau\right\} e^{-\lambda_i^{(k)}t}\phi_{i2}^{(k)}(r,z) \tag{68}$$

For large t, the effect of g(z) and h(r,z) will disappear. Then we have for large t

$$c(z,t) = e^{\frac{Pe}{2}z}\sum_{i=1}^{\infty}\sum_{k=1}^{\infty}\frac{\mu_i}{\|\underset{\sim}{\psi}_i^{(k)}\|}\int_0^t e^{-\lambda_i^{(k)}(t-\tau)}\times f(\tau)\,d\tau\cdot\phi_{i2}^{(k)}(z) \tag{69}$$

$$c_p(r,z,t) = \frac{1}{r}\sum_{i=1}^{\infty}\sum_{k=1}^{\infty}\frac{\mu_i}{\|\underset{\sim}{\psi}_i^{(k)}\|}\int_0^t e^{-\lambda_i^{(k)}(t-\tau)}\times f(\tau)\,d\tau\cdot\phi_{i2}^{(k)}(r,z) \tag{70}$$

Equations (69) and (70) are also the solutions for zero initial conditions, i.e., for g(z)=0 and h(r,z)=0. Thus the unit step respones and the impulse response can be calculated from Eqs. (69) and (70) by setting $f(\tau)=u(\tau)$ and $f(\tau)=\delta(\tau)$, respectively. The solutions for other feed functions can likewise be obtained.

ILLUSTRATIVE NUMERICAL EXAMPLE

We give a numerical example to show how the analytical solution can be used to obtain the time-domain response for a given feed function. We investigate the impulse response of c(z,t) at z=1 (the reactor exit). The numerical values of the parameters are taken from the studies of Wakao and coworkers on pulse chromatography [13, 14]. The values are

Pe=22,	α=57,	β=0.14
Φ^2=0.0,	K_A=6.0,	
ε_b=0.40,	ε_p=0.34	
g(z)=0,	h(r,z)=0	

subject to f(t)= δ(t). For z = 1, we have

$$\phi_{i1}^{(k)}(1) = (-1)^{i+1}\frac{\mu_i}{\|\underset{\sim}{\phi}_i^{(k)}\|} \tag{71}$$

Then Eq. (69) becomes

$$c(1,t) = \sum_{i=1}^{\infty}\sum_{k=1}^{\infty}(-1)^{i+1}\frac{\mu_i^2}{\|\underset{\sim}{\phi}_i^{(k)}\|^2}\cdot e^{(\frac{Pe}{2}-\lambda_i^{(k)}t)} \tag{72}$$

This function is computed and plotted in Figure 1 for the given set of numerical values.

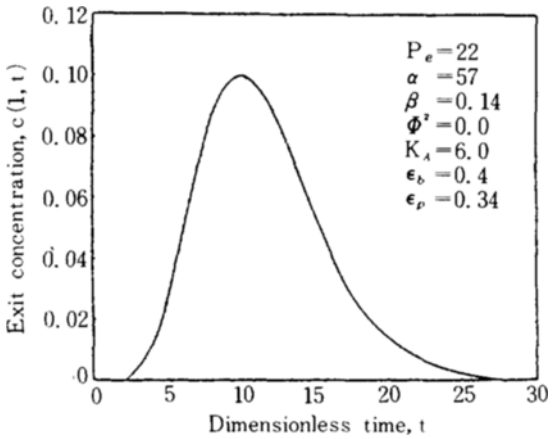

Fig. 1. Impulse Response c(1, t) at the Reactor Exit for f(t) = δ(t) (Pe = 22, α = 57, β = 0. 14, Φ^2 = 0. 0, K_A = 6. 0, ϵ_b = 0. 40, ϵ_p = 0. 34).

CONCLUSION

By means of Linear operator theory we have obtained the general transient solution for a finite axial dispersion reactor packed with spherical catalyst particles. The key steps were to define a Hilbert space and an operator so as to make the operator self-adjoint and positive definite in the space. Then by finding the eigenvalues and the eigenvectors of the operator, the solution was constructed from the orthonormal basis of the space.

ACKNOWLEDGEMENT

Financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

NOMENCLATURE

$\underset{\sim}{a}(r,z)$: dimensionless initial condition vector defined in Eq. (28)
$\underset{\sim}{b}(t)$: dimensionless boundary condition vector defined in Eq.(29)
C : concentration of flowing phase
C_a : concentration of adsorbed phase in catalyst particles
C_p : concentration in catalyst particles
C_o : reference concentration
c(z,t) : dimensionless concentration of flowing phase
$c_p(r,z,t)$: dimensionless concentration in catalyst particles
$C^o[0,1]$: the space of continuous functions over[0.1]
$C^2[0,1]$: the space of twice continuously differentiable functions over [0,1]
D : domain of $\underset{\sim}{L}$ defined in Eq. (35)
D* : domain of $\underset{\sim}{L}^*$
D_t : domain defined in Eq. (59)
D_e : effective intraparticle diffusivity
D_z : axial dispersion coefficient based on the void of the bed
$F(\bar{t})$: arbitrary time-varying feed concentration
f(t) : dimensionless $F(\bar{t})$
$G(\bar{z})$: arbitrary initial concentration of flowing phase
g(z) : dimensionless $G(\bar{z})$
H : Hilbert space H_t with no dependency on t
H_1 : Hilbert space, $=L_2[0,1]$
H_2 : Hilbert space, $= L_2[[0,1]\times[0,1]]$ with weighting factor $3(\epsilon_p + K_A)(\frac{1-\epsilon_b}{\epsilon_b})e^{-Pez}$ in the inner product
H_t : $H_1 \times H_2$
$H(\bar{r},\bar{z})$: arbitrary initial concentration in catalyst particles
h(r,z) : dimensionless $H(\bar{r},\bar{z})$
K_A : adsorption equilium constant
k : surface reaction rate
k_f : mass transfer coefficient between a catalyst particle and the flowing phase
$\underset{\sim}{L}$: operator defined in Eq. (21)
$\underset{\sim}{L}^*$: adjoint operator of L
$\underset{\sim}{L}^{-1}$: inverse operator of L
$L_2[0,1]$: the space of square integrable functions over [0,1]
l : reactor bed length $\frac{v\bar{l}}{\bar{D}z}$
Pe : axial Péclet number, $\frac{v\bar{l}}{\bar{D}z}$
R : radius of a catalyst particle
$\underset{\sim}{R}_1$: boundary operator degined in Eq. (24)
$\underset{\sim}{R}_2$: boundary operator defined in Eq. (25)
$\bar{r}$: radial variable in catalyst particles
r : dimensionless radial variable, $=\bar{r}/R$
$\bar{t}$: time
t : dimensionless time, $=\bar{v}t/\bar{l}$
$u_1(z,t)$: transformed dimensionless concentration of c by Eq. (11)
$u_2(r,z,t)$: transformed dimensionless concentration of Cp by Eq. (12)
$\underset{\sim}{u}$: vector concentration defined in Eq. (26)
u(t) : unit step function

v : interstitial velocity of the flowing phase
$\underset{\sim}{v}$: vector $(v_1\ v_2)^T$
$\underset{\sim}{w}$: vector $(w_1\ w_2)^T$
$\bar{z}$: axial variable along the reactor bed
z : dimensionless axial variable, $= \bar{z}/l$
$\underset{\sim}{Z}_1$: boundary operator defined in Eq. (22)
$\underset{\sim}{Z}_2$: boundary operator defined in Eq. (23)

Greek Letters

α : dimensionless group, $\dfrac{l\,De}{vR^2}$
β : mass transfer Biot number, $=\dfrac{Rk_f\varepsilon_p}{D_e}$
$\delta(t)$: delta function
ε_b : porosity of bed
ε_p : porosity of catalyst particles
θ : a positive constant, $= \min\{\dfrac{Pe}{4}, \dfrac{\alpha\Phi^2}{\varepsilon_p+K_A}\}$
λ : eigenvalue of $\underset{\sim}{L}$
$\lambda_i^{(k)}$: eigenvalues of $\underset{\sim}{L}$ given in Eq. (53) (i,k=1,2,3...)
μ : quantity defined in Eq. (51), $=\sqrt{\sigma}$
μ_i : the ith positive root of Eq. (51), (i=1,2,3...)
ν : quantity defined in Eq. (46)
$\nu_i^{(k)}$: quantities defined in Eq. (55)
σ : eigenvalue defined in Eq. (48)
τ : dummy variable of integration in time
Φ : Thiele modulus (or Jüttner modulus) $=R\sqrt{k\ K_A/De}$
$\phi_{i1}^{(k)}$: the first component of the eigenvector defined in Eq. (58)
$\phi_{i2}^{(k)}$: the second component of the eigenvector defined in Eq. (58)
$\underset{\sim}{\phi}_i^{(k)}$: orthonormal eigenvectors of $\underset{\sim}{L}$, defined in Eq. (58)
ψ_1 : the first component of the eigenvector defined in Eq. (40)
ψ_2 : the second component of the eigenvector defined in Eq. (40)
$\underset{\sim}{\psi}$: eigenvector of L defined in Eq. (40), $=(\psi_1\ \psi_2)^T$
ψ_{i1} : the first component of the eigenvector $\underset{\sim}{\psi}_i$ defined in Eq. (52)
$\psi_{i1}^{(k)}$: the first component of the eigenvector $\underset{\sim}{\psi}_i^{(k)}$ defined in Eq. (54)
$\psi_{i2}^{(k)}$: the second component of the eigenvector of $\underset{\sim}{\psi}_i^{(k)}$ defined in Eq. (54)
$\underset{\sim}{\psi}_i^{(k)}$: orthogonal eigenvectors of $\underset{\sim}{L}$ defined in Eq. (54) $=(\psi_{i1}^{(k)}\ \psi_{i2}^{(k)})^T$, (i,k=1,2,3,...)

Superscripts

T : transpose of a vector
− : upstream side
+ : downstream side

Symbols

$(\ ,\ )_1$: inner product in H_1 defined in Eq. (34)
$(\ ,\ )_2$: inner product in H_2 defined in Eq. (34)
$(\ ,\ )$: inner product in H_i defined in Eq. (34)
$(\ )^T$: column vector
$\|\ \|$: norm of a vector in H, $=\sqrt{(\ ,\ )}$

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