Fixed Bed Sorption with Recycle: Analytic Solutions for Linear Models

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In a recent article, Cooney and Shieh (1972) presented a process involving fixed bed sorption with recycle. Numerical solutions were obtained for the process dynamics based on the assumption of linear equilibrium and linear rate laws for the fixed bed operation. They mentioned the possibility of an analytic solution for such linear models and also pointed out that this analytic solution was not known. This note presents such an analytic solution and also shows the additional insight into the process dynamics one can obtain from this solution.

Following the notation used by Cooney and Shieh, the equations required to be solved are:

For the sorption bed

$$v\frac{\partial c}{\partial z}+\frac{\partial c}{\partial t}+\frac{1-\epsilon}{\epsilon}\,\frac{\partial q}{\partial t}=0 \tag{1}$$

$$\frac{\partial q}{\partial t}=K_pS_0\,(q^*-q) \tag{2}$$

$$q^*=\lambda c$$

For the reactor

$$F(c_{\text{out}}-c_{\text{in}})+R=V\frac{dc_{\text{in}}}{dt} \qquad (4)^\dagger$$

Equations (1), (2), and (4) can be normalized to dimensionless forms

$$\frac{\partial x}{\partial h}+\frac{\partial y}{\partial \theta}=0 \tag{5}$$

$$\frac{\partial y}{\partial \theta}=x-y \tag{6}$$

$$x_{\text{out}}-x_{\text{in}}+R'=a\frac{dx_{\text{in}}}{d\theta} \tag{7}$$

with initial and boundary conditions

$x(0,\theta)=x_{\text{in}}(\theta)$

$x(0,0)=x^0{}_{\text{in}}=1$

$y(h,0)=y^0$ (uniform presaturation in stationary phase)

by letting

$$h=\frac{K_pS_0z(1-\epsilon)Q^*}{v\,\epsilon\,c^0},\quad \theta=K_pS_0(t-z/v)$$

$$x=x(h,\theta)=c/c^0,\quad y=q/Q^*$$

$$x_{\text{in}}=x(0,\theta)=c_{\text{in}}/c^0,\quad x_{\text{out}}=x(H,\theta)=\frac{c_{\text{out}}}{c^0}$$

$$H=\frac{K_pS_0L(1-\epsilon)Q^*}{v\,\epsilon\,c^0},\quad a=VK_pS_0/F,\quad R'=\frac{R}{F\,c^0}$$

where L is the total sorber height, $Q^*/c^0=\lambda=q^*/c$ is the equilibrium distribution coefficient, c^0 is the initial concentration of species B in the reactor, and Q^* is the stationary phase concentration in equilibrium with c^0.

Laplace transforming Equations (5), (6), and (7) with respect to θ

$$\frac{d\,\overline{x}\,(h,s)}{dh}+s\,\overline{y}-y^0=0 \tag{8}$$

$$\overline{y}=\frac{y^0+\overline{x}}{s+1} \tag{9}$$

$$\overline{x}\,(H,s)=(as+1)\,\overline{x}\,(0,s)-ax^0{}_{\text{in}}-\frac{R'}{s} \tag{10}$$

Substituting (9) into (8) and solving the resulting equation with the aid of the integrating factor

$$\exp\left(\int\frac{s}{s+1}\,dh\right)$$

one obtains

$$\overline{x}\,(h,s)=\overline{x}\,(0,s)\,\exp\left(-\frac{sh}{s+1}\right)+\frac{y^0}{s}\left[1-\exp\left(-\frac{sh}{s+1}\right)\right] \tag{11}$$

Noting that at $h=H$, $x(h,s)=x(H,s)$, an explicit expression for $x(0,s)$ can be obtained by eliminating $x(H,s)$ from Equation (10) and Equation (11) at $h=H$. The resulting expression for $x(0,s)$, when substituted into (11), yields

$$\overline{x}\,(h,s)=\frac{y^0}{s}+\left[a(x^0-y^0)+\frac{R'}{s}\right]\frac{\exp\left(-\dfrac{sh}{s+1}\right)}{\left[1+as-\exp\left(-\dfrac{sH}{s+1}\right)\right]}$$

or

$$\overline{x}\,(h,s)=\frac{y^0}{s}+\left[a(x^0-y^0)+\frac{R'}{s}\right]\sum_{n=0}^{\infty}\left(\frac{1}{as+1}\right)^{n+1}\exp\left[\frac{-s}{s+1}\,(nH+h)\right] \tag{12}$$

by series expansion of the last factor.

The inversion of Equation (12) leads to the solution profiles for the inlet ($h=0$), the outlet ($h=H$), and also within the bed ($0<h<H$).

It is convenient to invert (12) by writing

$$\overline{x}\,(h,s)=\frac{y^0}{s}+a(x^0-y^0)\,(s\overline{G}+\overline{G})+R'\left(\overline{G}+\frac{\overline{G}}{s}\right)$$

where

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† R is the constant production rate of the species (B) being absorbed. This constant rate can arise in a variety of ways depending upon the nature of the reactor being considered.

$$\overline{G}(h, s) = \sum_{n=0}^{\infty} \overline{g}\,(n, h, s)$$

$$= \sum_{n=0}^{\infty} \left(\frac{1}{as+1}\right)^{n+1} \frac{\exp\left[-\dfrac{(nH+h)s}{s+1}\right]}{s+1}$$

The inversion of $\overline{g}$ is obtained by convolution

$$g(n, h, \theta) = \mathcal{L}^{-1}\,[\,\overline{g}\,(n, h, s)] = \frac{1}{n!}\left(\frac{1}{a}\right)^{n+1} \int_0^{\theta} (\theta - \xi)^n \exp\left(-\frac{\theta - \xi}{a} - \xi - nH - h\right) I_0(2\sqrt{(nH+h)\xi})\,d\xi \qquad (13)$$

where $I_0(.)$ is the modified Bessel function of the first kind of order zero.

Therefore, the inversion of $x(h, s)$ is

$$x(h, \theta) = y^0 + a(x^0 - y^0)\left(\frac{dG}{d\theta} + G\right) + R'\left[\,G + \int_0^{\theta} G\,d\theta\right] \qquad (14)$$

Equation (14) is an analytic solution but the determination of the derivative and integral terms by numerical methods is difficult and subject to large computational errors. An alternative series form, which avoids these problems is obtained by integrating $g(n, h, \theta)$ by parts (Appendix*):

$$g(n, h, \theta) = \left(\frac{1}{a-1}\right)^{n+1} \exp\left(-\frac{\theta}{a} + \frac{nH+h}{a-1}\right) \phi^{n+1}\left(b\theta, \frac{nH+h}{b}\right)$$

where $b = (a-1)/a$, and ϕ's are evaluated from

$$\phi^n(u, v) = \exp(-v) \sum_{K=0}^{\infty} A_K{}^n(u)\; v^K/\kappa!^2 \qquad (15)$$

with coefficients A's calculated from the following relations, where n are indices and κ are exponents when used in superscripts.

$$A_K{}^0 = \exp(-u)u^K$$

$$A_0{}^n = \frac{u^{n-1}}{(n-1)!} - A_0{}^{n-1}$$

$$A_K{}^n = \kappa\, A_{K-1}{}^n - A_K{}^{n-1}$$

The final solution is Equation (14) in series form

$$\begin{aligned} x(h, \theta) = y^0 + (x^0 - y^0)\Bigg\{ &\sum_{n=0}^{\infty} \left(\frac{1}{a-1}\right)^n \exp\left(-\frac{\theta}{a} + \frac{nH+h}{a-1}\right)\left[\,\phi^n\left(b\theta, \frac{nH+h}{b}\right) + \phi^{n+1}\left(b\theta, \frac{nH+h}{b}\right)\right]\Bigg\} + R'\Bigg\{\sum_{n=0}^{\infty} \phi^1(\theta, nH+h) \\ &+ \sum_{n=0}^{\infty} \exp\left(-\frac{\theta}{a} + \frac{nH+h}{a-1}\right) \Big/ (a-1) \left[\,\phi^{n+1}\left(b\theta, \frac{nH+h}{b}\right) \Big/ (a-1)^n - a \sum_{j=0}^{n} \phi^{j+1}\left(b\theta, \frac{nH+h}{b}\right) \Big/ (a-1)^j\,\right]\Bigg\} \end{aligned} \qquad (16)$$

The stationary phase concentration profile at any instant is obtained by substitution of Equation (12) in Equation (9) and following the inversion procedure outlined above:

$$\begin{aligned} y(h, \theta) = y^0 + a(x^0 - y^0)&\left\{\sum_{n=0}^{\infty} \left(\frac{1}{a-1}\right)^{n+1} \exp\left(-\frac{\theta}{a} + \frac{nH+h}{a-1}\right) \phi^{n+1}\left(b\theta, \frac{nH+h}{b}\right)\right\} \\ &+ R'\left\{\sum_{n=0}^{\infty} \phi^1(\theta, nH+h) - \frac{\exp\left(-\dfrac{\theta}{a} + \dfrac{nH+h}{a-1}\right)}{b} \sum_{j=0}^{n} \frac{\phi^{j+1}\left(b\theta, \dfrac{nH+h}{b}\right)}{(a-1)^j}\right\} \end{aligned} \qquad (17)$$

In certain cases (see discussion), only the first term of the series [which involves the tabulated J function only] is required. Equation (16) then becomes

$$\begin{aligned} x(h, \theta) = y^0 + (x^0 - y^0)&\left\{\exp\left(-\frac{\theta}{a} + \frac{h}{a-1}\right) \cdot J\left(\frac{h}{b}, b\theta\right)\right\} \\ &+ R'\left\{1 - J(\theta, h) - \exp\left(-\frac{\theta}{a} + \frac{h}{a-1}\right)\left[1 - J\left(b\theta, \frac{h}{b}\right)\right]\right\} \end{aligned} \qquad (18)$$

The $J(h/b, b\theta)$ term in Equation (18) arises from the use of the following identities:

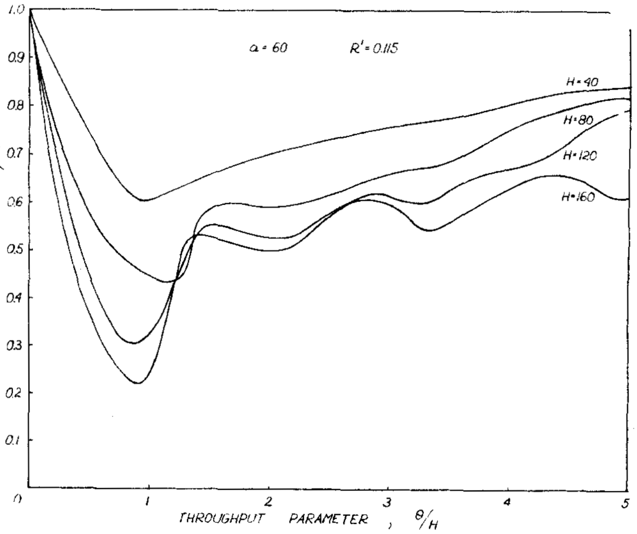

Fig. 1. Variation of inlet composition with throughput parameter.

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* The Appendix has been deposited as Document No. 01995 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 East 46th St., N.Y. 10017 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

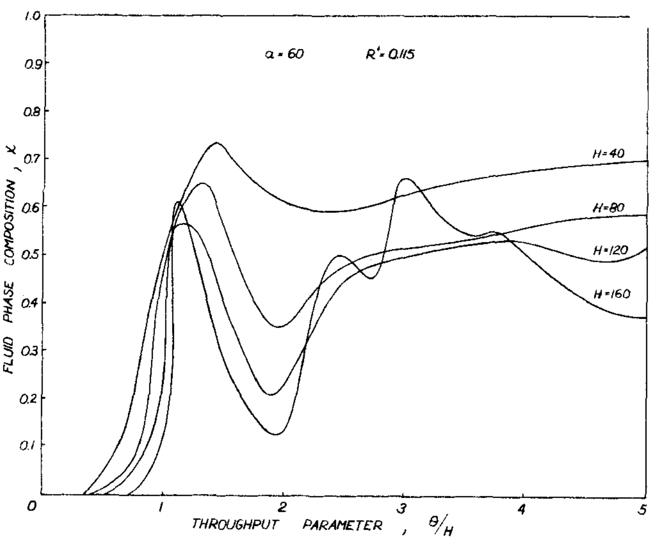

Fig. 2. Variation of outlet composition with throughput parameter.

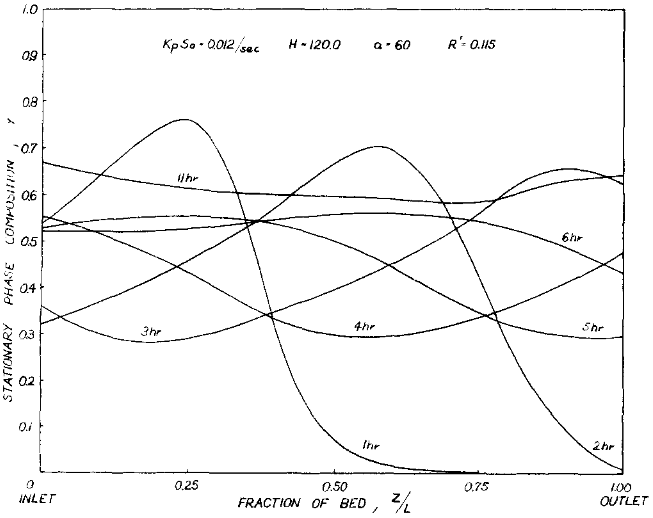

Fig. 3. Sorbent bed composition profiles.

$$\phi^1(u, v) = 1 - J(u, v)$$

$$\phi^0(u, v) = -\frac{d}{du} J(u, v) = J(u, v) + J(v, u) - 1$$

RESULTS AND DISCUSSION

Figures 1, 2, and 3 are obtained from Equations (16) and (17); the values of a and R' used in the calculations are identical to those used by Cooney and Shieh. The initial concentration profile in the stationary phase was assumed to be zero. The series of Equation (16) converges rapidly when $a = 60$, $H \leqq 100$, and $\theta/H \leqq 5$ and only three terms of the series are required for 0.1% accuracy. For $\theta/H \leqq 0.8$ only the first term of the series [Equation (18)] was required and was readily determined from the tabulated J function (Brinkley, 1951; Helfferich, 1962). The series converges less rapidly as a becomes smaller. For example, with $a = 10$ the stated accuracy with three terms was only obtained when $H \leqq 10$ and $\theta/H \leqq 3$.

The parametric effect of H on the instantaneous inlet and outlet concentrations of the adsorption bed is shown in Figures 1 and 2 respectively where the commonly adopted throughput parameter θ/H (Hiester and Vermeulen, 1952) is used as ordinate to yield more concise graphs. The transient development of the concentration profile in the stationary phase is shown in Figure 3.

The first term ($n = 0$) of the general solution for $x(h, \theta)$ is given by Equation (18), and for $h = 0$ and $y^0 = 0$ the solution is

$$x(0, \theta) = R' + (x^0 - R') \exp\left(-\frac{\theta}{a}\right)$$

This equation is identical to that derivable from Equation (7) with $x(H, \theta) = 0$ and describes a constant production rate reactor with a diluting stream. This equation is valid up to the time of initial adsorbent column breakthrough.

Equation (18) for the case of $h = H$ describes the elution profile for concurrent regeneration of an adsorbent column with time varying input. The feed concentration to the column during the initial stage is approximately given by $x^0 + \dfrac{R'}{a}\theta$ up to the time $t = \dfrac{L}{v}$, after this time and until some arbitrarily small breakthrough, the column is being eluted with a diluted stream whose concentration is given by $x(0, \theta)$ as previously stated.

Subsequent terms ($n > 0$) in the series of Equation (16) for $h = H$ are bell shaped functions of the form

$$\exp\left(-\frac{\theta}{a} + \frac{nH}{a-1}\right) \phi^n \left(b\theta, \frac{nH}{a-1}\right).$$

These functions can be considered to describe modified elution profiles. Each advance in counter n corresponds to one additional pass through the column. The separation between the peaks of the successive profiles becomes greater the larger the value of H, as would be expected for the elution of any adsorbent column. Although on a time basis the peaks will broaden more as they pass through a longer column, on a throughput basis the peaks will appear to sharpen. In Equation (7), a large reactor volume or a slow flowrate will tend to damp out both the disturbance term $x(H, \theta)$ and response term $x(0, \theta)$. Thus the smaller the magnitude of the normalized reactor residence time a the smaller will be the damping effect. Therefore smaller values of a and larger values of H will lead to a more oscillatory system behavior. As the throughput increases (and therefore loading of the column increases), the elution profiles must become broader, and the oscillatory behavior is eventually completely damped.

For the linear equilibrium considered here it can be seen by the application of final-value theorem to the transformed equations that $x(h, \theta)$ and $y(h, \theta)$ can increase without limit in time. Practical considerations suggest the application of some further constraint to the analytical solution, such as assuming a finite adsorbent capacity. In this case the bed will be completely saturated at some large value of θ, then it can be shown by a simple mass balance that

$$x(h, \theta) = x^0 - \frac{ALQ_c}{V c^0} + \frac{R'}{a}\theta,$$

$$\text{for} \quad 0 < h < H, \quad \theta \text{ very large}$$

where A and L are the cross section area and length of the column respectively, and Q_c is the capacity expressed as the maximum amount of solute that can be adsorbed per unit volume of the column.

It can be seen from Equation (14) that the analytical solution fails for the limiting case of $a = 1$. In this case, a different form can easily be obtained by applying the methods outlined directly to Equation (12).

The method of solution outlined is equally applicable to the cases of first-order reversible and nonreversible reactions in the reactor and also to open systems, but the Laplace transform inversions are more complicated. For nonlinear production rate equations, numerical methods must be used, but it is advisable to use normalized Equations (5), (6), and (7) rather than (1), (2), and (4).

NOTATION

A = coefficients in the series; cross section area of the column, cm^2
c = fluid phase concentration, g/cc
F = volumetric fluid phase flow rate, cc/s
K_p = overall stationary phase mass transfer coefficient, cm/s
L = total bed height of the sorbent bed, cm
q = stationary phase concentration, g/cc
R = solute production rate in source, g/s
s = Laplace transformation variable
S_0 = sorbent particle specific surface area, cm^{-1}
t = time, s
v = interstitial fluid phase velocity in sorbent bed, cm/s
V = volume of source, cc
x = normalized fluid phase concentration, dimensionless
y = normalized stationary phase concentration, dimensionless
ϵ = void fraction in sorbent bed, dimensionless
λ = equilibrium distribution coefficient, dimensionless

Subscripts and Superscripts

$*$ denotes an equilibrium concentration
n = index
κ = index, exponent
in denotes concentration at sorbent bed inlet
out denotes concentration at sorbent bed outlet
$-$ denotes a Laplace transformed variable

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On the Maximum Temperature Rise in Gas-Solid Reactions

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The temperature rise within a solid particle during gas-solid reactions, such as the reduction of metal oxides and the regeneration of catalyst pellets by burning off coke deposits, can be quite large. These temperature rises can introduce some difficulties. For instance, in the case of the metal oxide reduction, severe sintering may occur, thus retarding the reaction rate. The temperature rise during catalyst regeneration may cause damage to the catalyst.

Recently, Luss and Amundson (1969) reported the solution to the problem for diffusion-controlled shrinking-core systems. Their solution for a spherical pellet requires numerical integration. It is the purpose of this note to present an analytical solution for the temperature rise, which is exact for an infinite slab and is a good approximation for a spherical pellet. Asymptotic and approximate solutions for the maximum temperature rise that are more convenient to use and give more insight into the problem are also given.

The results of Luss and Amundson show that the maximum temperature rise within the pellet is quite insensitive to the modified Nusselt number, $Nu^* \equiv ha/\lambda_s$, for $Nu^* = 0 \sim 3$. Therefore, for the purpose of estimating the maximum temperature rise, it is reasonable to assume $Nu^* = 0$, that is, the resistance to the heat transfer within the pellet is much smaller compared to that between the solid and the fluid around the pellet. Under this condition the temperature within the pellet is uniform, and the governing equation becomes much simpler.

It was also shown by Luss and Amundson that, for $Sh^* \equiv k_c a/D_e$ greater than 10, the maximum temperature rise occurs a short period after the start of the reaction—when the reaction front is near the external surface. This suggests that, as a first approximation, we can neglect the curvature of the sphere in calculating the maximum temperature rise.

Using the same nomenclature used by Luss and Amundson, the temperature difference $T = T_s - T_g$ between a slab-like pellet and a gas is governed by the following relationship:

$$a\rho_s C_s \frac{dT}{dt} + hT = Q \qquad (1)$$

The position of the reaction front in a slab is given by the