An Approximate Approach to Design And Analysis of Fixed-Bed Catalytic Reactors

An approximate approach is proposed for the design and analysis of fixed-bed catalytic reactors in which the intraphase diffusion is important. This approach makes it possible to transform the design and analysis problem of nonisothermal reactors with inter- and intraphase mass and heat transfer resistances into one of simply integrating a single equation with respect to concentration. This transformation is applicable to general form of kinetics. Exceptions are reaction rate forms that can exhibit empirical or approximate negative order behavior. The transformation is based on a generalized effectiveness factor or a reactor point effectiveness factor. While the design and analysis of two-dimensional reactors requires simultaneous solution of conservation equations for mass and heat which are transformed into the equivalents of homogeneous reactors, the problem of one-dimensional reactors with axial dispersion involves simple integration of a single mass conservation equation.

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SCOPE

Rigorous design and analysis procedures of a fixed-bed catalytic reactor (Carberry, 1976; Froment and Bischoff, 1979) involve solving mass and heat conservation equations for the reactor. In order to solve these reactor conservation equations, pellet conservation equations have to be solved first at each point along the reactor. These solutions are then related to the reactor conservation equations through the mass and heat transfer across the pellet-bulk fluid interface. While the rigorous solution can be obtained, there are many difficulties with this rigorous approach. Time and effort involved in obtaining the rigorous solution are often prohibitive, especially when optimization problems are involved. These difficulties include: solving a nonlinear two-point boundary value problem at each point along the reactor, the stability problem of any numerical scheme used, and uncertainty on whether a converged solution is the true solution.

In order to alleviate these difficulties, an approach is proposed, which essentially transforms a heterogeneous reactor design problem into a homogeneous reactor problem for which straightforward integration procedures yield the solution. The transformation is based on a generalized effectiveness factor or a reactor point effectiveness factor which is expressed solely in terms of bulk fluid temperature and concentration. McGreavy and Cresswell (1969) were perhaps the first who attempted the use of generalized effectiveness factor for the catalyst pellet (Aris, 1965; Bischoff, 1965; Petersen, 1965) to simplify the heterogeneous reactor problem. Since then, a better understanding of intra- and interphase transport processes has been gained and it is now possible to express these transport effects in terms of bulk fluid conditions under certain simplifying assumptions. By expressing the bulk temperature in terms of the bulk concentration, one is then left with a mass conservation equation involving only the bulk concentration. A straightforward integration of the resulting equation yields the solution. The approach outlined above does necessarily involve approximations. These include: isothermality of the catalyst pellet (Carberry, 1975; Butt et al., 1977); negligible interphase mass transfer resistance based on the fact that in most realistic cases the mass Biot number is quite large; approximation of the concentration at the pellet center by the concentration corresponding to a pseudo, first-order reaction, and approximation of a rate constant ratio by the first-order term in Taylor series expansion. Because actual physical processes taking place do support all the approximations made, the proposed approach yields near-accurate results. Based on these approximations and the generalized effectiveness factor of Bischoff (1965) for isothermal pellets, the transformation is then made possible through the reactor point effectiveness factor.

In order to arrive at the simple design equation which involves only the bulk concentration, the bulk temperature has to be related to the bulk concentration. While this is straightforward for plug-flow reactors, it is not straightforward for the reactors with axial dispersion. Perturbation techniques are used for the relationship for reactors with axial dispersion.

CONCLUSIONS AND SIGNIFICANCE

The approach presented enables one to transform the difficult problem of designing and analyzing nonisothermal, diffusion-affected heterogeneous catalytic reactors into that of solving simple design equations. The transformation is applicable to general form of reaction kinetics. Exceptions are those exhibiting approximate negative order behavior. For plug-flow reactors, a single equation needs to be integrated with respect to concentration for the design and analysis. For reactors with axial dispersion, the results of plug-flow reactors lead directly to the desired solution. For reactors with radial dispersion, however, simultaneous solution of mass and heat conservation equations is required.

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Rigorous design and analysis of fixed-bed reactors in which heterogeneous catalytic reactions take place is not straightforward. In order to solve the problem, a nonlinear, two point boundary value problem has to be solved at each point along the reactor when no closed-form expression is available for the pellet effectiveness. This solution is related to the mass and energy conservation equations of the reactor through the mass and heat transfer across the pellet-fluid interface. While such a rigorous solution can be obtained, time and effort involved are often prohibitive, especially when optimization problems are analyzed through the sensitivity analysis of reaction parameters. There is also the problem of the stability of any numerical scheme used. Furthermore, there is no guarantee that a converged numerical solution is really the true solution.

A simple and yet quite accurate approach is proposed in this paper to alleviate the problems associated with the rigorous solution of the design and analysis problem. The approximate approach, which is rigorous under certain conditions, is based on the generalized effectiveness factor of Bischoff (1965) that was developed for the internal diffusion-reaction within a pellet. This generalized effectiveness factor is extended to include the mass and heat transfer resistances across the pellet-fluid interface for the reactor point effectiveness factor. The reactor point effectiveness factor is then expressed solely in terms of bulk concentration and physical parameters by eliminating the temperature in the expression. The net effect is that a single mass conservation equation results for the design and analysis of fixed-bed reactors, which contains only the concentration as a single dependent variable. For reactors with axial dispersion, however, more analysis and simplification have to be made for the approach taken. Perturbation techniques are used for near-accurate results.

REACTOR POINT EFFECTIVENESS FACTOR

Consider the internal effectiveness factor for an isothermal pellet. The pellet may be assumed isothermal in view of the work of Carberry (1975) and that of Butt et al. (1977). A general expression for the rate of reaction can be written as:

$$r(\underline{C}) = kg(C) \tag{1}$$

where C is the concentration of key species. Given the stoichiometry of reactions, the rate of formation given in terms of all species $\underline{C}$ can be expressed in terms of the key species C. A more general case in which the function g also depends on temperature will be considered later. For the general rate expression of Eq. 1, Bischoff (1965) derived a generalized internal effectiveness factor, which can be rewritten in terms of quantities at pellet surface:

$$\eta_{in} = \frac{\sqrt{2Dk_s}}{Lk_s g_s}\left[\int_{C_L}^{C_s} g(\alpha)d\alpha\right]^{1/2} \tag{2}$$

where the subscript s is for the quantity evaluated at surface conditions and C_L is the concentration at pellet center. The overall effectiveness factor is given by:

$$\begin{aligned}\eta &= \eta_{in}\left(\frac{k_s g_s}{kg}\right)\\ &= \left(\frac{1}{Lg}\right)\left(\frac{2D}{k}\right)^{1/2}\left(\frac{k_s}{k}\right)^{1/2}\left[\int_{C_L}^{C_s} g(\alpha)d\alpha\right]^{1/2}\end{aligned} \tag{3}$$

The ratio of rate constants is written as:

$$\left(\frac{k_s}{k}\right)^{1/2} = \exp\left\{-\frac{E_a}{2R_gT}\left(\frac{1}{T_s/T} - 1\right)\right\} \tag{4}$$

The ratio of surface temperature to bulk temperature T_s/T is quite close to unity. Therefore, Eq. 4 can be approximated by the first order term in the expansion of the right hand side of the equation in Taylor series:

$$\left(\frac{k_s}{k}\right)^{1/2} \approx 1 + \frac{E_a}{2R_gT}(T_s/T - 1)$$

A better approximation of Eq. 4 up to a value of unity for the argument of the exponential in Eq. 4 is:

$$\left(\frac{k_s}{k}\right)^{1/2} \approx 1 + \frac{1.2E_a}{2R_gT}(T_s/T - 1) \tag{5}$$

The error in using Eq. 5 in place of Eq. 4 is less than 1% up to the argument value of the exponential of 0.5.

The heat transferred across the pellet-fluid interface is equal to the heat generated by chemical reaction in the pellet:

$$h(T_s - T) = (-\Delta H)\mathcal{R}L = (-\Delta H)\eta kgL \tag{6}$$

where $\mathcal{R}$ is the global rate of reaction. From Eq. 6,

$$T_s/T - 1 = \frac{(-\Delta H)L\eta kg}{hT} \tag{7}$$

Substitution of Eq. 7 into Eq. 5 yields:

$$\left(\frac{k_s}{k}\right)^{1/2} = 1 + \frac{1.2E_a(-\Delta H)L\eta kg}{2hT^2R_g} \tag{8}$$

Substituting Eq. 8 into Eq. 3 and rearranging lead to:

$$\eta = \frac{\dfrac{1}{Lg}\left(\dfrac{2D}{k}\right)^{1/2}\left[\displaystyle\int_{C_L}^{C_s} g(\alpha)d\alpha\right]^{1/2}}{1 - \dfrac{1.2E_a(-\Delta H)\sqrt{2Dk}}{2hT^2R_g}\left[\displaystyle\int_{C_L}^{C_s} g(\alpha)d\alpha\right]^{1/2}} \tag{9}$$

It is seen that the reactor point effectiveness factor is completely general with the approximation made in Eq. 5 and thus applicable to general form of kinetics. On the other hand, it contains C_s and C_L which have to be related to bulk concentration before it can be incorporated into the conservation equations of the reactor. When the mass Biot number (of the order of 10^2 to 10^5 for typical conditions) is sufficiently high, the surface concentration C_s is essentially equal to the bulk concentration C. For first-order reactions, the mass Biot number is sufficiently high for the purpose of equating C_s to C when the Thiele modulus ϕ is much less than the mass Biot number. In most applications, this condition is met and C_s may be set equal to C. Let the kinetics be approximated by a pseudo, first-order kinetics:

$$r(C) \approx k_1C \tag{10}$$

Then, the surface concentration is related to the bulk concentration by:

$$C_s = \frac{C}{1 + \phi_1 \tanh \phi_1/B_m} \tag{11}$$

where

$$\phi_1 = L\sqrt{k_1/D} \tag{11a}$$

The concentration at pellet center C_L is given by:

$$C_L = \frac{C_s}{\cosh \phi_1} = \frac{C}{\cosh \phi_1(1 + \phi_1 \tanh \phi_1/B_m)} \tag{12}$$

Since B_m is large under realistic reaction conditions, we have:

$$C_L \approx C/\cosh \phi_1 \tag{12a}$$

These approximate relationships can be used to check whether C_s can be set equal to C, and C_L to zero. The value of ϕ_1 may be evaluated using the conditions at the reactor inlet. When the conditions are such that:

$$\phi_1 \tanh \phi_1/B_m << 1 \text{ and } \phi_1 >> 1 \tag{13}$$

the reactor point effectiveness factor can be written as:

$$\eta = \frac{\frac{1}{Lg}\left(\frac{2D}{k}\right)^{1/2}\left[\int_0^C g(\alpha)d\alpha\right]^{1/2}}{1 - \frac{1.2E_a(-\Delta H)\sqrt{2Dk}}{2hT^2R_g}\left[\int_0^C g(\alpha)d\alpha\right]^{1/2}} \tag{14}$$

As indicated earlier, the first condition of Eq. 13 is usually met under realistic reaction conditions. However, Eq. 12a should be used in Eq. 9 for the reactor point effectiveness factor when the second condition of Eq. 13 is not met.

REACTOR DESIGN AND ANALYSIS: PLUG-FLOW REACTORS

Consider the design and analysis of a plug-flow reactor. Steady-state conservation equations are:

$$\frac{dC}{dz} = -\tau\mathcal{R} \quad (0 \le z \le 1) \tag{15}$$

$$\frac{dT}{dz} = \frac{(-\Delta H)}{\rho C_p}\tau\mathcal{R} + \frac{(\rho C_p)_c}{\rho C_p}\frac{\tau}{\tau_c}\frac{dT_c}{dz} \tag{16}$$

$$-\frac{dT_c}{dz} = \frac{va}{(\rho C_p)_c}\tau_c(T - T_c) \tag{17}$$

Eq. 17 has been written for the countercurrent cooling. The fluid velocity is assumed constant. The global rate $\mathcal{R}$ is given by:

$$\mathcal{R} = \eta r(\underline{C}, T) = \eta kg \tag{18}$$

The diffusion-reaction taking place in the pellet is related to the reactor conservation equations through the heat and mass transfer across the pellet-fluid interface:

$$k_m(C - C_s) = \mathcal{R}L = -D\left.\frac{dy}{dx}\right|_{x=0} L \tag{19}$$

$$h(T_s - T) = (-\Delta H)\mathcal{R}L = (-\Delta H)D\left.\frac{dy}{dx}\right|_{x=0} L \tag{6}$$

The traditional approach is first to solve the diffusion-reaction problem within the pellet and then relate the result to the reactor conservation equations through Eqs. 6, 18 and 19. Instead, the reactor point effectiveness factor is used directly in the reactor conservation equations for the approach taken here. The global rate (Eq. 18) can be expressed as:

$$\mathcal{R} = \eta kg(C) = \frac{\frac{\sqrt{2Dk}}{L}\left[\int_0^C g(\alpha)d\alpha\right]^{1/2}}{1 - \frac{1.2E_a(-\Delta H)\sqrt{2Dk}}{2hT^2R_g}\left[\int_0^C g(\alpha)d\alpha\right]^{1/2}} \tag{20}$$

where Eq. 14 has been used for η. Then, Eq. 15 can be written as:

$$-\frac{dC}{dz} = \tau\left\{\frac{\frac{\sqrt{2Dk}}{L}\left[\int_0^C g(\alpha)d\alpha\right]^{1/2}}{1 - \frac{1.2E_a(-\Delta H)\sqrt{2Dk}}{2hT^2R_g}\left[\int_0^C g(\alpha)d\alpha\right]^{1/2}}\right\} \tag{21}$$

Eq. 21 can be used for parametric sensitivity studies, from which closed-form expressions for the sensitivity terms such as $(\partial C/\partial h)$ can be obtained. For the reactor design, the equation can be integrated from the inlet to the outlet of the reactor to yield:

$$\tau = \int_{C_{out}}^{C_{in}}\left\{\frac{1}{\frac{\sqrt{2Dk}}{L}\left[\int_0^C g(\alpha)d\alpha\right]^{1/2}} - \frac{1.2LE_a(-\Delta H)}{2hT^2R_g}\right\}dC \tag{22}$$

The right hand side of Eq. 22 can be integrated numerically or graphically to yield the reactor size (τ) for the desired conversion (C_{out}). For the integration with respect to C, however, T has to be expressed in terms of C. Consider Eqs. 15 and 16. Combining them and integrating the resulting equation from the reactor inlet to any point in the reactor yield:

$$T = T_{in} - \left(\frac{-\Delta H}{\rho C_p}\right)(C - C_{in}) + \frac{(\rho C_p)_c}{\rho C_p}\frac{\tau}{\tau_c}[T_c - (T_c)_{out}] \tag{23}$$

where $(T_c)_{out}$ is the coolant temperature at $z = 0$. It is seen that Eq. 23 provides the relationship necessary for the integration of Eq. 22. Because of the split boundary conditions on T and T_c, however, iterations on T_c are necessary as detailed below. Design equations for this general case are summarized in Table 1.

TABLE 1. DESIGN EQUATIONS FOR PLUG-FLOW REACTORS

$$r(C) = \mathrm{kg}(C)$$

Nonadiabatic, Nonisothermal Reactor

$$\int_{C_{in}}^{C}\left\{\frac{1}{\frac{\sqrt{2Dk}}{L}\left[\int_0^\xi g(\alpha)d\alpha\right]^{1/2}} - \frac{1.2LE_a(-\Delta H)}{2hT^2Rg}\right\}d\xi = -\tau z \tag{A}$$

$$k = k_o\exp(-E_a/R_gT) \tag{B}$$

$$T = T_{in} - \left(\frac{-\Delta H}{\rho C_p}\right)(C - C_{in}) + \frac{(\rho C_p)_c}{\rho C_p}\frac{\tau}{\tau_c}[T_c - (T_c)_{out}] \tag{C}$$

$$(T_c)_j = (T_c)_{j-1} - \frac{\tau_c\mathcal{U}a\Delta z}{(\rho C_p)_c}[T - T_c]_{j-1} \tag{D}$$

$$(T_c)_{j=0} = (T_c)_{out} = (T_c)_{z=0}$$

Adiabatic, Nonisothermal Reactor

$$\int_{C_{out}}^{C_{in}}\left\{\frac{1}{\frac{\sqrt{2Dk}}{L}\left[\int_0^C g(\alpha)d\alpha\right]^{1/2}} - \frac{1.2LE_a(-\Delta H)}{2hR_g[T_{in} - (-\rho H/\rho C_p)(C - C_{in})]^2}\right\}dC = \tau \tag{E}$$

$$k = k_0\exp\left\{(-E_a/R_g)/\left[T_{in} - \left(\frac{-\Delta H}{\rho C_p}\right)(C - C_{in})\right]\right\} \tag{F}$$

Isothermal Reactor

$$\int_{C_{out}}^{C_{in}}\frac{dC}{\frac{\sqrt{2Dk}}{L}\left[\int_0^C g(\alpha)d\alpha\right]^{1/2}} = \tau \tag{G}$$

When ϕ_1 is less than 3 where

$$\phi_1 = L\sqrt{k_1/D} \quad (r(C) \approx k_1C)$$

the limits of integration on $g(\alpha)$ should be set such that the integral is evaluated by

$$\int_{C_L}^{C} g(\alpha)d\alpha \text{ instead of } \int_0^C g(\alpha)d\alpha$$

where

$$C_L = \frac{C_s}{\cosh\phi_1} \quad (\phi_1 \text{ evaluated at reactor inlet})$$

Consider now the design of an adiabatic reactor. Eq. 23 reduces to:

$$T = T_{in} - \left(\frac{-\Delta H}{\rho C_p}\right)(C - C_{in}) \tag{24}$$

The rate constant k can be explicitly expressed in terms of C:

$$k = \exp\left\{(-E_a/R_g)/\left[T_{in} - \left(\frac{-\Delta H}{\rho C_p}\right)(C - C_{in})\right]\right\} \tag{25}$$

It is seen in Table 1 that the reactor volume (τ) can be obtained

TABLE 2. PARAMETERS FOR THE EXAMPLE REACTION

$k = \exp\left(-\frac{12{,}000}{T} + 14.6\right)$ (1/s), $E_a = 23.76$ kcal/mol

$\zeta = \exp\left(\frac{3{,}600}{T} + 3.86\right)$ (cm³/mol)

$T_{\text{in}} = 673°\text{K}$

$C_{\text{in}} = 1.81 \times 10^{-5}$ mol/cm³

$B_m = 2{,}500$ ($D_e = 1 \times 10^{-3}$ cm²/s, $L = 1$ cm, $k_m = 2.5$ cm/s)

$\left(\frac{-\Delta H}{\rho C_p}\right) = 4 \times 10^7$ °K cm³/mol

$h = 3.245 \times 10^{-4}$ cal/s · cm² · °K

$\phi_1 = 6.3$ at the reactor inlet

by simply integrating a function of C with respect to concentration when adiabatic reactors are involved. A simpler design equation results for isothermal reactors. These results are summarized in Table 1. Consider for illustration purposes an isothermal reactor for which the kinetics is given by a simple adsorption rate form:

$$r(C) = k\left(\frac{C}{\xi + C}\right)$$

$$g(C) = \frac{C}{\xi + C}\cdot$$

Utilizing the rate expression in Eq. G in Table 1 yields after integration:

$$\tau \int_{C_{\text{out}}}^{C_{\text{in}}} \frac{dC}{[C - \xi \ln(1 + C/\xi)]^{1/2} \frac{\sqrt{2Dk}}{L}}$$

The reactor volume (τ) required for a given conversion (C_{out}) can be obtained by integrating the right hand side of the above equation. The analysis procedures for a nonadiabatic, nonisothermal reactor can be stated as follows: Assume $(T_c)_{\text{out}}$. Calculate $(T_c)_j$ from Eq. D in Table 1, which is the Euler version of Eq. 17 for numerical calculation. Obtain $T_j = f(C_j)$ from Eq. C. Use this T_j relationship in Eqs. B and A in Table 1 for the integration of the left hand side of (A). The value of C_j corresponding to z_j is obtained by selecting a value of C_j that yields the known value of $(-\tau z_j)$ when this value of C_j is used for the numerical integration. Proceed to $z = 1$. These procedures are repeated until an assumed value of $(T_c)_{\text{out}}$ gives the calculated $(T_c)_{\text{in}}$ that matches the actual $(T_c)_{\text{in}}$. A table of τ vs. C_{out} can be generated using the above procedures. A value of τ corresponding to the desired conversion (C_{out}) is then selected for the specification of τ.

Consider as an example the design and analysis of an adiabatic plug-flow reactor in which a reaction takes place according to the kinetics:

$$r(C) = k\frac{C}{1 + \zeta C}$$

Complete description of the kinetics and parameters is given in Table 2. The design equations given in Table 1 (Eq. E) reduce to:

$$\int_{C}^{C_{\text{in}}} \left\{ \frac{1}{\sqrt{2Dk/\zeta}\left[C - \frac{1}{\zeta}\ln(1 + \zeta C)\right]^{1/2}} - \frac{5.326 \times 10^{11}}{T^2} \right\} dC = \tau z$$

$$T = T_{\text{in}} + 4 \times 10^7 (C_{\text{in}} - C)$$

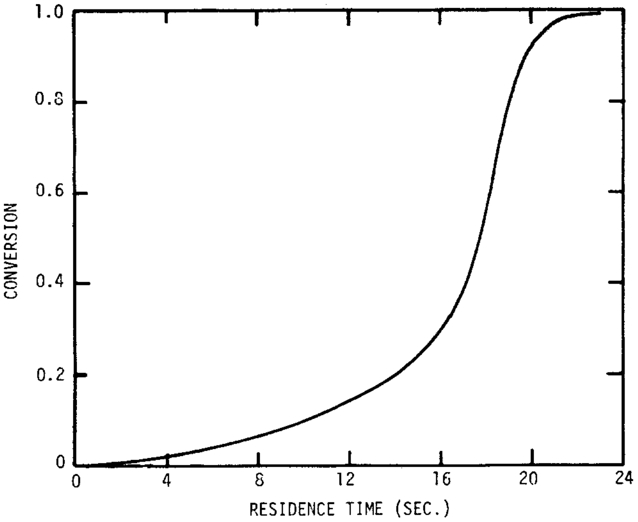

Figure 1. Conversion vs. residence time.

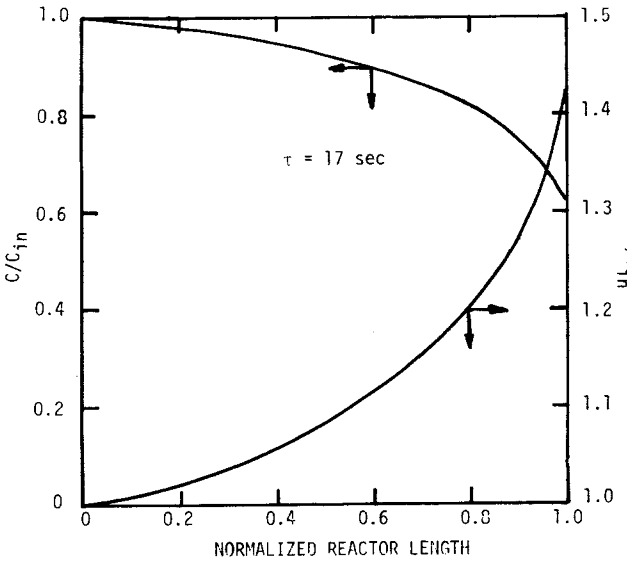

Figure 2. Normalized reactor concentration and temperature.

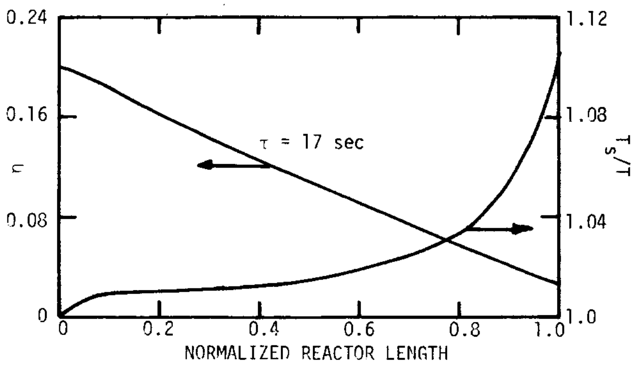

Figure 3. Reactor point effectiveness and pellet surface temperature.

In view of the value of B_m and that of ϕ_1, the surface concentration can be set equal to the bulk concentration and the pellet center concentration can be set equal to zero. A relationship between conversion and residence time or equivalently reactor size was obtained by integrating the above equation. The result is shown in Figure 1. It is seen that there exists a critical size of reactor above which the incremental increase in conversion due to an increase in reactor size accelerates. This size corresponds to the residence time of approximately 17 seconds. Detailed calculations were carried out for the reactor with 17 seconds of residence time and the results are shown in Figures 2 and 3. The ratio of pellet surface temperature to bulk fluid temperature was calculated using Eq. 17. The reactor point effectiveness factor was calculated using Eq. 14. Bulk fluid temperature was used for the temperature dependence of the equilibrium constant ζ. This is discussed in detail in the section to follow. It is seen that the ratio (T_s/T) increases rather rapidly as the conversion accelerates whereas the reactor point effectiveness factor decreases monotonically.

This example clearly demonstrates how simple it is to design and analyze a fixed-bed catalytic reactor using the approach proposed. A simple integration of the equation given above gave the results shown in Figures 1 through 3.

ADEQUACY OF APPROXIMATIONS

Consider the approximations made in arriving at the reactor point effectiveness factor. These approximations include: isothermality of catalyst pellet, negligible interphase mass transfer resistance, representation of the pellet center concentration by the concentration corresponding to a pseudo, first-order reaction and the approximation of Eq. 5. The adequacy of the first two approximations has already been discussed in detail. Consider the representation of the pellet center concentration by Eq. 12a. When C_L is relatively small, which is usually true for diffusion-affected reactions, the integrated value of $g(C)$ is not materially affected by an error in C_L. Consider as an example a second-order reaction. The maximum relative error in the integrated value of $g(C)$ due to an error in C_L is at most of the order of $|3C_L^2 \Delta C_L/C^3|$ where ΔC_L is the error involved in approximating true C_L. Even with 50% error in C_L and moderate diffusional effect (say $\phi_1 = 3$), the maximum relative error is of the order of 1%. Therefore, the approximation made in representing the pellet center concentration by means of a pseudo first-order reaction is quite adequate. Consider the approximation made in writing Eq. 5. As indicated earlier, the error involved in using Eq. 5 in place of Eq. 4 is less than 1% for the value of $[(E_a/2R_gT)(1/(T_s/T) - 1)]$ up to 0.5. For most reactions, the value of $(E_a/2R_gT)$ is less than 10 (Carberry, 1976). This in turn means that the error involved in using Eq. 5 is less than 1% up to (T_s/T) value of 1.05 for exothermic reactions for which $(E_a/2R_gT)$ is 10. In most cases, the value of $[(E_a/2R_gT)(1/(T_s/T) - 1)]$ is less than 0.5. In the example problem considered in the previous section, the value of the quantity at the reactor outlet is 0.6 ($E_a = 23.76$ kcal/mol, $T_s/T = 1.107$, $T = 957$°K). The error in using Eq. 5 can be calculated to be approximately 1%. It is noted, however, that the error can be much larger than 1% in unusual cases.

It was noted in the previous section that the bulk fluid temperature was used for the evaluation of equilibrium constant. The rate expression of Eq. 1 shows no temperature dependence of the function g. In more general cases, the function g contains equilibrium constants, as was the case in the example reaction, which are dependent on temperature. However, the equilibrium constants are less sensitive to temperature changes than the rate constant k in the reaction temperature range of interest. More important is the fact that the equilibrium constants have much less effect on the rate of reaction than the rate constant in the temperature range of interest. Therefore, bulk temperature may be used in place of surface temperature as an approximate way of representing the temperature dependence of the equilibrium constants.

AXIAL DISPERSION: ADIABATIC FIXED-BED REACTORS

For adiabatic fixed-bed reactors with axial dispersion, steady state conservation equations are:

$$-\frac{1}{P_m}\frac{d^2C}{dz^2} + \frac{dC}{dz} = -\tau\mathscr{R} \tag{26}$$

$$-\frac{1}{P_h}\frac{d^2T}{dz^2} + \frac{dT}{dz} = \frac{(-\Delta H)}{\rho C_p}\tau\mathscr{R} \tag{27}$$

where $\mathscr{R}$ is given by Eq. 14. The Peclet numbers are relatively large for most reactors of interest. For such cases, the equations can be rewritten as:

$$-\epsilon\frac{d^2C}{dz^2} + \frac{dC}{dz} = -\tau\mathscr{R} \tag{28}$$

$$-\beta\frac{d^2T}{dz^2} + \frac{dT}{dz} = \left(\frac{-\Delta H}{\rho C_p}\right)\tau\mathscr{R} \tag{29}$$

where $\epsilon = 1/P_m << 1$ and $\beta = 1/P_h << 1$. Boundary conditions are:

$$C_{\text{in}} = C - \epsilon\frac{dC}{dz}\,,\ T_{\text{in}} = T - \beta\frac{dT}{dz} \quad \text{at } z = 0 \tag{30}$$

$$\frac{dC}{dz} = \frac{dT}{dz} = 0 \quad \text{at } z = 1 \tag{30a}$$

If a relationship between T and C can be found, this relationship can be used to decouple Eqs. 26 and 27. For such a decoupled equation, the results of Burghardt and Zaleski (1968) can be used for a near-accurate solution. The relationship between T and C is to be obtained based on the perturbation method (Bellman, 1966).

Consider perturbation of the solution of Eqs. 28 and 29 around $\epsilon = \beta = 0$. Let

$$C = \sum_{i=0}^{n} \epsilon^i C_i \tag{31}$$

$$T = \sum_{i=0}^{n} \beta^i T_i \tag{32}$$

The right hand side of Eq. 28 [$\mathscr{R}$] is expanded in a Taylor series about the concentration and temperature for $\epsilon = \beta = 0$, i.e., about the solution of Eqs. 28 and 29 when $\epsilon = \beta = 0$:

$$\mathscr{R}(C, T) = \mathscr{R}(C_0, T_0) + (C - C_0)\mathscr{R}_c(C_0, T_0) + (T - T_0)\mathscr{R}_T(C_0, T_0) + \ldots \tag{33}$$

where the subscripts C and T indicate differentiation with respect to C and T, respectively. Eq. 33 becomes, upon inserting Eqs. 31 and 32 into Eq. 33:

$$\mathscr{R}(C, T) = \mathscr{R}(C_0, T_0) + (\epsilon C_1 + \epsilon^2 C_2 + \ldots)\mathscr{R}_C(C_0, T_0) + (\beta T_1 + \beta^2 T_2 + \ldots)\mathscr{R}_T(C_0, T_0) + \ldots \tag{34}$$

Utilizing Eqs. 31, 32 and 34 in Eqs. 28 and 29, and collecting zeroth- and first-order terms yield:

$$\frac{dC_0}{dz} = -\tau\mathscr{R}(C_0, T_0) \tag{35}$$

$$\frac{dT_0}{dz} = \frac{(-\Delta H)}{\rho C_p}\tau\mathscr{R}(C_0, T_0) \tag{36}$$

and

$$-\epsilon\frac{d^2C_0}{dz^2} + \epsilon\frac{dC_1}{dz} = -\tau\{\epsilon\mathscr{R}_C(C_0, T_0)C_1 + \beta\mathscr{R}_T(C_0, T_0)/T_1\} \tag{37}$$

$$-\beta\frac{d^2T_0}{dz^2} + \beta\frac{dT_1}{dz}$$

$$= \frac{(-\Delta H)\tau}{\rho C_p}\{\epsilon \mathscr{R}_C(C_0, T_0)C_1 + \beta \mathscr{R}_T(C_0, T_0)T_1\} \tag{38}$$

It is seen that the zeroth-order equations (Eqs. 35 and 36) are those for plug-flow reactors. Combining Eqs. 35 and 36 yields:

$$\frac{dT_0}{dC_0} = -\left(\frac{-\Delta H}{\rho C_p}\right) \tag{39}$$

Eqs. 37 and 38 yield:

$$\frac{dT_1}{dz} - \frac{d^2T_0}{dz^2} = -\left(\frac{-\Delta H}{\rho C_p}\right)\left(\frac{\epsilon}{\beta}\right)\left\{\frac{dC_1}{dz} - \frac{d^2C_0}{dz^2}\right\} \tag{40}$$

The boundary conditions (Eq. 30) dictate that:

$$C_{\text{in}} = C_0 + \epsilon C_1 - \epsilon \frac{dC_0}{dz} + \ldots$$

$$T_{\text{in}} = T_o + \beta T_1 - \beta \frac{dT_0}{dz} + \ldots$$

For the solutions of Eq. 39 and 40, therefore, the above conditions become:

$$C_0 = C_{\text{in}},\ T_0 = T_{\text{in}} \quad \text{at } z = 0 \tag{41}$$

$$C_1 = \frac{dC_0}{dz},\ T_1 = \frac{dT_0}{dz} \quad \text{at } z = 0 \tag{41a}$$

The solution of Eq. 39 with the condition (Eq. 41) is:

$$T_0 = T_{\text{in}} - \left(\frac{-\Delta H}{\rho C_p}\right)(C_0 - C_{\text{in}}) \tag{42}$$

while the solution of Eq. 40 with the condition (Eq. 41a) is:

$$T_1 - \frac{dT_0}{dz} = -\left(\frac{-\Delta H}{\rho C_p}\right)\left(\frac{\epsilon}{\beta}\right)\left(C_1 - \frac{dC_0}{dz}\right) \tag{43}$$

Eqs. 31 and 32 can be rewritten after neglecting the terms of order higher than unity:

$$C = C_0 + \epsilon C_1 \tag{44}$$

$$T = T_0 + \beta T_1 \tag{45}$$

Utilizing Eqs. 42, 43 and 44 in Eq. 45 yields:

$$T - T_{\text{in}} = (C_{\text{in}} - C)\left(\frac{-\Delta H}{\rho C_p}\right) + \left(\frac{-\Delta H}{\rho C_p}\right)(\epsilon - \beta)\frac{dC_0}{dz} \tag{46}$$

Since the first term in the right hand side of Eq. 46 represents the temperature change when there is no axial dispersion, the second term is the first order correction term for the effect of dispersion on the relationship between T and C.

Consider the solution of Eq. 28. If Eq. 46 is used in the right hand side of Eq. 28 to express T in terms of C, we have

$$-\epsilon \frac{d^2C}{dz^2} + \frac{dC}{dz} = -f(C) \tag{47}$$

where

$$f(C) = \tau \mathscr{R} \tag{48}$$

The solution obtained by Burghardt and Zaleski (1968) for Eq. 47 is:

$$C = C_0 + \epsilon f(\ln f_i/f - 1) + (\epsilon^2) \tag{49}$$

where C_0 is the solution when $\epsilon = \beta = 0$ (plug-flow reactor) and

$$f = \tau\left\{\frac{\sqrt{\dfrac{2Dk}{L}}\left[\displaystyle\int_0^{C_0} g(\alpha)d\alpha\right]^{1/2}}{1 - \dfrac{1.2E_a(-\Delta H)\sqrt{2Dk}}{2hT^2R_g}\left[\displaystyle\int_0^{C_0} g(\alpha)d\alpha\right]^{1/2}}\right\} \tag{50}$$

TABLE 3. DESIGN EQUATIONS FOR FIXED-BEDS WITH AXIAL DISPERSION

$$C = C_0 + \epsilon f\{\ln f_i/f - 1\} \tag{A}$$

$$f = +\tau\left\{\frac{\sqrt{\dfrac{2Dk}{L}}\left[\displaystyle\int_0^{C_0} g(\alpha)d\alpha\right]^{1/2}}{1 - \dfrac{1.2E_a(-\Delta H)\sqrt{2Dk}}{2hT^2R_g}\left[\displaystyle\int_0^{C_0} g(\alpha)d\alpha\right]^{1/2}}\right\} \tag{B}$$

$$f_i = \tau\left\{\frac{\sqrt{\dfrac{2Dk_{\text{in}}}{L}}\left[\displaystyle\int_0^{C_{\text{in}}} g(\alpha)d\alpha\right]^{1/2}}{1 - \dfrac{E_a(-\Delta H)\sqrt{2Dk_{\text{in}}}}{2hT^2_{\text{in}}R_g}\left[\displaystyle\int_0^{C_{\text{in}}} g(\alpha)d\alpha\right]^{1/2}}\right\} \tag{C}$$

$$k = k_0 \exp(-E_a/R_gT),\ k_{\text{in}} = k_0 \exp(-E_a/R_gT_{\text{in}}) \tag{D}$$

$$T = T_{\text{in}} - (C_0 - C_{\text{in}})\left(\frac{-\Delta H}{\rho C_p}\right) - \left(\frac{-\Delta H}{\rho C_p}\right)(\beta - \epsilon)\frac{dC_0}{dz} \tag{E}$$

$$\frac{dC_0}{dz} = \tau\left\{\frac{\sqrt{\dfrac{2Dk}{L}}\left[\displaystyle\int_0^{C_0} g(\alpha)d\alpha\right]^{1/2}}{1 - \dfrac{1.2E_a(-\Delta H)\sqrt{2Dk}}{2hT^2R_g}\left[\displaystyle\int_0^{C_0} g(\alpha)d\alpha\right]^{1/2}}\right\} \tag{F}$$

$$k = k_0 \exp\{(-E_a/R_g)/[T_{\text{in}} - \left(\frac{-\Delta H}{\rho C_p}\right)(C_0 - C_{\text{in}})]\} \tag{G}$$

$$f_i = f\big|_{\text{inlet conditions}} \tag{51}$$

Equations necessary for the design and analysis of adiabatic fixed-bed reactors with axial dispersion are summarized in Table 3. Eqs. F and G in Table 3 are those for plug-flow reactors. C_0 and dC_0/dz are first obtained from Eqs. F and G for the analysis. These results are then used in Eqs. B, C, D and E for the calculation of f and f_i. Finally, Eq. A is used for the concentration C. For the design, the exit concentrations corresponding to different values of τ can be tabulated. From these tabulated values, the value of τ that yields the desired conversion (desired exit concentration) can be found.

REACTORS WITH RADIAL DISPERSION

When the reactor point effectiveness factor is used for the reactors with radial dispersion, design equations become

$$\frac{\partial C}{\partial z} - \frac{\tau D_r}{r_o^2}\left(\frac{\partial^2 C}{\partial \bar{r}^2} + \frac{1}{\bar{r}}\frac{\partial C}{\partial \bar{r}}\right) = -\tau \mathscr{R} \tag{52}$$

$$\frac{\partial T}{\partial z} - \frac{\tau K_r}{r_o^2}\left(\frac{\partial^2 T}{\partial \bar{r}^2} + \frac{1}{\bar{r}}\frac{\partial T}{\partial \bar{r}}\right) = \left(\frac{-\Delta H}{\rho C_p}\right)\tau \mathscr{R} \tag{53}$$

where

$$\mathscr{R} = \frac{\sqrt{\dfrac{2Dk}{L}}\left[\displaystyle\int_0^{C} g(\alpha)d\alpha\right]^{1/2}}{1 - \dfrac{1.2E_a(-\Delta H)\sqrt{2Dk}}{2hT^2R_g}\left[\displaystyle\int_0^{C} g(\alpha)d\alpha\right]^{1/2}} \tag{14}$$

The radial boundary conditions are:

$$\frac{\partial C}{\partial \bar{r}} = \frac{\partial T}{\partial \bar{r}} = 0 \quad \text{at } \bar{r} = 0 \tag{54}$$

$$\frac{\partial C}{\partial \bar{r}} = 0,\ -\frac{\partial T}{\partial \bar{r}} = \frac{\mathscr{U}_w}{r_o\rho C_pK_r}(T - T_c) \quad \text{at } \bar{r} = 1 \tag{54a}$$

Again, the design equations for heterogeneous reactors are transformed into those for homogeneous reactors. It is apparent that no simple design equations such as those developed for one-dimensional reactors result and that the conservation equations for mass and heat have to be solved simultaneously. While the transformed design equations can be solved as such, they become particularly useful when combined with approximate methods of solution such as the collocation method (Finlayson, 1972).

Consider the use of Eqs. 52 through 54a for the average conversion at the reactor outlet. Multiplying Eqs. 52 and 53 by $\bar{r}$ and integrating the results with respect to $\bar{r}$ from zero to unity for the average values, we obtain:

$$\frac{\partial \bar{C}}{\partial z} = -2\tau \int_0^1 \bar{r}\mathscr{R}\, d\bar{r} \tag{55}$$

$$\frac{\partial \bar{T}}{\partial z} = 2\tau\left(\frac{-\Delta H}{\rho C_p}\right) \int_0^1 \bar{r}\mathscr{R}\, d\bar{r} - \frac{2\tau \mathscr{U}_w}{r_o \rho C_p}(T_w - T_c) \tag{56}$$

where the boundary conditions (Eqs. 54 and 54a were used and $T_w = T|_{\bar{r}=1}$. The global rate $\mathscr{R}$ is a function of C and T. If the radial profiles are expressed in polynomials of $\bar{r}$, the quantity ($\int_0^1 \bar{r}\mathscr{R} d\bar{r}$) can be evaluated at each point in the reactor, thereby reducing the problem essentially to that of a plug-flow reactor. This is not to imply that the two-dimensional reactor problem for the average conversion is equivalent to that of a plug-flow reactor since the parameters in the polynomials involve the quantities at the center and wall of the reactor, which have to be solved for separately. However, the design problem is greatly simplified. It is of interest to note from Eqs. 55 and 56 that the two-dimensional design problem is equivalent to that of a plug-flow reactor if

$$2\int_0^1 \bar{r}\mathscr{R} d\bar{r} = \mathscr{R}|_{T=\bar{T}, C=\bar{C}}$$

and if the overall heat transfer coefficient is based on the average temperature ($\mathscr{U}$) instead of the wall temperature ($\mathscr{U}_w$) so that the heat transferred away from the reactor to the coolant is written as $\mathscr{U}a(\bar{T} - T_c)$ instead of $\mathscr{U}_w a(T_w - T_c)$. It has been shown for homogeneous reactors (Froment, 1967; Finlayson, 1972) that one-dimensional model is capable of accounting for the influence of parabolic radial profiles if the wall heat transfer coefficient is chosen properly.

CONCLUSION

It is clear that the results obtained are applicable only to diffusion-limited reactions. The problem of kinetically controlled heterogeneous reactors is rather simple since then it is essentially a homogeneous reactor problem. As demonstrated by Petersen (1965) using realistic values of the mass transfer and diffusion parameters, the external transport limitations will never exist unless internal diffusion limitations are also present. Therefore, the problem is essentially a homogeneous reactor problem. The approximation of C_L (Eq. 12a) is an important one and should be treated as given in Table 1.

The general expression for η (Eq. 14) has its limitation. This is due to the fact that certain reaction rate forms can lead to unusual behavior, that is not well represented by the general internal effectiveness factor (Eq. 2), over the entire range of modulus values. These are associated with rate equations that can exhibit empirical or approximate negative order behavior. For instance, Roberts and Satterfield (1965) have shown that a rate equation showing apparent negative order behavior can lead to more than one solution to the steady-state mass balance equations for certain ranges of the parameters.

NOTATION

a = 2/tube radius
B_m = mass Biot number
C = bulk fluid concentration, concentration of key species
$\bar{C}$ = $\int_0^1 \bar{r} C d\bar{r} / \int_0^1 \bar{r} d\bar{r}$
C_p = specific heat capacity
D = effective diffusivity
D_a = axial dispersion coefficient for mass
D_r = radial dispersion coefficient for mass
E_a = activation energy
f = quantity defined by Eq. 50
f_i = f evaluated at inlet conditions
$f(C)$ = function of C defined by Eq. 48
$g(C)$ = function of C defined in Eq. 1 for the rate of reaction
h = film heat transfer coefficient
$(-\Delta H)$ = heat of reaction
k = rate constant
k_1 = rate constant for pseudo, first-order reaction, Eq. 10
k_m = film mass transfer coefficient
K_a = axial dispersion coefficient for heat
K_r = radial dispersion coefficient for heat
L = characteristic length of pellet
P_m = mass Peclet number, ZU/D_a
P_h = heat Peclet number, ZU/K_a
r = intrinsic rate of formation based on volume
r_o = radius of tube
$\mathscr{R}$ = global rate of formation based on volume
$\mathscr{R}_C$ = $\partial\mathscr{R}/\partial C$
$\mathscr{R}_T$ = $\partial\mathscr{R}/\partial T$
$\bar{r}$ = radius of tube normalized with respect to r_o
R_g = gas constant
T = bulk fluid temperature, temperature
$\bar{T}$ = $\int_0^1 \bar{r} T d\bar{r} / \int_0^1 \bar{r} d\bar{r}$
T_w = T at $\bar{r} = 1$
U = fluid velocity
$\mathscr{U}$ = overall heat transfer coefficient based on average temperature
$\mathscr{U}_w$ = overall heat transfer coefficient based on wall temperature
x = pellet coordinate normalized with respect to L
y = pellet concentration
z = reactor axial coordinate normalized with respect to Z
Z = reactor length

Greek Letters

α = dummy variable for integration
β = $1/P_h << 1$
ϵ = $1/P_m << 1$
η_{in} = pellet internal effectiveness factor, observed rate/$k_s g(C_s)$
η = reactor point effectiveness factor, observed rate/$kg(C)$
ϕ_1 = Thiele modulus for pseudo first-order reaction fluid density
ρ = fluid density
τ = residence time, Z/U
ζ, ξ = equilibrium constant

Subscripts

c = coolant side
j = grid point in z
s = pellet surface
L = pellet center
in = at $z=0$ for reactant, at $z=1$ for coolant
out = at $z=1$ for reactant, at $z=0$ for coolant
0 = zeroth order in perturbation method
1 = first order in perturbation method
2 = second order in perturbation method

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A Framework for Description of Mechanical Mixing of Fluids

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Mechanical mixing of fluids interpreted as deformation of contact interfaces between materials or originally designated material surfaces, can be described by continuum mechanical arguments. The idea is developed at two levels.

Part I: Exact kinematical description of mixing of fluids with negligible interfacial tension.
Part II: Description of mixing of fluids with negligible interfacial tension in terms of intermaterial area density.

The approach provides a unified mathematical description of the mechanical mixing of fluids.

SCOPE

Liquid-liquid mixing is a broad and important subject covering a variety of coupled physical phenomena: fluid mechanics, diffusion, and chemical reaction. Important special cases are obtained by the presence or absence of one or two of these three mechanisms. Mixing without diffusion is important in the processing of viscous liquids; mixing with diffusion and complex chemical reactions is an essential part of reaction engineering analysis; and mixing in turbulent flow fields is relevant to the fields of combustion, air pollution and atmospheric science.

However, mixing of fluids has lacked a sound theoretical description, due in large measure to coupling of processes and the complex geometry and time dependent topology of the mixing of moving fluids. Understanding and modeling of the physics of mixing has lagged far behind practical applications. Theories, models, and experiments suggested by a sufficient analytical description are now needed to supply at least qualitative understanding. Customarily different mixing processes are treated by different theories. With few exceptions no attempt has been made to propose a unified view. The consequences of a unified view would be a correct framing with a single perspective for a variety of physical phenomena which on first viewing appear to be unrelated.

This work presents a mathematical description of mechanical mixing of fluids. The only restriction to the analysis is the one of negligible interfacial tension between the fluids being mixed, i.e., "drop formation" is not allowed.

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