# An Analytic Solution for the Dynamics of a Packed Adiabatic Chemical Reactor

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Locally linearized equations for dynamic disturbances from a steady state have been solved analytically for an adiabatic chemical reactor with chemically inert packing and a homogeneous chemical reaction. The solutions, in the form of transfer functions, include the effects of heat capacity of the packing and heat transfer between the packing and the fluid, as well as the coupling effects of chemical reaction and the associated heat generation.

Several limiting cases of the transfer functions are discussed and the transfer functions are simplified by an approximation of the temperature dependence of the reaction rate. Frequency responses and step responses of the reactor are calculated from the transfer functions.

The first mathematical analyses of thermal dynamics in a packed bed (heat regenerator) were made by Anzelius (*3*) and Nusselt (*14*) and independently by Schumann (*17*). Their results were confirmed experimentally by Furnas (*11*) and extended mathematically by Brinkley (*6*) to a packed catalytic reactor in which the rate of heat generation in the packing is a linear function of packing temperature. Amundson (*2*) expanded Brinkley's solution to account for radial gradients within the bed.

These analyses do not include, however, an important feature of many chemical reactors: the interaction of temperature and reactant concentration. For most chemical reactions, the reaction rate depends upon both temperature and reactant concentration, and the rate of heat generation does also. These dependences are usually nonlinear.

This temperature and concentration interaction has, however, been included in a study of the dynamics of unpacked reactors by Bilous and Amundson (*5*). Furthermore, Douglas and Eagleton (*10*) have given analytic solutions for the dynamics of adiabatic unpacked reactors. These results for unpacked reactors cannot be readily extended, however, to packed reactors, because it has been shown that the exchange of heat between the fluid and the packing has important effects upon the dynamics of packed reactors (*19*, *20*, *9*).

In the present paper, an approximate analytic solution to the dynamics of an adiabatic packed reactor is presented. This solution shows the dynamic effects of packing heat capacity, heat transfer between the packing and the fluid, and interaction of concentration and temperature through the chemical reaction and associated heat generation. This analytic solution applies only to small disturbances from steady state operating conditions.

The reactor considered here is not a catalytic reactor, however; it is a reactor that contains chemically inert packing and a homogeneous chemical reaction occurring in the fluid phase, which is here a liquid. Such reactors, which have recently been studied experimentally (*20*, *19*, *18*), have the advantage of exhibiting some of the dynamic features of catalytic reactors while avoiding many of the experimental and analytical difficulties of the latter.

An important immediate application of this solution is to studies of the control of reactors in which the dynamic effects of the phenomena listed above are dominant. Such a study is presently in progress in these laboratories.

## SYSTEM EQUATIONS AND SOLUTION

The dimensionless unsteady state equations of the adiabatic reactor considered here are:

Material balance on the reactant

$$\frac{\partial c}{\partial t} + \frac{\partial c}{\partial x} = -r(c, T) = -\exp\left[AT/(T_o + T)\right]c \qquad (1)$$

Heat balance on the fluid

$$\frac{\partial T}{\partial t} + \frac{\partial T}{\partial x} = r + Hp(T_p - T) \qquad (2)$$

Heat balance on the packing

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$$\frac{\partial T_p}{\partial t} = HpB(T - T_p) \quad (3)$$

The representation of the reactor behavior by these equations rests upon a number of assumptions and restrictions: the chemical reaction is irreversible and of first order, with an Arrhenius form of the reaction rate; and liquid velocity, densities, heat capacities, and the heat transfer coefficient are constant. The thermal capacitance of the reactor wall is assumed negligible or, when appropriate, combined with the thermal capacitance of the packing. Also, the effects of radial gradients, turbulent axial diffusion, and conduction of heat from particle to particle are assumed negligible, while the rate of heat conduction within the particle is assumed large. These simplifications are supported by present experimental and computational evidence (*20*, *19*, *18*, *9*).

Only small disturbances from the steady state operating conditions are considered here. The equations describing the reactor at steady state are

$$\frac{dc_s}{dx} = -r_s = -\exp\,[AT_s/(T_o + T_s)]c_s \quad (4)$$

and

$$\frac{dT_s}{dx} = r_s \quad (5)$$

with the boundary conditions

$$\text{at } x = 0, \qquad c_s = 1,\ T_s = 0 \quad (6)$$

The solution to these equations, given by Douglas and Eagleton (*10*), is

$$c_s + T_s = 1 \quad (7)$$

and

$$\begin{aligned}&\{Ei[AT_o(1 - T_s)/(T_o + T_s)(T_o + 1)] -\\ &\quad \exp[-AT_o/(T_o + 1)]\,Ei[AT_o/(T_o + T_s)]\} =\\ &\quad \{Ei[A/(T_o + 1] - \exp[-AT_o/(T_o + 1)]Ei(A)\} -\\ &\qquad \exp[A/(T_o + 1)]x \quad (8)\end{aligned}$$

Equations for the disturbances from the steady state are

$$\frac{\partial \delta c}{\partial t} + \frac{\partial \delta c}{\partial x} = -r(c_s + \delta c,\ T_s + \delta T) + r_s \quad (9)$$

$$\frac{\partial \delta T}{\partial t} + \frac{\partial \delta T}{\partial x} = r(c_s + \delta c,\ T_s + \delta T) - r_s + Hp(\delta T_p - \delta T) \quad (10)$$

$$\frac{\partial \delta T_p}{\partial t} = HpB(\delta T - \delta T_p) \quad (11)$$

Because the disturbances are assumed to be small, the reaction rate may be linearized locally (*5*) about the steady state. The linearized approximation to the reaction rate is

$$r \cong r_s + r_c\,\delta c + r_T\,\delta T \quad (12)$$

where

$$r_c \equiv \frac{\partial r_s}{\partial c_s} = \exp\,[AT_s/(T_o + T_s)] \quad (13)$$

and

$$r_T \equiv \frac{\partial r_s}{\partial T_s} = \exp\,[AT_s/(T_o + T_s)]c_s\,AT_o/(T_o + T_s)^2 \quad (14)$$

With this linearization, Equations (9), (10), and (11) become

$$\frac{\partial \delta c}{\partial t} + \frac{\partial \delta c}{\partial x} = -r_c\,\delta c - r_T\,\delta T \quad (15)$$

$$\frac{\partial \delta T}{\partial t} + \frac{\partial \delta T}{\partial x} = r_c\,\delta c + r_T\,\delta T + Hp(\delta T_p - \delta T) \quad (16)$$

$$\frac{\partial \delta T_p}{\partial t} = HpB(\delta T - \delta T_p) \quad (17)$$

Because the coefficients of $\delta c$ and $\delta T$ are functions of $x$ according to Equations (7), (8), (13), and (14), this linearization retains the important variations in sensitivity of the reaction rate to concentration and temperature throughout the bed.

The validity of Equations (15), (16), and (17) has been confirmed experimentally by other workers. Tinkler and Lamb (*20*), Sinai (*19*), and Simpkins (*18*) have demonstrated, by comparing numerical solutions of these equations to experimental measurements, that this set of equations adequately models the principal dynamic features of the reactor considered here. Although this set of equations can be solved numerically without much difficulty, it also has an exact analytic solution.

The steps to the solution of these equations are as follows. Application of the Laplace transformation to the above equations yields

$$\delta\bar{T}_p = HpB \cdot \delta\bar{T}/(s + HpB) \quad (18)$$

$$\frac{d\delta\bar{c}}{dx} + s\delta\bar{c} = -r_c\,\delta\bar{c} - r_T\,\delta\bar{T} \quad (19)$$

$$\frac{d\delta\bar{T}}{dx} + s\delta\bar{T} = r_c\,\delta\bar{c} + \left[r_T - \frac{Hp \cdot s}{s + HpB}\right]\delta\bar{T} \quad (20)$$

The initial values of the disturbances are not shown bebecause they are zero for step responses and of no consequence for frequency responses, the two cases of importance here. Equations (19) and (20) are readily combined to give a second-order, linear, homogeneous, ordinary differential equation for $\delta\bar{T}$, with variable coefficients.* A particular solution of this equation is $\delta\bar{T} = r_s\,e^{-sx}$; this solution was originally found by guessing, by looking for a solution independent of $Hp$. When a particular solution of a second-order, linear differential equation is known, the general solution can be obtained by reduction of order (*13*). The two constants of integration are evaluated with the boundary conditions, which here are the feed disturbances $\delta\bar{c}(s,0)$ and $\delta\bar{T}(s,0)$. The resulting solution in terms of the variables $\delta\bar{c}$ and $\delta\bar{T}$ is

$$\delta\bar{c}(s,x) = G_{cc}(s,x)\,\delta\bar{c}(s,0) + G_{cT}(s,x)\,\delta\bar{T}(s,0) \quad (21)$$

$$\delta\bar{T}(s,x) = G_{Tc}(s,x)\,\delta\bar{c}(s,0) + G_{TT}(s,x)\,\delta\bar{T}(s,0) \quad (22)$$

with the transfer functions

$$\begin{aligned}G_{cc}(s,x) &\equiv \exp[-sx - Hp \cdot sx/(s + HpB)] -\\ &\quad [1 - Hp \cdot sc_s/r_s(s + HpB)] \times e^{-sx}\,r_s\bar{T}(s,x) \quad (23)\end{aligned}$$

$$\begin{aligned}G_{cT}(s,x) &\equiv [1 - Hp \cdot s/(s + HpB)] \times\\ &\quad \exp[-sx - Hp \cdot sx/(s + HpB)] -\\ &\quad [1 - Hp \cdot sc_s/r_s(s + HpB)]\,e^{-sx}r_s -\\ &\quad [1 - Hp \cdot s/(s + HpB)] \times\\ &\quad [1 - Hp \cdot sc_s/r_s(s + HpB)]\,e^{-sx}r_s\bar{T}(s,x) \quad (24)\end{aligned}$$

$$G_{Tc}(s,x) \equiv e^{-sx}\,r_s\,\bar{T}(s,x) \quad (25)$$

and

$$G_{TT}(s,x) \equiv e^{-sx}\,r_s + [1 - Hp \cdot s/(s + HpB)]\,e^{-sx}\,r_s\bar{T}(s,x) \quad (26)$$

where

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*Tabular material has been deposited as document No. 9644 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D.C., and may be obtained for $1.25 for photoprints or for 35 mm. microfilm.

$$\overline{T}(s,x) \equiv \int_0^x \exp\,[-Hp \cdot sy/(s+HpB)]\; dy/c_s(y) \tag{27}$$

Transfer functions can also be obtained in this manner for small disturbances in fluid velocity (*8*).

The relationship between the above solution and the original nonlinear Equations (1), (2), and (3) may be seen more clearly in terms of certain partial derivatives. In this respect, it is useful to consider the response of the reactor to step disturbances in the feed; for example, a step change in the feed concentration from 1 to a new, time-invariant value $c_i$ when $t = 0$. When Equation (9), which is not in linearized form, is divided by the step size $(c_i - 1)$, and the limit is taken as $c_i$ approaches 1, the result is

$$\begin{aligned}\frac{\partial}{\partial t}\left(\frac{\partial c}{\partial c_i}\right) + \frac{\partial}{\partial x}\left(\frac{\partial c}{\partial c_i}\right) &= -\lim_{c_i \to 1}\left[\frac{r(c_s + \delta c,\ T_s + \delta T) - r_s}{c_i - 1}\right] \\ &= -r_c\left(\frac{\partial c}{\partial c_i}\right) - r_T\left(\frac{\partial T}{\partial c_i}\right)\end{aligned} \tag{28}$$

The derivatives $(\partial c/\partial c_i)$ and $(\partial T/\partial c_i)$ in this equation are at $c_i = 1$ and $T_i = 0$. This equation is quite similar to Equation (15), but the local linearization approximation was not used in its derivation. The transfer function $G_{cc}$, then, is simply the Laplace transformation of the partial derivative $(\partial c/\partial c_i)$ at $c_i = 1$ and $T_i = 0$. And this partial derivative is exact; that is, it is independent of the linearization introduced above and is consistent with the original set of nonlinear Equations (1), (2), and (3). The other transfer functions are similarly interpreted.

Through this partial derivative approach may be seen the relationship between linear and nonlinear aspects of the reactor dynamics. The reactant concentration $c$, for example, at a particular point in the reactor and at a particular time, and in response to step disturbances in the feed, may be expanded in a Taylor's series with respect to the step sizes $(c_i - 1)$ and $T_i$. The solutions presented above, then, give the coefficients in the first-order terms in this expansion. The higher order terms in the expansion are important only when the feed disturbances are large enough for the reactor to exhibit nonlinear behavior. The coefficients of these terms are derivatives of higher order, such as $\partial^2 c/\partial c_i \partial T_i$; these derivatives are not easily determined and have not been considered here.

In the expressions for the transfer functions, the factor

$$G_H(s,x) \equiv \exp[-sx - Hp \cdot sx/(s + HpB)]$$

appears frequently. This function is the transfer function for the heat regenerator and is seen to have considerable influence upon the above four transfer functions, particularly through the integral $\overline{I}$. In fact, the influences of the packing heat capacity and solid-fluid heat transfer resistance appear in every transfer function but always in the combination $Hp \cdot s/(s + HpB)$. These transfer functions demonstrate the complicated influence of heat capacities, heat transfer, and chemical reaction and contrast sharply with transfer functions for unpacked reactors, which have the form of a simple delay (*5, 10*). The complicated behavior of temperature and concentration disturbances which results from these influences has been given physical interpretation by Sinai (*19*) in terms of interfering traveling waves.

For certain limiting values of the reactor parameters, the reactor can be reduced to certain simpler reactors and the transfer functions reduce to those of the simpler reactors. For the unpacked reactor, as a first example, $B$ is infinite and therefore the expression $Hp \cdot s/(s + HpB)$ in the transfer functions is replaced by zero. As a second example, for a packed reactor in which there is no resistance to heat transfer between the fluid and the packing (*8, 9*), $Hp$ is infinite and the expression $Hp \cdot s/(s + HpB)$ becomes $s/B$.

## APPLICATIONS OF TRANSFER FUNCTIONS

These transfer functions may be used in a variety of ways. They can be inverted, for example, to give the time behavior of the reactor in response to certain feed disturbances. In this application, the step response of the heat regenerator is of use. The inversion of $G_H/s$, giving the temperature response to a unit step in the feed temperature, yields

$$\mathcal{L}^{-1}\left\{\exp[-sx - Hp \cdot sx/(s + HpB)]/s\right\} = \begin{cases} 0 & ,\ t < x \\ J[Hp \cdot x,\ HpB(t - x)], & t \geq x \end{cases} \tag{29}$$

where $J(x,y)$ is the function studied by Goldstein (*12*)

$$\begin{aligned} J(x,y) &= 1 - \int_0^x e^{-y-\tau} I_0(2\sqrt{\tau y})\, d\tau \\ &= e^{-x} + \int_0^y e^{-x-\tau} I_1(2\sqrt{\tau x})\, (\sqrt{x/\tau})\, d\tau \end{aligned} \tag{30}$$

Tables of the $J(x,y)$ function have been prepared by Opler and Hiester (*15*). For a step input to the chemical reactor, the Laplace transforms of the feed conditions are

$$\begin{aligned} \delta\overline{c}(s,0) &= \delta c_o/s \\ \delta\overline{T}(s,0) &= \delta T_o/s \end{aligned} \tag{31}$$

The step responses of the chemical reactor are as follows [the expressions given here are valid for $t \geq x$; for $t < x$, $\delta c(t,x)$ and $\delta T(t,x)$ are zero]:

$$\begin{aligned} \delta c(t,x) = \Big\{ & J[Hp \cdot x,\ HpB(t-x)] - [1 - Hp \cdot c_s/r_s] r_s I(t-x,x) \\ & -Hp^2 B c_s \int_0^{t-x} \exp[-HpB(t - x - \tau)] \times \\ & I(\tau,x)\, d\tau \Big\}\, \delta c_o \\ & + \Big\{ [1 - Hp]\, J[Hp \cdot x,\ HpB(t-x)] \\ & +Hp^2 B \int_0^{t-x} \exp[-HpB(t - x - \tau)] \times \\ & J[Hp \cdot x,\ HpB\tau]\, d\tau \\ & - [1 - Hp \cdot \exp[-HpB(t-x)] c_s/r_s] r_s \\ & - [1 - Hp][1 - Hp \cdot c_s/r_s] r_s\, I(t-x,x) \\ & - [1 + (1 - 2Hp) c_s/r_s] Hp^2 B r_s \times \\ & \int_0^{t-x} \exp[-HpB(t - x - \tau)]\, I(\tau,x) d\tau \\ & -Hp^4 B^2 c_s \int_0^{t-x} (t - x - \tau) \exp[-HpB(t - x - \tau)] \times \\ & I(\tau,x)\, d\tau \Big\}\, \delta T_o \end{aligned} \tag{32}$$

$$\begin{aligned} \delta T(t,x) = \{r_s I(t-x,x)\}\delta c_o + \Big\{ & r_s + [1 - Hp] r_s I(t-x,x) + \\ & Hp^2 B r_s \int_0^{t-x} \exp[-HpB(t - x - \tau)] I(\tau,x) d\tau \Big\}\, \delta T_o \end{aligned} \tag{33}$$

where

$$I(t,x) = \int_0^x J(Hp \cdot y,\ HpBt) dy/c_s(y) \tag{34}$$

Unless approximations to the integrals are introduced, it is unlikely that these forms offer any significant computational advantage over direct numerical integration of the partial differential equations. These step response expressions may, however, be of use in further studies of this and related problems, and for this reason they are recorded here.

Limiting behavior of the step responses at very small times and at very large times can be obtained directly from the transfer functions, without inversion, on application of the initial and final value theorems (*21*). A step change in the feed at $t = 0$ has no effect on points in the reactor for which $x > t$, because the fastest disturbances travel at the velocity of the fluid. Therefore the first response to a step change is seen when $t = x$. From the initial value theorem, the responses at $t = x$ are

$$\begin{aligned}\delta c(x,x) &= \lim_{s\to\infty} se^{sx}\delta\overline{c}(s,x) \\ &= [e^{-Hp\cdot x} - (1 - Hp\cdot c_s/r_s)r_s \overline{T}(\infty, x)]\,\delta c_o \\ &\quad + [(1 - Hp)\,e^{-Hp\cdot x} - (1 - Hp\cdot c_s/r_s)r_s \\ &\quad - (1 - Hp)(1 - Hp\cdot c_s/r_s)r_s \overline{T}(\infty, x)]\,\delta T_o \end{aligned} \tag{35}$$

and

$$\delta T(x, x) = [r_s \overline{T}(\infty, x)]\,\delta c_o + [r_s + (1 - Hp)r_s \overline{T}(\infty, x)]\,\delta T_o \tag{36}$$

where

$$\overline{T}(\infty, x) = \int_0^x e^{-Hp\cdot y}\, dy/c_s(y) \tag{37}$$

Because $\delta c$ and $\delta T$ are zero for $t < x$, the expressions given above represent the sizes of the discontinuities that occur at $t = x$. These discontinuities are inherent in the mathematical model used here; they do not exist in actual reactors because they are dispersed by turbulent axial mixing (9). The expressions given above are useful, however, because they are estimates of upper bounds to the initial step responses in actual reactors. It is apparent, from Equation (35), that these expressions also represent the high-frequency limits of the transfer functions' frequency responses.

As time continues to increase after a step disturbance in the feed, the reactor eventually approaches a new steady state that is consistent with the new feed conditions. While the new steady state may be determined exactly by use of Equations (7) and (8) with the new feed conditions, estimates of the new steady state may be made through use of the final value theorem applied to the transfer functions. From the final value theorem, the final steady states for the disturbances are

$$\begin{aligned}\delta c(\infty, x) &= \lim_{s\to 0} s\delta\overline{c}(s, x) \\ &= [1 - r_s \overline{T}(0, x)]\,\delta c_o + [1 - r_s - r_s\overline{T}(0, x)]\,\delta T_o\end{aligned} \tag{38}$$

and

$$\delta T(\infty, x) = [r_s\overline{T}(0, x)]\,\delta c_o + [r_s + r_s\overline{T}(0, x)]\,\delta T_o \tag{39}$$

where

$$\overline{T}(0, x) = \int_0^x dy/c_s(y) \tag{40}$$

These expressions obey the conservation equation

$$\delta c(\infty, x) + \delta T(\infty, x) = \delta c_o + \delta T_o \tag{41}$$

The factors in Equations (38) and (39) also represent the low frequency limit of the transfer functions' frequency responses, as well as the final steady states of the partial derivatives of $c$ and $T$ with respect to $c_i$ and $T_i$. The factor $[1 - r_s\overline{T}(0, x)]$ in Equation (38), for example, is $G_{cc}(j\omega, x)$ in the limit as $\omega$ decreases to zero, and also is the exact partial derivative $(\partial c/\partial c_i)$ at $c_i = 1$, $T_i = 0$, and infinite $t$.

Equations (35), (36), (38), and (39) can also be obtained directly from the solution of the appropriate forms of the original differential equations, Equations (15), (16), and (17). For example, at $t = x$, these equations become

$$\left(\frac{d\delta c}{dx}\right)_{t=x} = \frac{\partial\delta c}{\partial t}\left(\frac{dt}{dx}\right)_{t=x} + \frac{\partial\delta c}{\partial x} = -r_c\delta c - r_T\,\delta T \tag{42}$$

and

$$\left(\frac{d\delta T}{dx}\right)_{t=x} = r_c\,\delta c + [r_T - Hp]\,\delta T \tag{43}$$

The variable $\delta T_p$ can easily be shown (*8*) to be zero at $t = x$. These ordinary differential equations can be solved in the same manner that Equations (19) and (20) were.

The equations for the packed reactor for which $Hp$ is infinite may also be treated in this manner. This case is of interest because it leads to determination of the limiting magnitudes of the low-frequency temperature disturbances, the slowest moving of all disturbances in the reactor. Application of the initial value theorem to the transfer functions of this reactor is considerably more difficult than direct solution of the differential equations. This reactor is described by Equation (15) and

$$\left(1 + \frac{1}{B}\right)\frac{\partial\delta T}{\partial t} + \frac{\partial\delta T}{\partial x} = r_c + r_T\,\delta T \tag{44}$$

which replaces Equations (16) and (17). This system of equations has two characteristics, or paths in space-time along which discontinuities travel. Along the first characteristic, the line $t = x$, the temperature is continuous for step inputs in either feed temperature or feed concentration while the concentration exhibits a discontinuity if there is a step change in feed concentration (9). Thus along the line $t = x$

$$\delta T(x, x) = 0 \tag{45}$$

and by integration of Equation (42) with $\delta T$ zero

$$\delta c(x, x) = c_s\delta c_o \tag{46}$$

These relations replace Equations (35) and (36) when $Hp$ is infinite. The second characteristic is the line $t = (1 + 1/B)x$ along which the concentration deviation $\delta c$ takes on its final steady state value $\delta c(\infty, x)$ and is continuous while the temperature exhibits a discontinuity if there is a step change in feed temperature (9). Thus along the line $t = (1 + 1/B)x$

$$\delta c(x + x/B, x) = \delta c(\infty, x) \tag{47}$$

and integration of Equation (44), with $\delta c$ given by Equation (47), yields

$$\delta T(x + x/B, x) = \delta T(\infty, x) - r_c\,\delta T_o \tag{48}$$

where $\delta c(\infty, x)$ and $\delta T(\infty, x)$ are given in Equations (38) and (39). It is easy to show that with a step change in $\delta T_o$ only (no step disturbance in feed concentration), $\delta T(x + x/B, x)/\delta T_o$ is always negative; this confirms the nonmonotonic behavior of temperature in this reactor as discussed previously (9). These results further indicate that this behavior, which makes control more difficult, may also be observed in reactors with finite but large values for $Hp$. The magnitude of the temperature discontinuity along this second characteristic is

$$\delta T(\infty, x) - \delta T(x + x/B, x) = r_c\,\delta T_o$$

because it can be shown (*8*, 9) that $\delta T(t, x)$ is equal to $\delta T(\infty, x)$ for $t > (1 + 1/B)x$. The amplification factor for a step disturbance in feed temperature in this chemical reactor therefore is $r_c$, the sensitivity of reaction rate to the concentration.

## REACTION RATE APPROXIMATION

An important step in this analysis, as well as in other reactor analyses, is the following simplification of the temperature dependence of the reaction rate:

$$\exp\,[AT/T_o + T)] \cong \exp\,(\kappa T) \qquad (49)$$

The simplified form on the right, the linear exponential form, has been used by Barkelew (*4*), Chambré (7), and Vermeulen (*22*). Aris (*1*, *1a*) has discussed this approximation, pointing out its two major advantages: it reduces the number of reactor parameters and it allows analytic solution of, or at least simplifies, certain reactor problems.

The simplification of the present problem that follows the use of this approximation can be seen by substituting it into the above equations. All of the above equations remain valid, with the following modifications. The reaction rate that appears in Equations (1) and (2) becomes

$$r = e^{\kappa T} c \qquad (50)$$

The reaction rate at steady state that appears in Equation (4) and in the following equations becomes

$$r_s = e^{\kappa T_s} c_s \qquad (51)$$

The derivatives of the reaction rate therefore are given by

$$r_c \equiv \left(\frac{\partial r_s}{\partial c_s}\right) = e^{\kappa T_s} \qquad (52)$$

$$r_T \equiv \frac{\partial r_s}{\partial T_s} = \kappa\, e^{\kappa T_s} c_s \qquad (53)$$

instead of Equations (13) and (14). Finally, integration of Equations (4) and (5) shows that the steady state concentration and temperature are described by Equation (7) and

$$Ei\,(\kappa c_s) = Ei(\kappa) - e^{\kappa} x \qquad (54)$$

instead of Equation (8). The expressions in all other equations given previously remain unchanged.

Comparison of Equations (8) and (54) shows the degree of simplification that the approximation brings to the problem. With the introduction of an inverse exponential integral function, Equation (54) gives $c_s$ as an explicit function of $x$; with a graph of the exponential integral, the steady state concentration profile is easily obtained by hand calculation. Other methods of determining steady state concentration profiles include application of well-known root-finding techniques to Equations (8) and (54) and numerical integration of the original Equations (4) and (5). Numerical integration was used here.

Figure 1 shows steady state concentration profiles, according to Equation (54), for various values of $\kappa$. This figure indicates that $\kappa$ is a measure of the degree of interaction of temperature and reactant concentration through the chemical reaction. This observation is reinforced by an approximate relationship that was found (*8*) between $\kappa$ and the reactor parameters $A$ and $T_o$:

$$\kappa \cong (A - 0.5972)/(T_o + 0.2701) \qquad (55)$$

The numerical parameters in this expression were chosen to minimize the square of the error between the approximate concentration profiles, given by Equation (54), and the true profiles, given by Equations (7) and (8). Vermeulen (*22*) has proposed other relationships between $\kappa$ and the reaction parameters. In terms of dimensional parameters, Equation (55) is

$$\kappa \cong \left(\frac{-\Delta H c_r}{\rho_f c_f}\right)\left[\frac{E - 0.5972\,RT_r}{RT_r(T_r + 0.2701\,\Delta T_a)}\right] \qquad (56)$$

In this expression $\kappa$ increases with both the activation energy $E$ and the exothermic heat of reaction $(-\Delta H)$, the two parameters that indicate the effects of temperature and reactant concentration upon each other. Because $\kappa$ is an *approximate measure of the extent of reaction coupling*, it is called here the *coupling parameter*.

The accuracy of the coupling parameter approximation given in Equation (49) and the further approximation in Equation (55) may be seen in Figure 2, which compares corresponding true and approximate concentration profiles. As this figure indicates, Equations (49) and (55) are useful approximations when $\kappa$ is less than six and $A$ is greater than eight, even though the reaction rate at a point within the reactor may be twenty-five times its value at the reactor inlet.

A further advantage of the coupling parameter approximation in this analysis is that it allows analytic evaluation of the integral in Equation (40):

$$\bar{T}(0, x) = \kappa x - 1 + 1/r_s \qquad (57)$$

Equations (38) and (39), which describe the final steady state after a step change in feed conditions, become

$$\delta c\,(\infty, x) = [(1 - \kappa x)\, r_s]\,\delta c_o - [\kappa x r_s]\,\delta T_o \qquad (58)$$

$$\delta T\,(\infty, x) = [1 - (1 - \kappa x)\, r_s]\,\delta c_o + [1 + \kappa x r_s]\,\delta T_o \qquad (59)$$

Equation (58) shows that there exists a point in the reactor, located at

$$x = 1/\kappa \qquad (60)$$

at which the reactant concentration at the final steady state is not affected by changes in the feed concentration. This point, the concentration node point (9), is important dynamically because it divides the reactor into two regions,

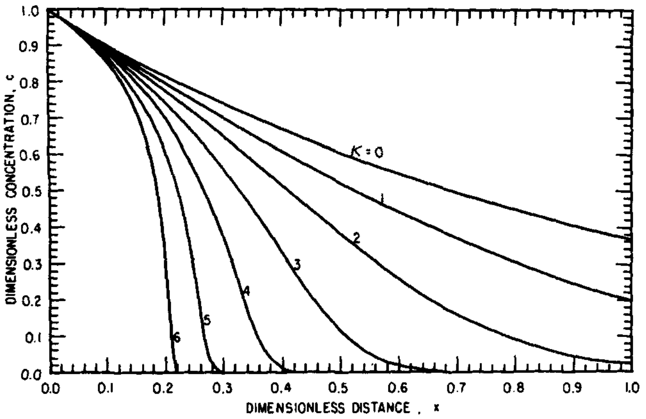

Fig. 1. Concentration profiles at steady state.

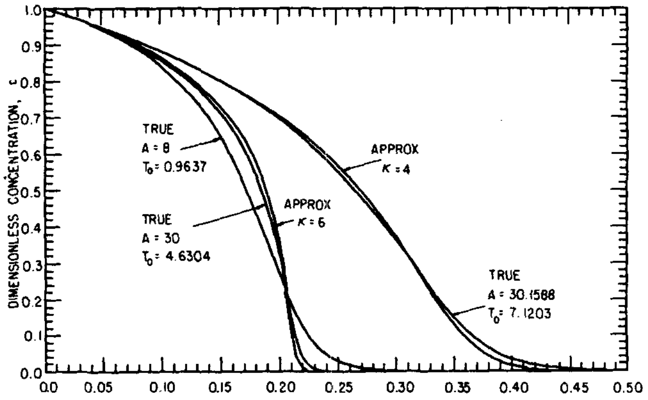

Fig. 2. Comparison of true and approximate concentration profiles at steady state.

and an increase in the feed concentration ultimately results in a decrease in reactant concentration in the region downstream of the concentration node point. In terms of partial derivatives, the node point is the point in the reactor at which $\partial c/\partial c_i$ (at $c_i = 1$, $T_i = 0$, and infinite $t$) passes through zero. Contrary to that stated previously (*9*), the product concentration and the degree of conversion do not exhibit similar node points. Furthermore, the reactant concentration at the node point at intermediate times is not constant, but varies with time in a manner similar to the concentration at other points in the reactor.

A concentration node point is easily determined numerically as the intersection of two concentration profiles, with different feed concentrations, at steady state. In this manner, locations of node points in nonadiabatic reactors have been determined (*8*). Furthermore, concentration node points may also be found in catalytic reactors, since the latter can often be described by the same steady state equations as is the present reactor (*16*). But determination of a node point in this manner reveals that its position is slightly dependent upon the magnitude and direction of the feed disturbance; this is a nonlinear effect that may be estimated (*8*) through the second derivative, $\partial^2 c/\partial c_i^2$. There is therefore a small region in the reactor (rather than a point) in which the steady state reactant concentration is insensitive to a disturbance in the feed concentration, and if the reactor is adiabatic Equation (60) gives a good estimate of its location.

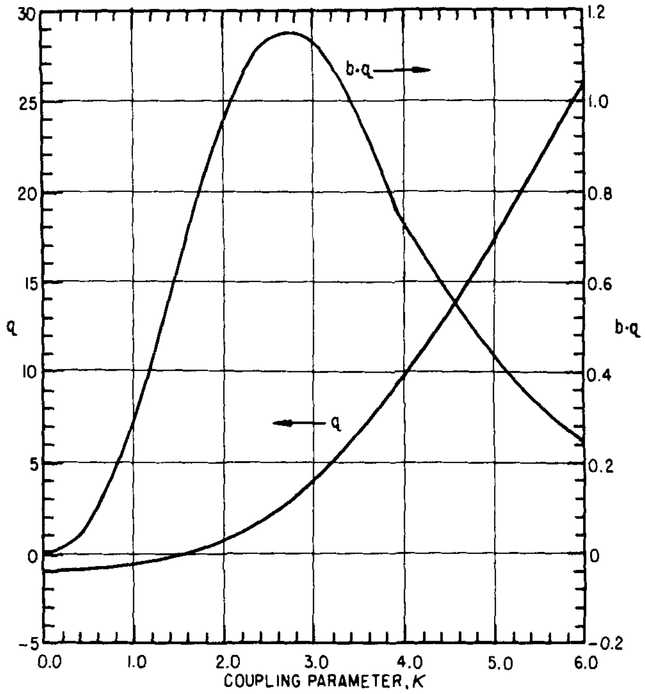

Fig. 4. The parameter $q$ and the product $b \cdot q$ as a function of the coupling parameter $\kappa$.

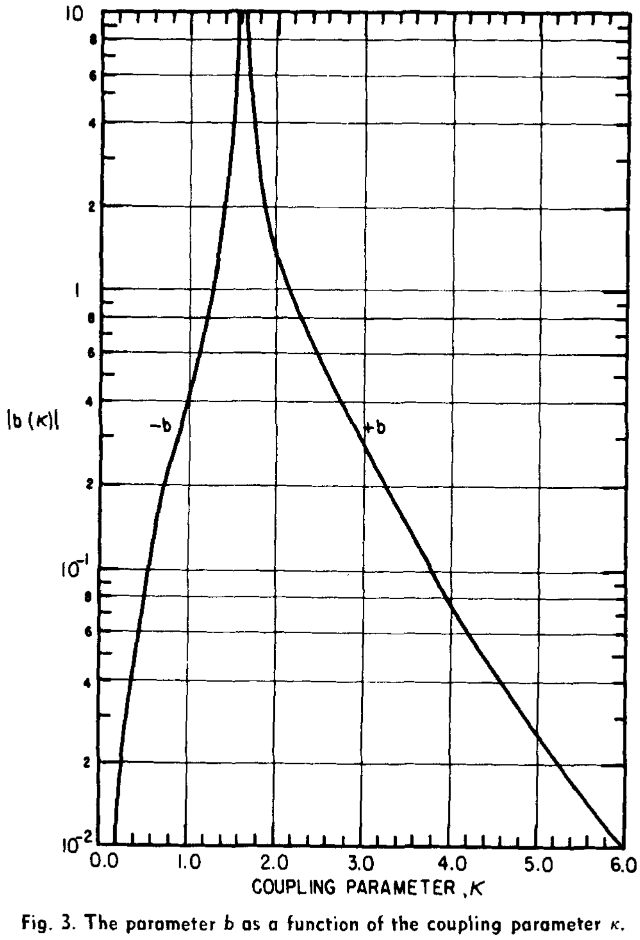

Fig. 3. The parameter $b$ as a function of the coupling parameter $\kappa$.

## FREQUENCY RESPONSES OF THE TRANSFER FUNCTIONS

In addition to the coupling parameter approximation for frequency response calculations, the integral $\overline{I}(s, x)$ can be approximated by a series of exponential functions to avoid repeated numerical quadrature (*8*). In this approximation, the function $1/c_s$ in the integral $\overline{I}(s, x)$ is replaced by

$$1/c_s(x) \cong 1/c_s^*(x) = \{[\exp (e^{\kappa} x) - 1]/c_{sa}\} + \{1 + b(e^{qx} - 1)\} \quad (61)$$

where the first term represents the asymptotic expansion of $1/c_s(x)$ for large values of $x$ and the second term has the form of an approximation to $1/c_s(x)$ for small values of $x$. The two adjustable parameters $b$ and $q$ were determined as functions of $\kappa$ such that the maximum percentage deviation of the approximate integral

$$\overline{I}^*(s, x) \equiv \int_0^x \exp [-Hp \cdot sy/(s + HpB)] \, dy/c_s^*(y) \quad (62)$$

from the integral $\overline{I}(s, x)$ is minimized. The parameter $b$ is shown as a function of $\kappa$ in Figure 3, and the parameter $q$ and the product $bq$ are shown in Figure 4. Although $b$ exhibits a pole in the neighborhood of $\kappa = 1.622$, the product $bq$ in Figure 4 verifies that $1/c_s^*(x)$ remains well behaved for values of $\kappa$ in this neighborhood. Because $b$ and $q$ originate in an approximation for the steady state concentration profile, they should be independent of $Hp$, $B$, and the transform parameter $s$. Therefore they were determined, as described above, only for $s = 0$, and these values were used in frequency response calculations, where $s$ takes on nonzero imaginary values. Evaluation of these parameters in this manner is justified because the behavior of a transfer function in the neighborhood of $s = 0$ is associated with low-frequency and long-time behavior of the process. This behavior is particularly important in packed-bed reactors because the major disturbances travel with the slowly moving temperature wave. This approach is further justified by the accuracy of the approximate frequency responses that are presented below.

Frequency responses of the transfer functions, Equations (23) through (26), are readily obtained by equating $s$ to $j\omega$ and calculating the complex values of the transfer functions over the range of $\omega$. Frequency responses of $G_{cc}$ and $G_{Tc}$ are shown in Figures 5, 6, 7, and 8. The solid lines in the figures represent the transfer functions with $r_s$ given by Equation (4) and $c_s$ given by Equations (7) and (8); the broken lines represent the approximate transfer functions with $r_s$ given by Equation (51) and $c_s$ given

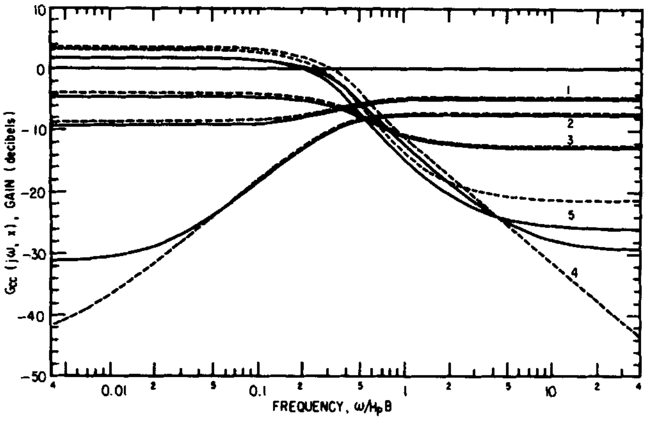

Fig. 5. Frequency response of $G_{cc}$, gain.

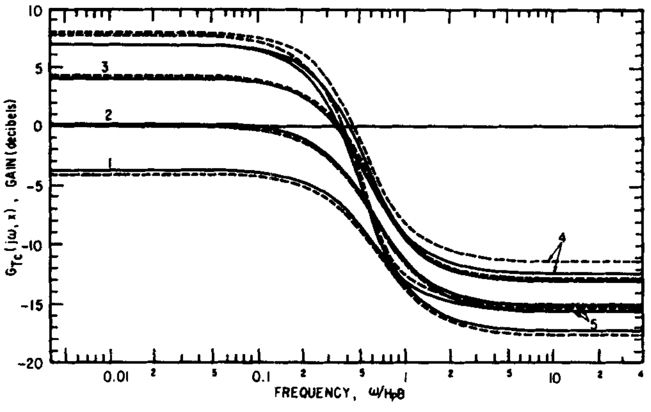

Fig. 7. Frequency response of $G_{Tc}$, gain.

by Equation (54) and with the approximation of $I(s, x)$ given by Equation (62). Frequency responses are shown for these five positions in the reactor:

Position 1: $x = 0.2126$
2: $x = 0.2500$ (concentration node point)
3: $x = 0.2874$
4: $x = 0.3248$ (point of maximum reaction rate)
5: $x = 0.3623$

The parameter values used in these calculations are close to those measured by Sinai (*19*): $Hp = 20$, $B = 1.5$; $A = 30.1588$, $T_o = 7.1203$, and the corresponding $\kappa = 4$. For a characteristic time $(e^A/k)$ of 14.08 seconds, $\omega = 1$ corresponds to 0.0113 cycle/sec.

Figures 5 and 7 give the gain of the transfer functions, which is defined, for $G_{cc}$ for example, as $20 \log_{10}|G_{cc}(j\omega, x)|$. Figure 5 shows the effect of the node point on the frequency response; the gain at the node point, position 2, becomes very small at low frequencies. Figure 6 shows that, at low frequencies, the phase approaches 0 deg. at points upstream of the node point, but approaches +180 deg. at points downstream. It should be noted that the phases shown here do not include the phase contributions of the dead-time factor, exp $(j\omega x)$; this additional phase lag can be as much as 20,756 deg. here.

Figure 5 also exhibits a high-frequency node point near position 4. This behavior is not so important, however, because the model used here becomes inaccurate at high frequencies because it does not include the high-frequency phenomena of turbulent mixing, heat conduction through the packing (that is, from particle to particle), and the finite rate of heat conduction inside each packing particle.

The frequency responses of the other three transfer functions, including $G_{Tc}$ shown in Figures 7 and 8, resemble the frequency response of $G_H$. The phase response (exclusive of the dead-time phase lag) for $G_H$ exhibits a minimum in the neighborhood of $\omega/HpB = 1$; this minimum is lower for larger $x$. Combination of this phase behavior with the dead-time phase lag gives an overall phase lag that can exhibit a local minimum followed by a local maximum, as was observed experimentally by Tinkler and Lamb (*20*). The corresponding gain of $G_H$ decreases monotonically, and the point of greatest decrease is in the neighborhood of $\omega/HpB = 1$. Calculations with $Hp = 40$ reveal, however, a peak in the gain of $G_{TT}$. Sinai (*19*) has attributed such behavior to the effect of frequency upon the interference between concentration and temperature waves.

The solid lines in these figures represent the response of the mathematical model given by Equations (15), (16), and (17) that was confirmed experimentally by Tinkler and Lamb (*20*), Sinai (*19*), and Simpkins (*18*). These workers in fact compared experimentally determined transfer functions with the transformed Equations (19) and (20) integrated on analog and digital computers. Thus, these figures show that the approximate transfer functions (the dashed lines), which include the coupling parameter approximation and the further approximation of $I(s, x)$ by Equation (62), are quite satisfactory representations of the physical process.

## CONCLUDING REMARKS

The primary objective of this paper has been to present an analytic solution that displays some of the principal effects of concentration and temperature interaction in packed-bed reactors in unsteady state operation. The reactor model used here is the simplest continuum model that accounts for a stationary and distributed thermal capacitance, finite rates of heat transfer between the fluid and

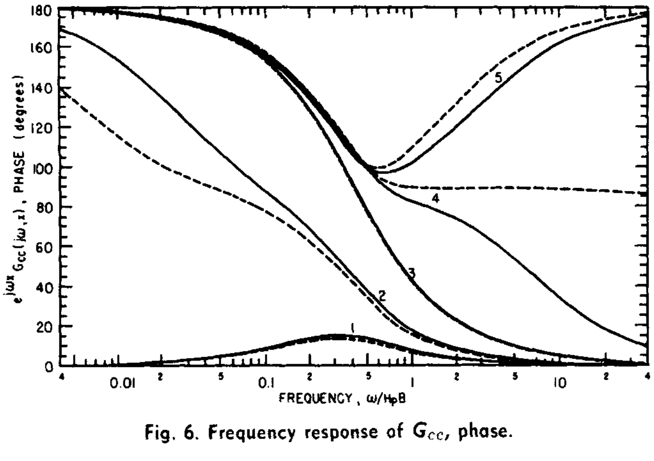

Fig. 6. Frequency response of $G_{cc}$, phase.

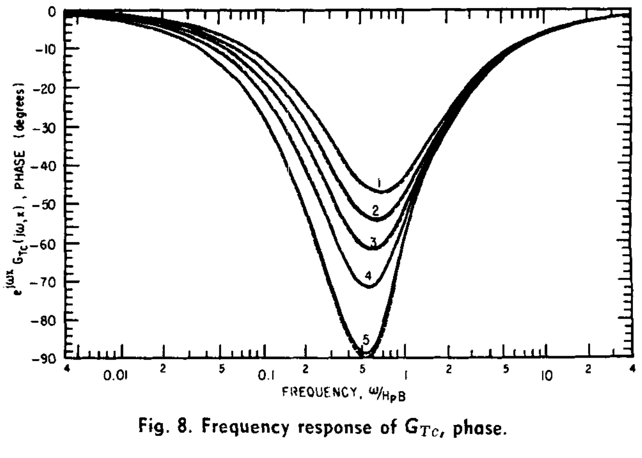

Fig. 8. Frequency response of $G_{Tc}$, phase.

that capacitance, and realistic reaction coupling of the temperature and the reactant concentration. Although the local linearization approximation restricts the results to small disturbances (*18 to 20*), it allows an analytic solution that nevertheless retains the important coupling in the reaction rate. Useful extensions would include reactions having rates dependent on the concentration of more than one species and heat transfer with the surroundings.

Also, there are many refinements that may be made of the basic reactor model used here, but they are usually of secondary importance. Axial fluid mixing, for example, usually has only small influence on the dynamic behavior of these reactors (9).

Of greater importance is the extension of this analysis to a packed catalytic reactor, in which the heat from the chemical reaction is generated in the packing rather than in the fluid. Analysis of such a reactor, however, is complicated by problems of instabilities and multiple steady states, and the authors know of no analytic solution of catalytic reactor dynamics analogous to the solution presented here.

## ACKNOWLEDGMENT

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## NOTATION

$A$ = dimensionless Arrhenius parameter, $E/RT_r$
$a_p$ = specific surface area of the packing
$B$ = dimensionless heat capacity parameter, $\rho_f c_f \varepsilon / \rho_p c_p (1-\varepsilon)$
$b$ = adjustable parameter in $c_s^*$
$c$ = dimensionless concentration of the reactant, $c^*/c_r$
$c_f$ = heat capacity of the fluid
$c_i$ = dimensionless, time-invariant reactant concentration in the feed after a step change in the feed
$c_p$ = heat capacity of the packing
$c_r$ = constant reference concentration that is representative of the feed concentration; for example, if the feed concentration varies sinusoidally, $c_r$ is its average value
$c_s$ = dimensionless reactant concentration in reactor at steady state
$c_{sa}$ = asymptotic parameter in $c_s^*$, $\exp\left[Ei(\kappa) - \gamma - \ln(\kappa)\right]$
$c^*$ = concentration of the reactant
$c_s^*$ = approximation to $c_s$ given in Equation (61)
$E$ = activation energy of the reaction
$Ei(x)$ = exponential integral function, $\int_{-\infty}^{x} e^y dy/y$
$f$ = a frequency, rad./time unit
$G_{cc}, G_{cT}, G_{Tc}, G_{TT}$ = transfer functions given in Equations (23) through (26)
$G_H$ = heat regenerator transfer function
$Hp$ = dimensionless heat transfer parameter, $h_p a_p (1-\varepsilon)/\rho_f c_f \varepsilon k e^{-A}$
$h_p$ = solid-fluid heat transfer coefficient
$I$ = integral given in Equation (34)
$\bar{I}$ = integral given in Equation (27)
$I_0, I_1$ = modified Bessel functions of the first kind, of orders zero and one
$J$ = function given in Equation (30)
$j$ = imaginary unit, $\sqrt{-1}$
$k$ = frequency factor of the reaction rate
$q$ = adjustable parameter in $c_s^*$
$R$ = gas constant
$r$ = dimensionless reaction rate
$r_c$ = sensitivity of reaction rate to reactant concentration. $(\partial r_s/\partial c_s)$
$r_s$ = dimensionless reaction rate at steady state
$r_T$ = sensitivity of reaction rate to temperature, $(\partial r_s/\partial T_s)$
$s$ = Laplace transform parameter
$T$ = dimensionless temperature of the fluid, $(T^* - T_r)/\Delta T_a$
$T_i$ = dimensionless, time-invariant feed temperature after a step change in the feed
$T_o$ = dimensionless reactor parameter, $T_r/\Delta T_a$
$T_p$ = dimensionless temperature of the packing, $(T_p^* - T_r)/\Delta T_a$
$T_r$ = constant reference temperature that is representative of the feed temperature
$T_s$ = dimensionless temperature at steady state
$T^*$ = temperature of the fluid
$T_p^*$ = temperature of the packing
$t$ = dimensionless time, $t^* k e^{-A}$
$t^*$ = time
$v$ = average true velocity of the fluid
$x$ = dimensionless distance, $(x^*/v) k e^{-A}$
$x^*$ = distance from the inlet of the reactor

### Greek Letters

$(-\Delta H)$ = thermodynamic heat of reaction
$\Delta T_a$ = adiabatic temperature rise, $(-\Delta H) c_r/\rho_f c_f$
$\delta c$ = disturbance in reactant concentration, $c - c_s$
$\delta\bar{c}$ = Laplace transform of $\delta c$
$\delta c_o$ = size of a step disturbance in feed concentration
$\delta T$ = disturbance in fluid temperature, $T - T_s$
$\delta\bar{T}$ = Laplace transform of $\delta T$
$\delta T_o$ = size of a step disturbance in feed temperature
$\delta T_p$ = disturbance in packing temperature, $T_p - T_s$
$\delta\bar{T}_p$ = Laplace transform of $\delta T_p$
$\varepsilon$ = void fraction of packed bed
$\gamma$ = Euler's constant = 0.577215...
$\kappa$ = coupling parameter
$\rho_f$ = density of the fluid
$\rho_p$ = density of the packing
$\omega$ = dimensionless frequency, $f/ke^{-A}$

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