A MODEL OF THE CASCADE OF STIRRED REACTORS WITH A HETEROGENEOUS DIFFUSION-CONTROLLED REACTION

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A mathematical model has been derived of the cascade of ideally stirred tank reactors with chemical reaction between dispersed solid particles and a continuous fluid medium. The kinetics of the reaction is controlled by diffusion within the particles and by the transport of mass from the particle surface into the bulk of the continuous phase.

The mass transfer between solid particles and a continuous fluid phase is encountered in many operations of chemical technology. Equipment for such operations may be often simulated by a cascade of ideally stirred tank reactors (in the following: CSTR) in which the kinetics is controlled by diffusion from within the particles to the surface and by the convective transport from the surface into the bulk of the continuous phase, *i.e.* by the inner and outer diffusion.

The papers that have been published on the subject have been concerned only with such conditions under which the reaction kinetics is not affected by concentration in the continuous phase[1-4], or have dealt with batch reactors[5,6]. In the preceding communication[7] we examined counter-current extraction in a cascade of CSTR's where the rate of extraction was controlled by diffusion within the particles, while the resistance of the boundary layer on the particle surface was negligible. The subject of the presented paper is a so far uninvestigated general case of mass transfer between solid particles and a fluid in a cascade of CSTR's when the kinetics of the process is controlled simultaneously by the outer and inner diffusion.

THEORETICAL

The model is formulated on the following assumptions:

1. the system consists of a sequence of k equal CSTR's operating under steady state regime;

2. the solid particles are isotropically porous spheres (porosity equals ε) of equal radius R; no change of volume or particle break-down occurs during the process;

3. the concentration of the reactant within the pores is governed by the second Fick's law with an effective diffusivity D;

4. the resistance of the boundary layer on the particle surface exerts its effect through the mass transfer coefficient h;

5. the concentration of the reactant in the feed to the first CSTR of the cascade (the reactors are numbered in the direction of flow of the solid phase) equals $c_{s,0}$.

Under these assumptions the concentration of the reactant within the pores of the solid particles at the outlet of the i-th CSTR is given by the following parabolic partial differential equation

$$\partial c_{s,i}/\partial \tau_i = D[\partial^2 c_{s,i}/\partial r^2 + (2/r)\, \partial c_{s,i}/\partial r] \tag{1}$$

with the initial and boundary conditions

$$\tau_i = 0: \quad c_{s,i} = c_{s,i-1}(r; \tau_1; \ldots; \tau_{i-1}), \tag{2}$$

for $i = 1$ we have

$$c_{s,1} = c_{s,0}; \tag{3}$$

$$r = 0: \quad c_{s,i} \neq \infty, \qquad r = R: \quad -D\, \partial c_{s,i}/\partial r = h(c_{s,i} - c_{f,i}) \tag{4), (5}$$

(τ_1 through τ_i are the residence times of particles in individual CSTR's). On introducing new dimensionless variables

$$x = r/R, \qquad t_i = D\tau_i/R^2, \tag{6), (7}$$

$$u_i = c_{f,i}/c_{s,0}, \qquad y_i = x(c_{s,i}/c_{s,0} - u_i). \tag{8), (9}$$

Eqs (*1*) through (*5*) transform into

$$\partial y_i/\partial t_i = \partial^2 y_i/\partial x^2, \tag{10}$$

$$t_i = 0: \; y_i = x[(1/c_{s,0})\, c_{s,i-1}(xR; t_1 R^2/D; \ldots; t_{i-1} R^2/D) - u_i] = f_i(x; t_1; \ldots; t_{i-1}) \tag{11}$$

for $i = 1$ we have

$$y_1 = x(1 - u_1); \tag{12}$$

$$x = 0: \quad y_i = 0; \qquad x = 1: \quad \alpha\, \partial y_i/\partial x = -y_i, \tag{13), (14}$$

where

$$\alpha = (hR/D - 1)^{-1}. \tag{15}$$

The Laplace transform of a general solution to Eq. (*10*) for distribution of the dimensionless concentrations within the pores of the particles exiting from the i-th CSTR, y_i, has the form of an infinite series

$$\{y_i(x; p; t_1; \ldots; t_{i-1})\} = \sum_{n=1}^{\infty} A_n \sin(\lambda_n x) \int_0^1 f_i(x; t_1; \ldots; t_{i-1}) \sin(\lambda_n x)\, dx\,, \tag{16}$$

where p is an argument of the Laplace transform defined as

$$\{y_i(x; p; t_1; \ldots; t_{i-1})\} = \int_0^{\infty} y_i(x; t_1; \ldots; t_i) \exp(-pt_i)\, dt_i\,. \tag{17}$$

The coefficients A_n in Eq. (*16*) are determined by

$$A_n = [(\lambda_n^2 + p) \int_0^1 \sin^2(\lambda_n x)\, dx]^{-1} \tag{18}$$

and λ_n are roots of the characteristic equation

$$\mathrm{tg}(\lambda_n) = -\alpha\lambda_n\,. \tag{19}$$

The dimensionless concentrations y_i in a particle exiting from the i-th CSTR are functions of the coordinate x and the dimensionless residence times of the given particle in the first i reactors, *i.e.* $t_1 - t_i$. Corresponding variables $\{y_i\}$ are functions of x, the Laplace parameter p and the dimensionless residence times in first $(i - 1)$ CSTR's, *i.e.* $t_1 - t_{i-1}$. Distribution function of the dimensionless residence times in the i-th stage of the cascade of k equal CSTR's is

$$\Phi(t_i) = (k/\bar{t}) \exp(-kt_i/\bar{t})\,, \tag{20}$$

where

$$\bar{t} = D\bar{\tau}/R^2 \tag{21}$$

and $\bar{\tau}$ is the average residence time in the whole cascade. In the following we shall concentrate on determining the time-averaged values of the dimensionless concentration in the dispersed phase on exit from the i-th reactor, which we shall denote as $\bar{y}_i$. This quantity depends on the coordinate x only and it is given by the following multiple (i) integral

$$\bar{y}_i(x) = (k/\bar{t})^i \underbrace{\int_0^{\infty} \ldots \int_0^{\infty}}_{i} y_i(x; t_1; \ldots t_i) \exp(-kt_1/\bar{t}) \ldots \exp(-kt_i/\bar{t})\, dt_1 \ldots dt_i\,. \tag{22}$$

On taking the Laplace variable in Eq. (*17*) so as to have

$$p = k/\bar{t}\,, \tag{23}$$

one can arrange Eq. (*22*) by making use of Eq. (*16*) and with the aid of

$$f_i(x; t_1; \ldots; t_{i-1}) = y_{i-1}(x; t_1; \ldots; t_{i-1}) + x(u_{i-1} - u_i) \tag{24}$$

to obtain an expression for $\bar{y}_i(x)$

$$\bar{y}_i(x) = p^i \sum_{n=1}^{\infty} A_n \sin(\lambda_n x) \int_0^1 [\sin(\lambda_n x) \,.\, \underbrace{\int_0^{\infty} \ldots \int_0^{\infty}}_{i-1} y_{i-1}(x; t_1; \ldots; t_{i-1}) \exp(-pt_1) \ldots$$

$$\ldots \exp(-pt_{i-1})\, dt_1 \ldots dt_{i-1}]\, dx + p(u_{i-1} - u_i) \sum_{n=1}^{\infty} A_n \sin(\lambda_n x) \int_0^1 x \sin(\lambda_n x)\, dx =$$

$$= p \sum_{n=1}^{\infty} A_n \sin(\lambda_n x) \int_0^1 \bar{y}_{i-1}(x) \sin(\lambda_n x)\, dx +$$

$$+ p(u_{i-1} - u_i) \sum_{n=1}^{\infty} A_n \sin(\lambda_n x) \int_0^1 x \sin(\lambda_n x)\, dx \,. \tag{25}$$

The advantage of this approach rests in that the expression for the average dimensionless concentration $\bar{y}_i$ could have been derived directly on the basis of the transformed $\{y_i\}$ without recourse to the explicit expression of the dimensionless concentrations y_i. Eq. (*25*) will now be used to find relation for the fraction of unconverted species, I_i, in particles leaving the *i*-th CSTR. This fraction, which from technological point of view is the most important variable, is defined by

$$I_i = 3 \int_0^1 x \bar{y}_i(x)\, dx + u_i \,. \tag{26}$$

Eq. (*25*) is now multiplied by $\sin(\lambda_m x)$ and both sides integrated with respect to x in limits $0-1$. With respect to the orthogonality of the functions $\sin(\lambda_n x)$ over the interval $0 \leqq x \leqq 1$ one obtains, after changing from m to the original subscript n, a relation

$$\int_0^1 \bar{y}_i(x) \sin(\lambda_n x)\, dx = B_n \int_0^1 \bar{y}_{i-1}(x) \sin(\lambda_n x)\, dx + (u_{i-1} - u_i)\, B_n C_n \,, \tag{27}$$

where

$$B_n = p/(p + \lambda_n^2) \,, \tag{28}$$

$$C_n = \int_0^1 x \sin(\lambda_n x)\, dx = -(1 + \alpha)\, \lambda_n^{-1} \cos(\lambda_n) \,. \tag{29}$$

For $i = 1$ Eq. (*27*) reduces to

$$\int_0^1 \bar{y}_1(x) \sin(\lambda_n x)\, dx = (1 - u_1)\, B_n C_n \,. \tag{30}$$

From Eqs (27) and (30) we now have

$$\int_0^1 \bar{y}_{i-1}(x) \sin(\lambda_n x) \,dx = (1 - u_1) B_n^{i-1} C_n + \sum_{m=2}^{i-1} (u_{m-1} - u_m) B_n^{i-m} C_n . \quad (31)$$

On combining Eqs (25), (26) and (31) and making use of

$$\int_0^1 \sin^2(\lambda_n x) \,dx = 0{\cdot}5(1 + \alpha + \alpha^2 \lambda_n^2) \cos^2(\lambda_n) \quad (32)$$

one obtains after some algebra the final expression for I_i

$$I_i = 6 \sum_{n=1}^{\infty} X_n [(1 - u_1) B_n^i + \sum_{m=1}^{i-1} (u_m - u_{m+1}) B_n^{i-m}] + u_i , \quad (33)$$

where

$$X_n = (1 + \alpha)^2 \lambda_n^{-2} / (1 + \alpha + \alpha^2 \lambda_n^2) . \quad (34)$$

However, the thus far undetermined dimensionless concentrations of the reactant in the continuous phase, $u_1 - u_i$, still appear in Eq. (33). The necessary relations for the calculation of these concentrations, or their elimination, are obtained from mass balances in individual CSTR's. The form of the balance equations depends on the arrangement of flows of the continuous and dispersed phase.

Counter-current flow. In case of the counter-current flow the mass balances in individual CSTR's are

$$\begin{aligned}
&z_1 + z_2 + z_3 + \ldots \quad \ldots + z_{k+1} = 1 - u_{k+1} , \\
&a_1 z_1 - z_2 = 0 , \\
&a_2 z_1 + a_1 z_2 - z_3 = 0 , \\
&\vdots \\
&a_k z_1 + a_{k-1} z_2 + a_{k-2} z_3 + \ldots - z_{k+1} = 0 ,
\end{aligned} \quad (35)$$

where

$$\begin{aligned}
z_1 &= 1 - u_1 , \\
&\vdots \\
z_i &= u_{i-1} - u_i , \quad (i = 2, 3, \ldots, k) \\
&\vdots \\
z_{k+1} &= u_k - u_{k+1} .
\end{aligned} \quad (36)$$

In these expressions it is assumed that u_{k+1} is known and the coefficients a_i $(i = 1, 2, \ldots, k)$ are determined by

$$a_i = 6q \sum_{n=1}^{\infty} B_n^{i-1}(1 - B_n) X_n . \tag{37}$$

The relation for a_i was obtained from Eq. (*33*) and the set of Eqs (*35*) after an arrangement which utilized the following relations

$$I_1 = 6(1 - u_1) \sum_{n=1}^{\infty} B_n X_n + u_1 , \tag{38}$$

$$\lim_{p \to \infty} (I_1 - u_1)/(1 - u_1) = 6 \sum_{n=1}^{\infty} X_n = 1 . \tag{39}$$

Eq. (*39*) is dictated by the fact that in limit $p \to \infty$ (*e.g.* for very low values of the effective diffusivity D) the fraction of the unreacted species in the whole system approaches unity.

The set (*35*) is solved (similarly as in paper[7]) by substitution

$$b_i = z_{i+1}/z_1 , \qquad (i = 1, 2, \ldots, k) , \tag{40}$$

leading to equations

$$\begin{aligned} \sum_{i=1}^{k} b_i &= (1 - z_1 - u_{k+1})/z_1 = (u_1 - u_{k+1})/(1 - u_1) , \\ b_1 &= a_1 , \\ b_2 &= a_2 + a_1 b_1 , \\ b_3 &= a_3 + a_2 b_1 + a_1 b_2 , \\ &\vdots \\ b_k &= a_k + a_{k-1} b_1 + a_{k-2} b_2 + \ldots + a_1 b_{k-1} . \end{aligned} \tag{41}$$

Calculation of the quantities b_i from Eqs (*41*) is then easy; individual values of u_i are then found by subsequent substitution into Eqs (*40*) and (*36*).

Co-current flow. The mass balances at co-current flow are as follows

$$\begin{aligned} q(1 - I_1) &= u_1 - u_0 , \\ q(I_1 - I_2) &= u_2 - u_1 , \\ &\vdots \\ q(I_{k-1} - I_k) &= u_k - u_{k-1} . \end{aligned} \tag{42}$$

It is assumed again that the dimensionless concentration in the continuous phase at the inlet (u_0) is given. The set (*42*) is arranged by introducing coefficients a_i

$$\begin{aligned}
&(1 - u_1)\, a_1 + u_0 - u_1 &&= 0\,,\\
&(1 - u_1)\, a_2 + (u_1 - u_2)\, a_1 + u_1 - u_2 &&= 0\,,\\
&\vdots\\
&(1 - u_1)\, a_k + (u_1 - u_2)\, a_{k-1} + \ldots + (u_{k-1} - u_k)\, a_1 + u_{k-1} - u_k &&= 0\,.
\end{aligned} \tag{43}$$

Individual u_i are calculated from Eqs (*43*) by successive elimination; the values of I_i then follow from Eqs (*42*).

Cross flow. The balance equations for the cross flow are

$$\begin{aligned}
q(1 - I_1) &= u_1 - u_0\,,\\
q(I_1 - I_2) &= u_2 - u_0\,,\\
&\vdots\\
q(I_{k-1} - I_k) &= u_k - u_0\,.
\end{aligned} \tag{44}$$

The value of u_0 is assumed again to be known. After substituting for the coefficients a_i one obtains

$$\begin{aligned}
&(1 - u_1)\, a_1 + u_0 - u_1 &&= 0\,,\\
&(1 - u_1)\, a_2 + (u_1 - u_2)\, a_1 + u_0 - u_2 &&= 0\,,\\
&\vdots\\
&(1 - u_1)\, a_k + (u_1 - u_2)\, a_{k-1} + \ldots + (u_{k-1} - u_k)\, a_1 + u_0 - u_k &&= 0\,.
\end{aligned} \tag{45}$$

The sets (*44*) and (*45*) are solved again by successive elimination.

RESULTS

The derived relations enable the reaction yields in a cascade of CSTR's with a given arrangement of flows of the continuous and dispersed phase (counter-current, co-current and cross flow) to be computed provided that the above listed simplifying assumptions are met. The input data for the calculations are: the number of CSTR's in the cascade k, the average residence time of particles in the cascade $\bar{\tau}$, concentration of the reactant in both phases in the feed $c_{s,0}$ and $c_{f,k+1}$ or $c_{f,0}$, the ratios D/R^2 and hR/D (the calculation does not require the knowledge of D, h and R themselves – see Eqs (*15*) and (*21*)), and finally q, that is the ratio of volume flow rates of the dispersed and continuous phase multiplied by particle porosity. The ratios D/R^2 and hR/D may be determined for a given system from measurements on a laboratory batch reactor by evaluating the dependence of the unconverted fraction on the residence time and the mixing Reynolds number[4]. The relations for recalculation of hR/D at changed intensity of mixing are available in the literature[8].

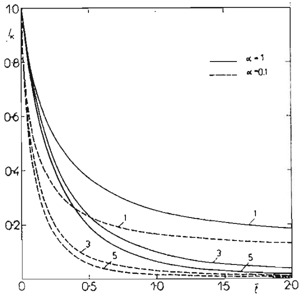

FIG. 1

The Dependence of I_k on $\bar{t}$ and α for Counter-Current Flow of Phases

$q = 0{\cdot}1$; $u_{k+1} = 0$; k is indicated on curves.

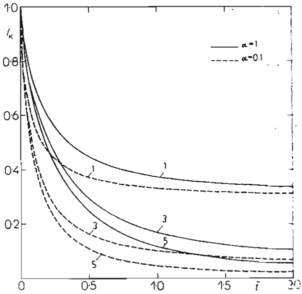

FIG. 2

The Dependence of I_k on $\bar{t}$ and α for Counter-Current Flow of Phases

$q = 0{\cdot}4$; $u_{k+1} = 0$; k is indicated on curves.

To calculate the fractions of unconverted species at the outlet of individual CSTR's, one determines first the dimensionless parameters α, $\bar{t}$ and p from definitions (*15*), (*21*) and (*23*). Further, the coefficients a_i are computed by means of Eq. (*37*). To evaluate the infinite series in Eq. (*37*) one uses Eqs (*28*) and (*34*) to find B_n and X_n, while the roots λ_n are given by solution of Eq. (*19*). The coefficients a_i are then substituted into the balance equations for a given arrangement of flows of the dispersed and continuous phase (Eqs (*35*), (*36*), (*40*) and (*41*) for counter-current arrangement, (*42*) and (*43*) for co-current arrangement and Eqs (*44*) and (*45*) for the cross flow) and their solution provides the values of the fractions I_i.

The relations for the counter-current arrangement were programmed for a computer in Algol 60 language. The quantities α, q and u_{k+1} were fed as the input data; the result were the values of the fractions I_k in the product of the cascade of k reactors for preselected values of k and $\bar{t}$. The coefficients λ_n, which are not functions of k and $\bar{t}$, were conveniently evaluated at the beginning of the computation. 30 to 50 terms of the infinite series in Eq. (*37*) had to be taken in order that the coefficients a_i be computed to 5 digits. A part of the results reflecting the dependence of I_k on $\bar{t}$, k, α and q is presented in graphical form in Figs 1 and 2.

LIST OF SYMBOLS

A_n, a_i	coefficients defined in Eqs (*18*) and (*37*)
B_n, b_i	coefficients defined in Eqs (*28*) and (*40*)
C_n	coefficients defined in Eq. (*29*)

$c_{f,i}$	concentration of reactant in continuous phase in the i-th CSTR (mol/cm^3)
$c_{s,i}$	concentration of reactant in particle pores at the outlet of the *i*-th CSTR (mol/cm^3)
D	effective diffusivity of reactant in dispersed phase (cm^2/s)
$f_i(x; t_1; \ldots; t_{i-1})$	value of y_i at zero residence time in the i-th CSTR (Eq. (*11*))
h	mass transfer coefficient between particle surface and the bulk of continuous phase (cm/s)
I_i	fraction of unconverted reactant in dispersed phase at the outlet of the *i*-th CSTR (with reference to concentration in dispersed phase at the inlet of the cascade)
k	number of reactors in the cascade
$p = k/\bar{t}$	Laplace variable
q	volume fraction of flow rates of dispersed and continuous phase times particle porosity
R	particle radius (cm)
r	distance from center of particle (cm)
$t_i = D\tau_i/R^2$	dimensionless residence time in the *i*-th CSTR
$\bar{t} = D\bar{\tau}/R^2$	dimensionless average residence time in the cascade
$u_i = c_{f,i}/c_{s,o}$	dimensionless concentration of reactant in continuous phase in the *i*-th CSTR
X_n	coefficient defined in Eq. (*34*)
$x = r/R$	dimensionless distance from center of particle
y_i	dimensionless concentration of reactant in particle pores at the outlet of the *i*-th CSTR, see Eq. (*9*)
$\bar{y}_i$	value of y_i averaged over all particle residence times in the first to *i*-th CSTR's, see Eq. (*22*)
z_i	coefficients defined in Eqs (*36*)
α	parameter defined in Eq. (*15*)
ε	particle porosity (volume of pores as a fraction of the macroscopic volume of particle)
λ_n	roots of Eq. (*19*)
τ_i	particle residence time in the *i*-th CSTR (s)
$\bar{\tau}$	average residence time in a cascade of *k* equal reactors (s)
$\Phi(t_i)$	distribution function of the dimensionless particle residence time in single CSTR

Subscripts

f	fluid phase
i, k	*i*-th or *k*-th CSTR (counted in direction of flow of the solid phase)
j, m, n	summation indices
s	solid phase

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