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Axial Dispersion in Nonisothermal Packed Bed Chemical Reactors

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A criterion is developed to predict when axial dispersion is important in nonisothermal packed-bed reactors with cooling or heating at the walls. In contrast to the isothermal problem, the criterion does not depend on the length of the reactor, so that the importance of axial dispersion cannot be minimized by increasing the length of the reactor. An increase in flow rate does decrease the importance of axial dispersion. The criterion is applied to the experimental data presented by Schuler, *et al.* (1954), for SO₂ oxidation on an alumina catalyst impregnated with platinum, and the criterion suggests that axial dispersion is important. The experimental data apparently cannot be reconciled with a model excluding axial dispersion, but a model including both axial and radial dispersion correctly predicts the data.

Mathematical models of chemical reactors are useful for predicting the conversion and temperature profiles in packed bed reactors. While very general models can be written down, these are not often used either because of the computational complexity or because it is difficult or impossible to estimate the parameters in the model. We are concerned here with a cylindrical tube, which is cooled or heated at the walls, and which is packed with catalyst. We wish to determine when axial dispersion is important in such a reactor and relate the results to experimental data.

The importance of axial dispersion is shown below to depend on the type of reactor, and reactors with cooling or heating have a different criterion than isothermal or adiabatic reactors. To understand this difference we first examine the known information about the importance of axial dispersion in isothermal and adiabatic reactors.

For a first-order reaction in an isothermal reactor, Carberry (1958), Epstein (1958) and Levenspiel and Bischoff (1963) provide criteria for the neglect of axial dispersion effects. Levenspiel and Bischoff give, in the notation of this paper

$$\frac{C}{C_P} = 1 + \left(\frac{\rho \rho_B k^*}{G} \right)^2 \frac{d_p L}{Pe_{m,z}}$$

where C is the outlet concentration from a reactor of length L with axial dispersion and C_P is the concentration at length L in a reactor without axial dispersion. Levenspiel and Bischoff and Carberry present the above result in terms of the nominal residence time. This notational convention is not followed here since the residence time is proportional to the reactor length, and we wish to display the reactor length directly. We can

rearrange this result to be expressed in terms of the concentration difference.

$$X_P - X = \frac{C - C_P}{C_0} = \left(\frac{\rho \rho_B k^*}{G} \right)^2 \frac{d_p L}{Pe_{m,z}} \times \exp \left[- \left(\frac{\rho \rho_B k^* L}{G} \right) \right] \ll 1 \quad (1)$$

For long enough reactors, axial dispersion can be neglected, since the difference in concentration approaches zero. In an isothermal reactor without the effect of axial dispersion, the exit concentration approaches the equilibrium concentration as the length is increased. The same is true for an isothermal reactor which includes the effects of axial dispersion. Thus the difference in the exit concentration from the two reactors must approach zero as the length is increased. Levenspiel and Bischoff also present a criterion based on the ratio of the reactor lengths required for a given conversion in the two cases. This type of criterion is best suited for design purposes, and the ratio is not a function of reactor length.

For adiabatic reactors Carberry and Wendel (1963) and Hlaváček and Marek (1966) indicate that axial dispersion effects are negligible provided the length is long enough. In the latter case the criterion is

$$Pe_{m,z} L / d_p > 100-400$$

with the number on the right-hand side depending on the reaction rate. A similar criterion must hold for the Peclet number for heat transfer. Here, too, the equilibrium conversion and adiabatic temperature are eventually reached

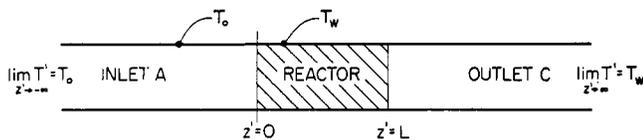


Figure 1. Reactor geometry

for a reactor of sufficient length. If we consider two hypothetical reactors, one including and the other neglecting the axial dispersion effect, the outlet conversion from the reactors approach the same quantity, the equilibrium conversion, if the reactors are long enough. Large axial temperature and conversion gradients within the reactors can result in significant discrepancies in the internal profiles, but the temperature and conversion at the outlet will approach the same values if the length is sufficiently long.

For reactors with cooling or heating at the wall (nonadiabatic) similar results are not necessarily expected, since cooling can quench the reaction so that the equilibrium conversion is never reached for any reasonable length. Calculations have been made for nonadiabatic models including axial dispersion, but with a radially uniform profile (Carberry and Wendel, 1963; Coste, *et al.*, 1961). Carberry and Wendel (1963) concluded that the criterion for isothermal reactors is sufficient and that axial dispersion is unimportant for long reactors ($L/d_p < 50$). It appears that the conclusions of Carberry and Wendel have found acceptance by others (Hlaváček, 1970; Valstar, 1969); the generally accepted criterion is based on the reactor length.

The conclusions of Carberry and Wendel are open to question, however. In their Figure 2 the concentration and temperature profiles are compared for two reactors, one without axial dispersion ($n \rightarrow \infty$) and one with axial dispersion corresponding to 100 mixing cells ($n = 100$), where n is defined in the notation of this paper as $(L/2d_p)Pe_{m,z} = 1/(2\gamma)$. This comparison is made while keeping $k_0\theta_0$ fixed, where k_0 is a first-order reaction rate constant and θ_0 is the residence time based on the inlet conditions; here $\theta_0 = L\rho/G$. Now if the comparison is to be for two reactors which are identical except for the length and the axial dispersion parameter, then the reaction rate constant, k_0 , and velocity, G/ρ , must be the same in both reactors. Since the same value of $k_0\theta_0 = k_0L\rho/G$ is used for both reactors in their Figure 2, L must be the same, too. Then the parameter

$$n = (L/2d_p)Pe_{m,z} = LG/(2\rho D_z)$$

and solutions for different n correspond to different values of D_z , not different values of L . The conclusion of their Figure 2 is correct: axial dispersion is unimportant for the case illustrated. It is incorrect, however, to extrapolate those results to the conclusion that axial dispersion is unimportant when $L/d_p > 50$. To test that conclusion it is necessary to change $k_0\theta_0$ at the same time n is changed, since *both* are proportional to the length.

We wish, therefore, to reexamine the question of the importance of axial dispersion in nonadiabatic reactors, and we include the effects of both axial and radial dispersion. First, we write the equations and derive the boundary conditions for this model. Next is derived the criterion which shows if axial dispersion is important. The criterion is applied to particular experimental data and we find that axial dispersion is important. Calculations are then made for this case using the general model, and the two-dimensional equations are solved with the orthogonal collocation method.

Reactor Model Equations

Consider the equations governing a packed-bed catalytic reactor under the assumptions of constant physical properties and plug flow and for a reaction rate governed by the conversion and temperature. The dimensionless equations are

$$\begin{aligned} \gamma \frac{\partial^2 X}{\partial z^2} - \frac{\partial X}{\partial z} + \frac{\alpha}{r} \frac{\partial}{\partial r} \left(r \frac{\partial X}{\partial r} \right) + \beta R(X, T) &= 0 \\ \gamma' \frac{\partial^2 T}{\partial z^2} - \frac{\partial T}{\partial z} + \frac{\alpha'}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \beta' R(X, T) &= 0 \\ \frac{\partial X}{\partial r} = \frac{\partial T}{\partial r} &= 0 \quad (r = 0) \\ \frac{\partial T}{\partial r} = -BiT, \frac{\partial X}{\partial r} &= 0 \quad (r = 1) \end{aligned} \quad (2)$$

The boundary conditions in the axial direction are not listed above, as these have apparently not been derived for cases of both axial and radial dispersion.

The axial boundary conditions when radial dispersion is important are derived in the same way as when radial dispersion is neglected (Bischoff, 1961; Levenspiel and Bischoff, 1963; Wehner and Wilhelm, 1956). The reactor is partitioned into three sections (Figure 1): inlet ($-\infty < z' < 0$), reactor ($0 \leq z' \leq L$), outlet ($L < z' < \infty$). The inlet and outlet regions are governed by the same differential equations as the reactor, but the generation term is zero ($R(X, T) = 0$). The parameters in the differential equations ($\alpha, \gamma, \alpha', \gamma', Bi$) are defined in the same manner as for the reactor, but are the values applicable to the inlet or outlet. At the inlet or outlet boundaries the fluxes of mass and energy and the concentration and temperature are continuous.

Since the reaction term is zero in the inlet and outlet regions, the differential equations governing the inlet and outlet regions are linear and uncoupled. They may be solved analytically to give an infinite series involving Bessel functions. The form of the solution is

$$v(z, r) = v_0 + \sum_{n=0}^{\infty} A_n \exp \left[\left(1 \pm \sqrt{1 + 4\alpha\gamma\lambda_n^2} \right) \frac{z}{2\gamma} \right] J_0(\lambda_n r) \quad (3)$$

where the eigenvalues are specified by

$$-\lambda_n J_1(\lambda_n) + Bi J_0(\lambda_n) = 0$$

The parameters α, γ , and Bi are taken appropriate to the equations for mass or heat in the inlet or outlet; *e.g.*, $Bi = 0$ for mass. The positive sign applies to the inlet, while the negative sign applies to the outlet. The term $v_0 = 1$ for the solution for temperature in the inlet ($z < 0$) whereas $v_0 = 0$ for the solutions for temperature in the outlet ($z > 1$) or for conversion in either inlet or outlet sections. At the inlet or outlet the temperature or conversion is required to be continuous, *e.g.*

$$v(0^+, r) = v(0^-, r) = v_0 + \sum_{n=0}^{\infty} A_n J_0(\lambda_n r)$$

This equation is multiplied by $J_0(\lambda_n r)r$ and integrated over r to give the $\{A_n\}$ in terms of integrals involving $v(0^+, r)$ and Bessel functions. The expressions for the $\{A_n\}$ are then substituted into the equations making the fluxes continuous, *e.g.*

$$\gamma_B \frac{\partial v}{\partial z}(0^+, r) = \gamma_A \frac{\partial v}{\partial z}(0^-, r)$$

to give the boundary conditions solely in terms of the unknown solution at the boundary $v(0, r)$ or $v(1, r)$.

Conversion

$$\begin{aligned} \gamma \frac{\partial X}{\partial z}(0, r) &= \sum_{n=0}^{\infty} (1 + \sqrt{1 + 4\alpha_A \gamma_A \lambda_n^2}) \times \\ &\quad \left[\int_0^1 X(0, r) J_0(\lambda_n r) r dr \right] \frac{J_0(\lambda_n r)}{J_0^2(\lambda_n)} \\ \gamma' \frac{\partial X}{\partial z}(1, r) &= \sum_{n=0}^{\infty} (1 - \sqrt{1 + 4\alpha_C \gamma_C \lambda_n^2}) \times \\ &\quad \left[\int_0^1 X(1, r) J_0(\lambda_n r) r dr \right] \frac{J_0(\lambda_n r)}{J_0^2(\lambda_n)} \end{aligned} \quad (4)$$

where the λ_n 's are determined by $J_1(\lambda_n) = 0$

Temperature

$$\begin{aligned} \gamma' \frac{\partial T}{\partial z}(0, r) &= \sum_{n=1}^{\infty} (1 + \sqrt{1 + 4\alpha_A' \gamma_A' \lambda_n^2}) \times \\ &\quad \left\{ \int_0^1 [T(0, r) - 1] J_0(\lambda_n r) r dr \right\} \frac{J_0(\lambda_n r)}{J_0^2(\lambda_n) \left[1 + \left(\frac{\text{Bi}_A}{\lambda_n} \right)^2 \right]} \end{aligned}$$

where the λ_n 's are the solutions of $\lambda_n = \text{Bi}_A J_0(\lambda_n) / J_1(\lambda_n)$.

$$\begin{aligned} \gamma' \frac{\partial T}{\partial z}(1, r) &= \sum_{n=1}^{\infty} (1 - \sqrt{1 + 4\alpha_C' \gamma_C' \lambda_n^2}) \times \\ &\quad \left[\int_0^1 T(1, r) J_0(\lambda_n r) r dr \right] \frac{J_0(\lambda_n r)}{J_0^2(\lambda_n) \left[1 + \left(\frac{\text{Bi}_C}{\lambda_n} \right)^2 \right]} \end{aligned}$$

where the λ_n 's are found from $\lambda_n = \text{Bi}_C J_0(\lambda_n) / J_1(\lambda_n)$. The subscripts *A* and *C* above are used to denote parameter values for the inlet and outlet region, respectively.

When there is no radial dispersion ($\alpha = \alpha' = 0$) the boundary conditions reduce to the usual ones (Bischoff, 1961; Wehner and Wilhelm, 1956)

$$\begin{aligned} \gamma \frac{\partial X}{\partial z} &= X; \quad \gamma' \frac{\partial T}{\partial z} = T - 1 \quad (z = 0) \\ \frac{\partial X}{\partial z} &= 0; \quad \frac{\partial T}{\partial z} = 0 \quad (z = 1) \end{aligned}$$

These boundary conditions have previously been stated to apply to eq 2 (Hlaváček, 1970), but we see here that they apply only when radial dispersion is unimportant in the inlet and outlet ($\alpha = \alpha' = 0$).

Due to the complicated nature of the exact boundary conditions, the orthogonal collocation method (Finlayson, 1971, 1972; Villadsen and Stewart, 1967) is used to approximate the exact boundary conditions. The first collocation approximation ($N = 1$) and an analysis similar to that used to derive eq 4 gives the following approximate boundary conditions

$$\begin{aligned} \gamma \frac{\partial X}{\partial z} &= X \quad (z = 0) \\ \frac{\partial X}{\partial z} &= 0 \quad (z = 1) \\ \gamma \frac{\partial T}{\partial z} &= \frac{1}{2} \left(1 + \sqrt{1 + \frac{24\alpha_A' \gamma_A' \text{Bi}_A}{\text{Bi}_A + 3}} \right) (T - 1) \quad (z = 0) \\ \gamma' \frac{\partial T}{\partial z} &= \frac{1}{2} \left(1 - \sqrt{1 + \frac{24\alpha_C' \gamma_C' \text{Bi}_C}{\text{Bi}_C + 3}} \right) T \quad (z = 1) \end{aligned} \quad (5)$$

The approximate boundary conditions above are equivalent to those that would be derived if all radial resistance to heat transfer were lumped at the wall in the inlet and outlet with an overall heat transfer coefficient of

$$\frac{1}{U} = \frac{1}{h_w} + \frac{r_0}{3k_r}$$

The approximate boundary conditions are also the same as those which would be derived by expressing the solution with only the first term in the infinite series, except that the first eigenvalue is approximated by orthogonal collocation. If desired a higher approximation ($N > 1$) can be derived using the orthogonal collocation method (Young, 1972). We note that the conversion boundary conditions are the same as when there is no radial dispersion, whereas the thermal boundary conditions are not unless $\text{Bi} = 0$ or $\alpha' = 0$ in the inlet or outlet sections. The model which includes the effects of both axial and radial dispersion has previously been designated the dispersed plug flow model (Levenspiel and Bischoff, 1963); for simplicity here we refer to it as the general model.

Solution of Equations

Due to the complicated nature of the exact boundary conditions (4), the approximate boundary conditions (5) are used here together with eq 2. The problem is seen to be a set of coupled nonlinear elliptic partial differential equations of the boundary value type in both the axial and radial directions. The boundary value nature of the problem would seem to make solution very difficult even for numerical techniques using the digital computer, and some investigators have used this fact for partial justification of simplifications (Beek, 1962; Hlaváček, 1970). The recently developed orthogonal collocation method has been found to be very efficient for the solution of boundary value problems and is used here.

Applying orthogonal collocation in both the axial and radial directions, we have

$$\begin{aligned} \gamma \sum_{j=1}^{M+2} B_{ij}^{(2)} X_{kj} - \sum_{j=1}^{M+2} A_{ij}^{(2)} X_{kj} + \\ \alpha \sum_{j=1}^{N+1} B_{kj}^{(r)} X_{jt} + \beta R_{kt} = 0 \end{aligned} \quad (6)$$

$$\begin{aligned} \gamma' \sum_{j=1}^{M+2} B_{ij}^{(2)} T_{kj} - \sum_{j=1}^{M+2} A_{ij}^{(2)} T_{kj} + \\ \alpha' \sum_{j=1}^{N+1} B_{kj}^{(r)} T_{jt} + \beta' R_{kt} = 0 \end{aligned}$$

$$\sum_{j=1}^{M+2} A_{1j}^{(2)} X_{kj} = \frac{1}{\gamma} X_{k1}$$

$$\sum_{j=1}^{M+2} A_{1j}^{(2)} T_{kj} = [T_{k1} - 1] \frac{1}{2\gamma'} \left(1 + \sqrt{1 + \frac{24\alpha_A' \gamma_A' \text{Bi}_A}{\text{Bi}_A + 3}} \right)$$

$$\sum_{j=1}^{M+2} A_{M+2,j}^{(2)} X_{kj} = 0$$

$$\begin{aligned} \sum_{j=1}^{M+2} A_{M+2,j}^{(2)} T_{kj} = T_{k,M+2} \left(\frac{1}{2\gamma'} \right) \times \\ \left(1 - \sqrt{1 + \frac{24\alpha_C' \gamma_C' \text{Bi}_C}{\text{Bi}_C + 3}} \right) \end{aligned}$$

$$\sum_{j=1}^{N+1} A_{N+1,j}^{(r)} X_{jt} = 0$$

$$\sum_{j=1}^{N+1} A_{N+1,j}^{(r)} T_{jt} = -\text{Bi} T_{N+1,t}$$

where $i = 2, 3, \dots, M + 1$; $k = 1, 2, \dots, N$; $X_{ji} = X(r_j, z_i)$; $T_{ji} = T(r_j, z_i)$; and $R_{ki} = R(X_{ki}, T_{ki})$. The matrices $B^{(2)}$ and $A^{(2)}$ approximate the axial Laplacian and first derivative, while the matrices $B^{(r)}$ and $A^{(r)}$ approximate the radial Laplacian and first derivative. The matrices are easily calculated with the algorithm described elsewhere (Finlayson, 1972; Villadsen and Stewart, 1967). The boundary conditions at $r = 0$ are satisfied by the trial functions, which are orthogonal polynomials in r^2 defined by the weighting function $w = 1 - r^2$ and described elsewhere (Finlayson, 1971, 1972).

From examination of eq 6, it is seen that orthogonal collocation reduces the problem to a set of coupled nonlinear algebraic equations which are easily solved using the digital computer. The solution algorithm is outlined here, while details may be found elsewhere (Young, 1972).

1. The boundary conditions are linear, so the temperature and conversion on the boundaries may be written in terms of the values at the interior points. The values on the boundaries are then eliminated from the equations for the interior points. The above simplifications reduce the problem to the following form

$$\sum_{j=2}^{M+1} V_{ij} X_{kj} + \sum_{j=1}^N Y_{kj} X_{ji} + \beta R_{ki} = 0$$

$$\sum_{j=2}^{M+1} V_{ij}' T_{kj} + \sum_{j=1}^N Y_{kj}' T_{ji} + \beta' R_{ki} = W_{ki}$$

2. The collocation points are then renumbered and the above matrices are rearranged to reduce the problem to the following form

$$\sum_{j=1}^{N \cdot M} P_{ij} X_j + \beta R_i = 0$$

$$\sum_{j=1}^{N \cdot M} P_{ij}' T_j + \beta' R_i = W_i$$

3. Either the Newton-Raphson or Picard iteration method is then applied to solve the above equations. The Newton-Raphson method converges rapidly but requires the inversion of an $(N \cdot M) \times (N \cdot M)$ matrix for each iteration, while the Picard method requires the inversion of two $(N \cdot M) \times (N \cdot M)$ matrices and converges more slowly.

From the above discussion it is seen that the axial dispersion effect can be included without undue difficulty when the orthogonal collocation method is used. It is common practice, however, to neglect the axial dispersion effect (Beek, 1962; Froment, 1967; Hlaváček, 1970). If this assumption is used then γ and γ' are set to zero in eq 2 and boundary conditions (5), and the governing equations reduce to

$$\frac{\partial X}{\partial z} = \frac{\alpha}{r} \frac{\partial}{\partial r} \left(r \frac{\partial X}{\partial r} \right) + \beta R(X, T)$$

$$\frac{\partial T}{\partial z} = \frac{\alpha'}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \beta' R(X, T)$$

$$\frac{\partial X}{\partial r} = \frac{\partial T}{\partial r} = 0 \quad (r = 0) \quad (7)$$

$$\frac{\partial X}{\partial r} = 0, \frac{\partial T}{\partial r} = -\text{Bi}T \quad (r = 1)$$

$$X = 0, T = 1 \quad (z = 0)$$

Equations 7 are a set of coupled nonlinear parabolic differential equations of the boundary value type in the radial direction, but of the initial value type in the axial direction. Since eq 7 are initial value problems in the axial direction, the equations may be integrated by standard methods, for example the Crank-Nicolson method, or by the orthogonal collocation

method as described elsewhere (Finlayson, 1971). For comparison with the general model, eq 7 are solved using orthogonal collocation in the radial direction and an improved Euler integration scheme in the axial direction. The model governed by eq 7 has commonly been referred to as the two-dimensional model but here it is designated the radial model to distinguish it from the general model.

The Importance of Axial Dispersion

The radial model has been used extensively in the literature, but except for the theoretical calculations of Feick and Quon (1970), the general model has not been used. Even Feick and Quon (1970) assumed no radial dispersion in the inlet and outlet sections. The reasons for ignoring the general model are apparently twofold: (1) axial dispersion has generally been considered unimportant (Beek, 1962, Froment, 1967; Hlaváček, 1970); (2) the general model is somewhat more complicated and has been considered too formidable to solve (Hlaváček, 1970; Lapidus, 1961).

The first criterion we develop depends on the conditions at the inlet to the reactor. Due to axial dispersion the temperature and concentration take values at $z = 0$ which differ from their inlet values (at $z = -\infty$). When axial dispersion is ignored, the temperature and concentration at $z = 0$ take the inlet values. Thus the two models give different results at the inlet. This difference can persist throughout the reactor if it is heated or cooled, because the equilibrium values of temperature and conversion need not be approached. The spatial distribution of temperature is all important. By contrast, however, in the isothermal or adiabatic reactor this difference must decrease if the length is sufficient, since the same equilibrium values are finally reached whether or not axial dispersion is important. The criterion for reactors with cooling or heating is therefore different from that for isothermal or adiabatic reactors and is derived as follows. We make several assumptions in order to obtain analytical results. We wish to solve one problem with axial dispersion and one without. Radial dispersion is neglected in both problems, on the ground that the effect of radial dispersion is similar in both cases. The reaction rate expression is linearized as follows. For the mass balance, $R(X, T) = (1 - X)R_0$, where we have written $R_0 = R(X, T)|_{z=0}$; for the energy balance, $R(X, T) = R_0$. The mass balances are then: Problem 1

$$\gamma \frac{d^2 X}{dz^2} - \frac{dX}{dz} + \beta R_0(1 - X) = 0$$

$$\gamma \frac{dX}{dz} = X \quad (z = 0) \quad (8)$$

$$\gamma \frac{dX}{dz} = 0 \quad (z = 1)$$

Problem 2

$$\frac{dX_P}{dz} - \beta R_0(1 - X_P) = 0 \quad (9)$$

$$X_P(0) = 0$$

The energy balances are: Problem 1

$$\gamma' \frac{d^2 T}{dz^2} - \frac{dT}{dz} + \beta' R_0 = 0$$

$$\gamma' \frac{dT}{dz} = T - 1 \quad (z = 0) \quad (10)$$

$$\gamma' \frac{dT}{dz} = 0 \quad (z = 1)$$

Problem 2

$$\frac{dT_P}{dz} - \beta'R_0 = 0 \quad (11)$$

$$T_P(0) = 1$$

The solution to eq 9 is

$$X_P = 1 - \exp(-\beta R_0 z)$$

and the solution to eq 8 is given by Wehner and Wilhelm (1956).

For γ small the parameter a used by Wehner and Wilhelm is given by

$$a = (1 + 4\gamma\beta R_0)^{1/2} \simeq 1 + 2\gamma\beta R_0$$

and the solution to eq 8 at the inlet reduces to

$$X = 1 - \frac{1}{1 + \gamma\beta R_0}$$

The error at the inlet is then

$$X - X_P \simeq \gamma\beta R_0$$

The same analysis for temperature gives the solutions as

$$T_P = 1 + \beta'R_0 z$$

$$T = 1 + \gamma'\beta'R_0 + \beta'R_0 z - \gamma'\beta'R_0 \exp[(z-1)/\gamma']$$

The difference in the temperatures at $z = 0$ for γ' small is

$$T - T_P = \gamma'\beta'R_0$$

In both cases the error is proportional to $\gamma\beta R_0$ or $\gamma'\beta'R_0$. In physical variables we have the necessary condition that axial dispersion is unimportant

$$\gamma\beta R_0 = \left(\frac{\rho}{G}\right)^2 \frac{D_z \rho_B}{C_0} R_0 = \frac{\rho \rho_B d_p}{GC_0 Pe_{m,z}} R_0 \ll 1$$

$$\gamma'\beta'R_0 = \frac{k_z(-\Delta H)\rho_B}{(GC_p)^2(T_0 - T_w)} R_0 = \frac{(-\Delta H)\rho_B d_p}{(T_0 - T_w)GC_p Pe_{h,z}} R_0 \ll 1 \quad (12)$$

This criterion is to be used as follows. If eq 12 are satisfied then axial dispersion is unimportant at the inlet. If either inequality is violated, axial dispersion is important at the inlet. In that case, axial dispersion could still be unimportant at the outlet. This is the case if the equilibrium concentration and temperature were approached, in spite of the heating or cooling. If, however, equilibrium values are not approached (for example the cooling might be sufficient to quench the reaction), then the spatial distribution of temperature is very important to the exit concentration, and axial dispersion must be included in the model. Equation 12 says the neglect of axial dispersion would lead to errors at the inlet, and these are propagated down the reactor. If either inequality 12 is not satisfied, the analyst has two choices. If he is concerned only with the exit conversion he can calculate using a model which neglects axial dispersion. Any results which do not approach the equilibrium conversion would be suspect and would have to be recalculated with a model including axial dispersion. Alternatively, he could calculate all results with a model including axial dispersion. Also, if the concentration and temperature distributions in the reactor were important (for example, the peak temperature), then the model must include axial dispersion if inequalities 12 are violated.

Notice that neither eq 12 depends on the length of the reactor. The γ and γ' are inversely proportional to the length, while β and β' are proportional to the length. Thus the products $\gamma\beta$ and $\gamma'\beta'$ are independent of length. Carberry and Wendel (1963) made calculations for various γ while holding β constant. This is equivalent to changing the effective diffusivity, as discussed above. For β constant, Carberry and Wendel do find that axial dispersion is unimportant for small γ , and this result is consistent with eq 12. For their Figure 2, $\gamma = 1/200$, $\beta R_0 = k_0 \theta_0 = 0.2$ so that $\gamma\beta R_0 = 0.001 \ll 1$ is satisfied. Thus in the case treated by Carberry and Wendel axial dispersion is unimportant at the inlet, as they found.

Discrepancies in the temperature and conversion profiles can also occur, even though eq 12 are satisfied, if the maximum axial temperature or conversion gradient occurs at a point other than the reactor inlet. Due to the extreme nonlinearity of the problem, for the interior of the reactor it is difficult to derive a rigorous criterion such as eq 12. An indication of the importance of axial dispersion in the interior of the reactor can be obtained by comparing the fluxes in the two cases, with and without axial dispersion. If axial dispersion is to be negligible, then the absolute difference in the fluxes for these two cases must be negligible.

$$\left| X_P - X + \frac{1}{Pe_{m,z}} \frac{dX}{d\left(\frac{z'}{d_p}\right)} \right| \ll 1$$

$$\left| T_P - T + \frac{1}{Pe_{h,z}} \frac{dT}{d\left(\frac{z'}{d_p}\right)} \right| \ll 1$$

Clearly the differences in the temperature and conversion for the two cases must also be small. Using this fact and requiring the inequality to hold for all z we obtain

$$\max_{z'} \left| \frac{1}{Pe_{m,z}} \frac{dX}{d\left(\frac{z'}{d_p}\right)} \right| \ll 1$$

$$\max_{z'} \left| \frac{1}{Pe_{h,z}} \frac{dT}{d\left(\frac{z'}{d_p}\right)} \right| \ll 1 \quad (13)$$

Since Peclet numbers do not vary widely for most packed bed reactors, eq 13 indicates that the importance of axial dispersion is primarily dependent on the magnitude of the maximum temperature and conversion gradients. Note that eq 13 is consistent with eq 12 for the special case of the reactor inlet. Note also that the length of the reactor does not appear in eq 13.

The criterion based on inlet conditions (eq 12) can be applied *a priori*, while eq 13 requires knowledge of temperature and conversion gradients. This information can be obtained either from experimental data or may be approximated from numerical computations using mathematical models which neglect axial dispersion.

We now address the question of the importance of axial dispersion in cases of heat transfer and no reaction. The case of heat transfer is important since the heat transfer parameters (k_r , h_w) are normally determined experimentally by heating or cooling of the bed, and the solutions to the reactor modeling equations are often very sensitive to these parameters (Froment, 1967; Valstar, 1969). The experimental method for heat transfer parameter determination normally involves a gas flowing at some temperature (T_0), and at some point ($z = 0$) the wall is heated or cooled at a different tem-

perature (T_w). The radial temperature profile is then measured at the outlet of several beds of different lengths. Wakao and Yagi (1959) have considered the importance of axial dispersion in this problem but used the boundary conditions of Wehner and Wilhelm (1956), which neglect radial dispersion in the inlet and outlet regions. Phillips, *et al.* (1960), considered both axial and radial dispersion, too, but used the boundary condition $T' = T_0$ at $z = 0$.

Here we model the problem by assuming two semiinfinite regions: an inlet region, $-\infty < z < 0$, and an outlet or cooling region, $0 < z < \infty$. In the inlet region the wall is maintained at a temperature T_0 , and in the cooling region the wall is cooled at a different temperature, T_w . We make the additional assumption that the parameters (γ' , α' , Bi) are the same in both regions. Under the above assumptions the governing equation for the cooling region is

$$\gamma' \frac{\partial^2 T}{\partial z^2} - \frac{\partial T}{\partial z} + \alpha' \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) = 0$$

$$\frac{\partial T}{\partial r} = 0 \quad (r = 0)$$

$$\frac{\partial T}{\partial r} = -\text{Bi}T \quad (r = 1)$$

$$\lim_{z \rightarrow \infty} T = 0$$

For the inlet region the differential equation is the same, but the boundary conditions are

$$\frac{\partial T}{\partial r} = 0 \quad (r = 0)$$

$$\frac{\partial T}{\partial r} = -\text{Bi}(T - 1) \quad (r = 1)$$

$$\lim_{z \rightarrow \infty} T = 1$$

The two additional conditions needed in the axial direction require the continuity of flux and temperature.

$$T(0^-, r) = T(0^+, r)$$

$$\frac{\partial T}{\partial z}(0^-, r) = \frac{\partial T}{\partial z}(0^+, r)$$

In the cooling region the solution to the above problem is given by

$$T(z, r) = \sum_{n=1}^{\infty} \left(\frac{1 + a_n}{a_n} \right) \left(\frac{\text{Bi}}{\lambda_n^2 + \text{Bi}^2} \right) e^{(1-a_n)z/2\gamma'} \frac{J_0(\lambda_n r)}{J_0(\lambda_n)}$$

$$a_n = \sqrt{1 + 4\alpha'\gamma'\lambda_n^2}; \lambda_n J_1(\lambda_n) = \text{Bi}J_0(\lambda_n)$$

For small γ' the parameter $a_n \simeq 1 + 2\alpha'\gamma'\lambda_n^2$. Assuming the approximation to a is valid, we subtract the above solution from the solution which assumes no axial dispersion ($\gamma' = 0$), and obtain the error in temperature by neglecting axial dispersion.

$$T_{P'} - T' = \frac{(T_0 - T_w)}{\text{Pe}_{n,z}\text{Pe}_{n,r}} \left(\frac{d_p}{r_0} \right)^2 \sum_{n=1}^{\infty} \times$$

$$\left(\frac{2\lambda_n^2 \text{Bi}}{\lambda_n^2 + \text{Bi}^2} \right) \frac{J_0(\lambda_n r)}{J_0(\lambda_n)} \exp \left[\frac{-\lambda_n^2 \left(\frac{d_p z'}{r_0^2} \right)}{\text{Pe}_{n,r}} \right] \quad (14)$$

A simpler result may be found by using the first collocation approximation in the radial direction and a similar analysis

$$T_{P'} - T' = \frac{(T_0 - T_w)}{\text{Pe}_{n,z}\text{Pe}_{n,r}r_0} \left(\frac{d_p}{r_0} \right)^2 \frac{6\text{Bi}}{(\text{Bi} + 3)^2} \times$$

$$[3 + 1.5\text{Bi}(1 - r^2)] \exp \left[\frac{-1}{\text{Pe}_{n,r}} \left(\frac{6\text{Bi}}{\text{Bi} + 3} \right) \left(\frac{d_p z'}{r_0^2} \right) \right] \quad (15)$$

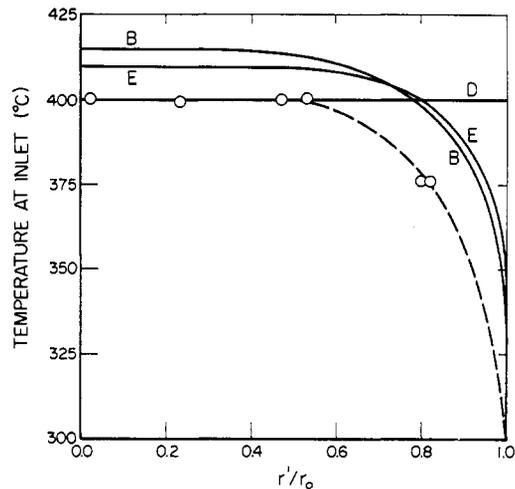


Figure 2. Experimental and predicted inlet temperature profiles: -○- -, experimental (cooling only, no reaction); —, theoretical B,D,E (with reaction)

For both cases the results for large z are similar. Since experimental data are usually measured at large z , the approximate result using orthogonal collocation can be used to determine whether axial dispersion is important.

Notice that the error is inversely proportional to the product of the Peclet numbers, decreases exponentially with z , and the error at the center of the reactor is $(1 + 1/2 \text{Bi})$ times larger than that near the wall. The error decreases with z since the axial gradient of temperature decreases with z . Thus the case of heat transfer without reaction is somewhat like that of isothermal or adiabatic reactors: if the packed bed is long enough the fluid attains the wall temperature, irrespective of whether axial dispersion is important or not. Thus length is relevant in determining if axial dispersion is important in heat transfer studies.

For example consider a reactor with the following parameter values: $(T_0 - T_w) = 150^\circ\text{C}$, $\text{Pe}_{n,z} = 1.5$, $\text{Pe}_{n,r} = 7.0$, $\text{Bi} = 5$, $d_p/r_0 = 0.20$. The error in temperature at a bed depth of 30 particle diameters is 1.48°C for the center of the reactor and 0.42°C at the reactor wall, while at a depth of 100 particle diameters the errors would be 0.33 and 0.09°C for the center and wall, respectively. The parameters used in the above example would not be unusual, and the effect of this error on the predicted heat-transfer parameters could be significant.

Equation 15 or 14 can be used to test any particular experimental situation, but we leave to future work the determination of a criterion based on errors incurred in estimating k_r and h_w when neglecting axial dispersion.

Application to an Experimental Reactor

Smith (1970) has presented the results of a theoretical and experimental study of a sulfur dioxide oxidation reactor. The radial model was used for the theoretical prediction, and errors as large as 25% were found between the experimental and predicted average conversion. This experimental reactor is studied here in an effort to determine the causes of this disagreement and to correct the theoretical analysis accordingly. In order to compare the model predictions with the experimental results, we must first point out some important features of the experimental method.

The experimental results were first published by Schuler, *et al.* (1954). The experimental method involved the measurement of the outlet temperature profiles and average con-

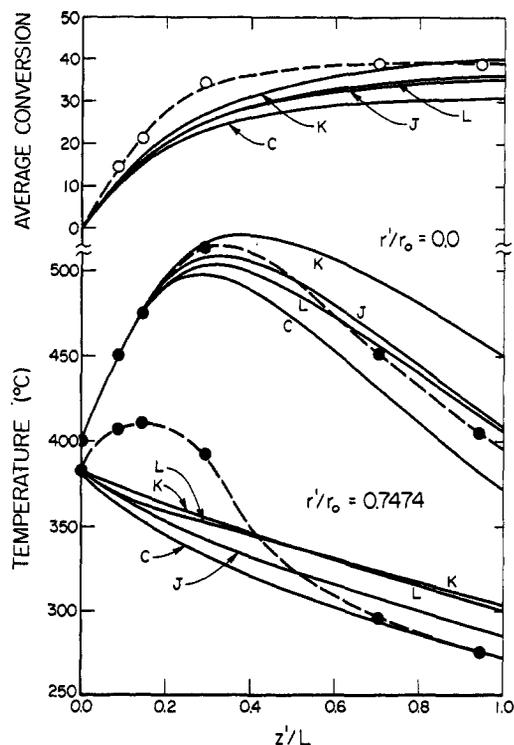


Figure 3. Comparison of radial model prediction with experimental data, using experimental inlet temperature profile: \circ , experimental conversion; —, theoretical prediction C,J,K,L; - - - - -, smoothed experimental data; \bullet , experimental temperature from smoothing of radial profiles

version for five bed depths, *i.e.*, for five reactors of different lengths. The model calculations are affected in the following way.

1. Since the general model is a two-point boundary value problem in the axial direction, the reactors of different lengths must be modeled separately in order to compare the calculations using the general model with the experimental reactors.

2. The radial model is an initial value problem, so the calculations using it are not affected. One calculation provides the solution for all different bed depths. A reactor with a short length is just the first part of a longer reactor.

The inlet temperature profile was measured for the case of cooling with no reaction, and it was found that the temperature varied radially. The experimental data are shown in Figure 2. The reason for this observed inlet temperature profile is an interesting question, since if there were no axial dispersion, the inlet boundary conditions in eq 7 should hold and we would expect a uniform inlet temperature profile like that of D in Figure 2. It appears that the discontinuity in wall temperature at the inlet causes strong enough axial temperature gradients so that axial dispersion is important near the wall, but the temperature at the center of the reactor is unaffected. We see that we are presented with somewhat of a dilemma as to the correct inlet temperature that should be used with the radial model calculations. Both the uniform and experimental inlet temperature profiles are used with the radial model to assess the significance of this discrepancy. When the general model is used this discrepancy is not encountered, since the dispersion boundary conditions (5) are used, and the temperature profile is predicted rather than assumed.

The experimental reactor has previously been studied by other investigators (Almond, 1959; Ohki, *et al.*, 1966; Richard-

Table I. Data Used and Parameters Estimated

$d_p = 0.0032 \text{ m}$	$C_p = 0.24 \text{ kcal/kg } ^\circ\text{C}$
$r_0 = 0.026 \text{ m}$	$\Delta H = -23,400 \text{ kcal/kg-mole}$
$L = 0.15 \text{ m}$	$\rho_B = 1080 \text{ kg/m}^3$
$T_0 = 400^\circ\text{C}$	$G = 1710 \text{ kg/m}^2 \text{ hr}$
$T_w = 197^\circ\text{C}$	$\rho/C_0 = 480 \text{ kg/kg-mole}$

1. Radial effective thermal conductivity
 $k_r = 0.32 \rightarrow 0.42 \text{ kcal/m hr } ^\circ\text{C}$
 $Pe_{h,r} = 4.0 \rightarrow 3.0$
 $\alpha' = 0.18 \rightarrow 0.23$
2. Axial effective thermal conductivity
 $k_z = 0.92 \rightarrow 1.35 \text{ kcal/m hr } ^\circ\text{C}$
 $Pe_{h,z} = 1.4 \rightarrow 0.95$
 $\gamma' = 0.015 \rightarrow 0.022$
3. Wall heat transfer coefficient
 $h_w = 51 \rightarrow \infty \text{ kcal/m}^2 \text{ hr } ^\circ\text{C}$
 $Bi = 3.1 \rightarrow \infty$
4. Radial mass Peclet number
 $Pe_{m,r} = 9.6$
 $\alpha = 0.074$
5. Axial mass Peclet number
 $Pe_{m,z} = 2.0$
 $\gamma = 0.010$
6. Generation parameters (including a heat and mass transfer resistance between the fluid and the catalyst)
 $\beta = 46.4 \text{ kg (cat.) hr/kg-mole}$
 $\beta' = 47.1 \text{ kg (cat.) hr/kg-mole}$
 $R(X, T) = 0.00853 (T_s' - T') \text{ kg-mole/kg (cat.) hr } ^\circ\text{K}$
 $= 0.730 (X_s - X) \text{ kg-mole/kg (cat.) hr}$
 $= \frac{(1.0 - X_s) \sqrt{1.0 - 0.166X_s - 2.20X_s/K_{eq}}}{(k_1 + k_2X_s)^2}$
 $K_{eq} = \exp\left[\frac{11,570^\circ\text{K}}{T_s'} - 11.02\right]$
 $k_1 = \exp\left[\frac{11,070^\circ\text{K}}{T_s'} - 14.96\right] \times$
 $\text{[kg (cat.) hr/kg-mole]}^{1/2}$
 $k_2 = \exp\left[\frac{2331^\circ\text{K}}{T_s'} - 1.331\right] \times$
 $\text{[kg (cat.) hr/kg-mole]}^{1/2}$
7. The parameters for the inlet and outlet regions are assumed to be equal to the corresponding parameters of the reactor
 $\gamma' = \gamma_A' = \gamma_C'$
 $\alpha' = \alpha_A' = \alpha_C'$
 $Bi = Bi_A = Bi_C$

son, 1963). Almond considered axial dispersion in an effort to achieve agreement; however, the correct boundary conditions were not used, and agreement was not achieved. Richardson performed calculations for a number of cases of radially varying parameters, including a velocity profile model, but apparently did not include the effect of axial dispersion. Richardson also considered the effect of the parameter values on the prediction, but good agreement was not achieved. Ohki, *et al.*, used a modified mixing cell model to obtain only fair agreement with experiment. It is pointed out that all of the above mentioned investigators used the experimental inlet temperature profile as in Figure 2.

Model parameters and the rate expression are given in Table I. The model parameters were calculated from available data and a number of correlations (Schuler, *et al.*, 1954; Smith, 1970; Yagi and Kunii, 1957, 1960; Yagi, *et al.*, 1960). The value of the heat transfer parameters varied depending on the correlation, data source, or estimation of physical properties. For this reason, the range of these values is given

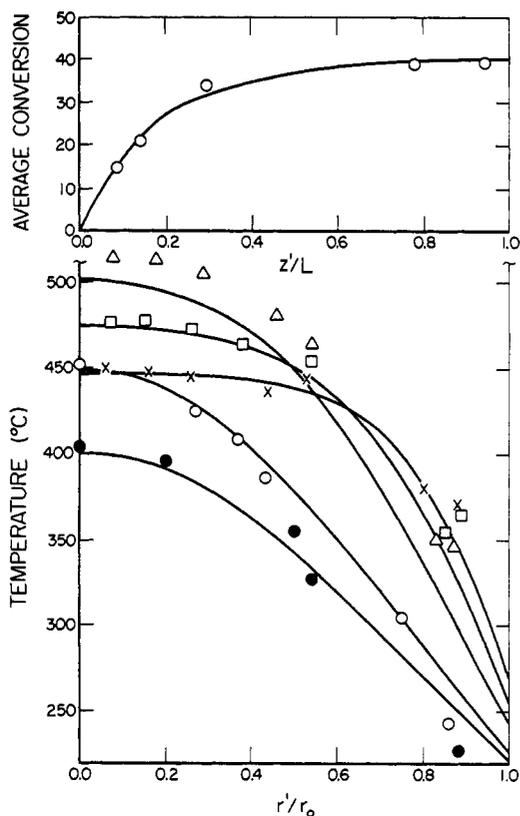


Figure 4. Comparison of general model prediction with experimental data: —, theoretical A. Experimental temperature at z'/L of: \times , 0.086; \square , 0.146; \triangle , 0.292; \circ , 0.708; \bullet , 0.946; experimental conversion, \circ

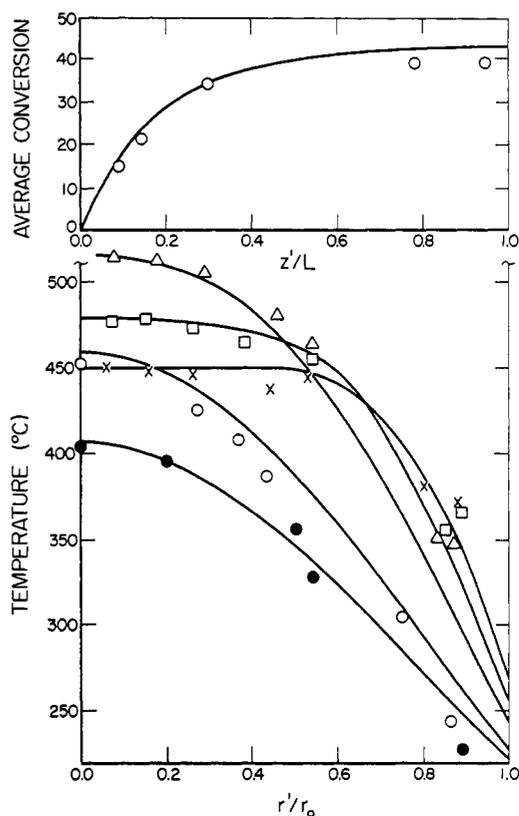


Figure 5. Comparison of radial model prediction with experimental data, uniform inlet temperature: —, theoretical D. Experimental temperature for z'/L of: \times , 0.086; \square , 0.146; \triangle , 0.292; \circ , 0.708; \bullet , 0.946; experimental conversion, \circ

in Table I, and these parameters are considered adjustable within these limits.

The rate expression shown in Table I was derived by an analysis of the reaction rate data given by Olson, *et al.* (1950). Since the assumption of differential reactor behavior could not be justified, the data were reanalyzed using the general model together with a nonlinear regression technique. The parameters of the general model and the external diffusion parameters were estimated from available information. The four parameters in the rate expression were then determined by minimizing the weighted sum of the squared error between the predicted and experimental average outlet conversions. Although the parameters of the general model were not known accurately for the reactors of Olson, *et al.* (1950), it was found that the predicted reaction rate parameters were not extremely sensitive to this uncertainty (Young, 1972). The rate expression given here includes the effect of external diffusion and is significantly different from the data given by Smith (1970). Smith's data embody the assumption of differential reactor behavior; however, the differences in these rate expressions were found to make little difference in the predicted temperature and conversion profiles (Young, 1972).

We now apply the criterion for determining whether axial dispersion should be important. From the data in Table I, we see that the reactor is 48 particle diameters long. Using the criterion based on the length to particle diameter ratio, we would expect axial dispersion to have a very small effect. Using the criterion developed above, eq 12 and $Pe_{h,z} = 0.945$, we find an approximate error of 0.034 and 15°C in the inlet conversion and temperature, respectively. The errors in conversion and temperature predict an error of 28% in the reaction rate at the inlet. An error of this magnitude cannot be

Calculation	α'	Bi	γ'	$\frac{\alpha' \text{Bi}}{\text{Bi} + 3}$	Inlet temp
A ^a	0.220	10.0	0.0218	0.169	...
B	0.220	10.0	0.0218	0.169	...
C	0.220	10.0	0.0	0.169	Exptl
D	0.220	10.0	0.0	0.169	400°C
E	0.220	10.0	0.0149	0.169	...
F	0.241	7.0	0.0218	0.169	...
G	0.203	15.0	0.0218	0.169	...
H	0.179	50.0	0.0218	0.169	...
J	0.190	10.0	0.0	0.146	Exptl
K	0.160	10.0	0.0	0.123	Exptl
L	0.210	5.0	0.0	0.131	Exptl

^a Calculation of separate reactors of different lengths.

neglected. Thus we expect axial dispersion to be important; however, the two criteria for the importance of axial dispersion can also be evaluated by solution of the governing equations for the two reactor models.

The calculated results are shown in Figures 2–8, while the parameters used are given in Table II. In Figure 3 the results calculated using the radial model and the experimental inlet temperature are shown. The heat transfer parameters are adjusted in an effort to achieve agreement with the experimental results, but no adjustment of these parameters gives reasonable agreement with the experimental results. In Figure 4, the results calculated using the general model are found to be in good agreement with the experimental results. Only the temperatures near the hot spot depart significantly from

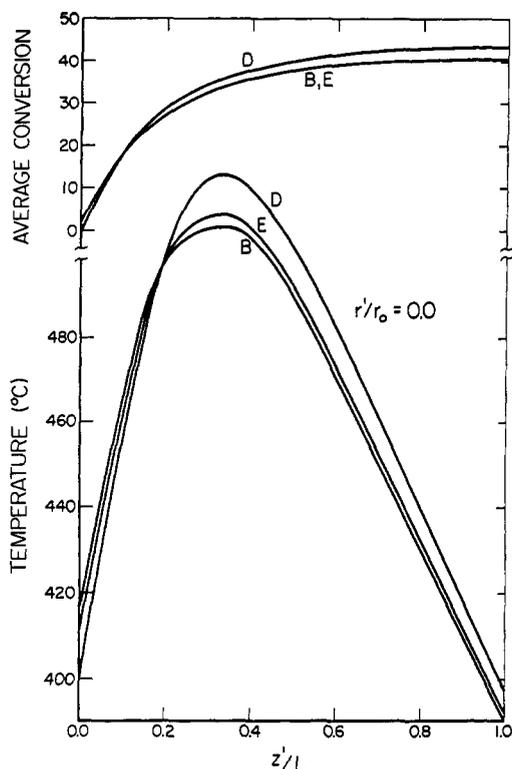


Figure 6. The effect of the axial dispersion terms. Curves B and E have axial dispersion; curve D does not

the experimental values. The calculations shown in Figure 5 are performed using the radial model and a uniform inlet temperature profile, and these results are found to be in good agreement with the experimental results. From the results shown in Figures 3, 4, and 5 it is apparent that poor results are obtained when the experimental inlet temperature profile is used in the radial model.

Of interest in the general model calculation is the calculated inlet temperature profile shown in Figure 2. It is seen that the predicted inlet temperature is 415°C near the center, as predicted by the criterion for neglecting axial dispersion. The temperature near the wall is much lower than 400°C , as was found experimentally for the case of cooling with no reaction. Since the experimental profile was measured for no reaction, the profiles would not be expected to agree, but it is found that the behavior near the wall is in qualitative agreement with the experimental results. The criterion for neglecting axial dispersion predicts the errors in conversion and temperature accurately at the inlet and near the center; however, the decreased temperature near the wall is not predicted by the criterion. Axial dispersion is also important due to the rapidly changing wall temperature at the inlet.

Since the axial effective thermal conductivity is only known within the range shown in Table I, it is important to know the sensitivity of the prediction to variations within this range, as shown in Figure 6. Also shown are the calculations for neglecting axial dispersion altogether. The prediction is affected by the value of γ' , but the effect is small compared to that found by neglecting axial dispersion altogether.

We summarize the evidence for the importance of axial dispersion in this reactor. Figure 6 shows that the calculated results change if axial dispersion is included. Figure 4 shows that the calculated results using the general model agree well with the experimental data, and the radial temperature profile at the inlet has the correct shape (Figure 2) even though no experimental results exist for direct comparison. Figure 5

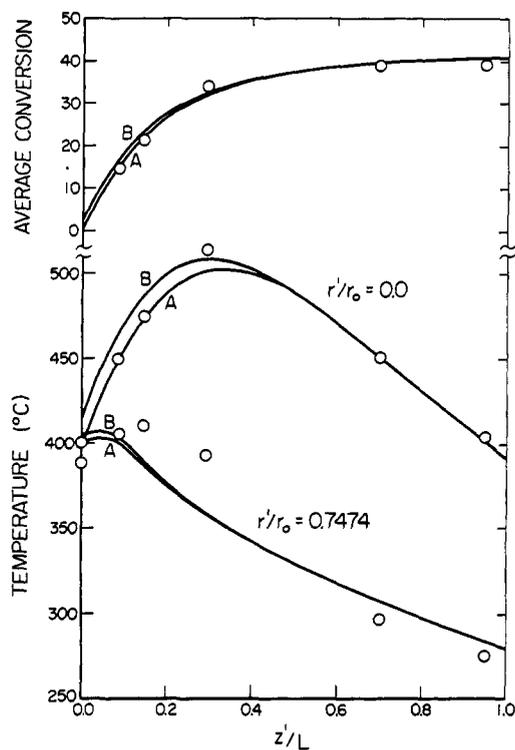


Figure 7. The effect of gathering data on different length reactors: O, experimental data. Curve B is for one long reactor; curve A is for a series of reactors of different lengths; both B and A include axial dispersion

shows that good agreement can also be obtained using the radial model with a flat radial temperature profile. Such a profile, however, is inconsistent with the experimental measurements, see Figure 2, which show a radial variation even when there is no chemical reaction. The radial model using the experimental profile cannot be made to fit the data (Figure 3). Thus we can rule out the possibility that the radial model is adequate and the inlet temperature profile is caused entirely by cooling, since in that case the radial model would fit the data in Figure 3 for some choice of parameters. The reason that the radial model with a flat (and unrealistic) temperature profile gives good agreement, too, is because the errors incurred at the wall are partially offset by opposing errors which occur on the center line.

In Figure 7 the significance of the experimental method is assessed. The data were taken at the outlet of five reactors differing only in length. The calculations presented in Figure 7 are performed using the general model. Curve B represents a single reactor of length 0.1514 m, whereas curve A represents the outlet values for calculations for reactors of five different lengths. The difference between curves A and B illustrates the errors possible when measuring the data in such a manner. It appears that if axial dispersion is important, the conversion and temperature out of a reactor of length L_1 will be different from the conversion and temperature at length L_1 when measured in a reactor of length $L_2 > L_1$. It is also clear from Figures 6 and 7 that an increase in reactor length will not decrease the importance of axial dispersion. As the reactor length is increased in the various calculations represented by curve A of Figure 7, the temperature profile does not approach that predicted for a model without axial dispersion. This is because axial dispersion affects the temperature at the inlet whereas increasing the length merely affects the cooling in the last part of the reactor.

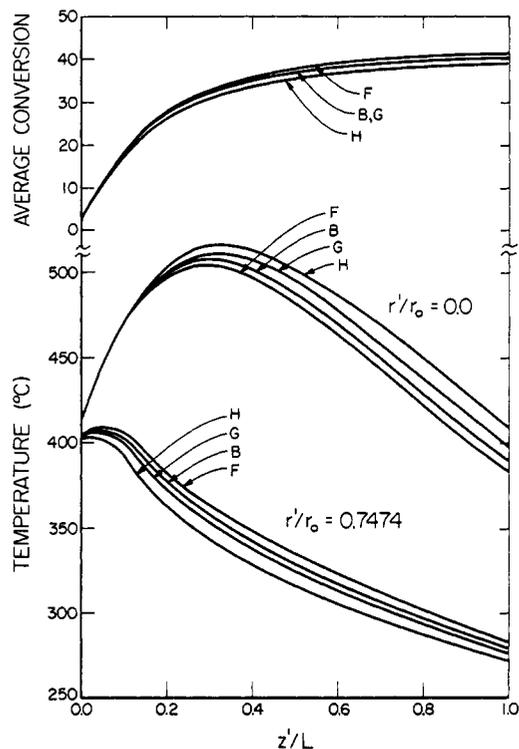


Figure 8. Sensitivity of the prediction to radial heat transfer parameters at constant $\alpha' Bi/(Bi + 3)$ or constant U defined by eq 16

It has been common practice to measure heat transfer coefficients by measuring the temperature out of packed beds of different lengths. The data are then interpreted as if they applied to a single bed with the longest length. It is clear that if axial dispersion is important the temperature profile developed at the inlet (see Figure 2) will influence the heat transfer data unless the inlet region is ignored. If the experimental reactor is used to study heat transfer without reaction, eq 15 says that significant (2.3°C) errors will occur for the longest reactor, if axial dispersion is neglected. This is reflected in the inlet temperature profile, too (Figure 2). Thus axial dispersion influences heat transfer data in this situation, although the effect is minimized if temperature profiles are only used for long reactors, as is often the case.

The radial heat transfer parameters could not be determined accurately, as shown in Table I. It has previously been shown by others (Froment, 1967; Valstar, 1969) that the solution to the governing equations is usually sensitive to the values of the radial effective thermal conductivity and the wall heat transfer coefficient. The reason for this phenomenon is due to the fact that these parameters determine the overall heat loss from the reactor, which generally has a large effect on the reaction rate. It has previously been shown (Finlayson, 1971), that the first collocation approximation in the radial direction is equivalent to lumping all radial resistance to heat transfer at the wall, with an overall heat transfer coefficient of

$$\frac{1}{U} = \frac{1}{h_w} + \frac{r_0}{3k_r} \quad (16)$$

In Figure 8, calculations are presented in which the radial effective thermal conductivity and wall heat transfer coefficient are varied, but the parameters are changed in a manner so that the overall heat transfer coefficient defined by eq 16 is held constant. Although the individual param-

eters are varied over a wide range, the results are not strongly affected, especially the average conversion. From these results, it appears that the above relationship gives a good qualitative idea of the overall heat loss from the reactor.

The calculated results are, of course, dependent on the accuracy of the numerical approximation. In the calculations using the general model, six interior collocation points were used in both the axial and radial direction. The calculations performed using the radial model employed six interior collocation points in the radial direction and 250 steps in the improved Euler scheme for the axial direction. Other computations suggest that the results are accurate within 1%.

As stated above, the solution algorithm for the general model employed the Newton-Raphson or Picard method to solve the nonlinear algebraic equations. When the initial guess in the solution algorithm was a constant conversion and temperature everywhere in the reactor, the solution was obtained in an average of five iterations using the Newton-Raphson method and twelve iterations using the Picard method. The calculation time in both cases was primarily due to the matrix inversions required. Computation time was approximately 23 and 10 sec for the Newton-Raphson and Picard methods, respectively, on the CDC-6400 computer.

Conclusions

Both axial and radial dispersion are important in the experimental SO_2 -oxidation reactor.

A criterion is developed, eq 12, to decide if axial dispersion is important at the inlet to a reactor which is heated or cooled. Even if eq 12 is violated, if the temperature and conversion approach their equilibrium values at the exit, then the influence of axial dispersion will not be great on the exit conversion and temperature, although it can affect the spatial distribution of those quantities. The criterion (13) can be used throughout the reactor in an *a posteriori* fashion. After calculating without axial dispersion, eq 13 can tell one if axial dispersion should have been included.

Orthogonal collocation is an efficient numerical method for solving the equations governing a reactor with axial and radial dispersion.

Nomenclature

$A_{ij}^{(r)}$	= matrix representing radial first derivative
$A_{ij}^{(z)}$	= matrix representing axial first derivative
$B_{ij}^{(r)}$	= matrix representing radial Laplacian
$B_{ij}^{(z)}$	= matrix representing axial Laplacian
Bi	= Biot number, $h_w r_0 / k_r$
C	= concentration, $\text{kg-mole}/\text{m}^3$
C_p	= heat capacity, $\text{kcal}/\text{kg } ^{\circ}\text{C}$
d_p	= particle diameter, m
D_r	= radial effective diffusivity, m^2/hr
D_z	= axial effective diffusivity, m^2/hr
G	= mass flow rate based on empty tube area, $\text{kg}/\text{m}^2 \text{ hr}$
h_w	= wall heat transfer coefficient, $\text{kcal}/\text{m}^2 \text{ hr } ^{\circ}\text{C}$
$-\Delta H$	= heat of reaction, $\text{kcal}/\text{kg-mole}$
J_i	= i th order Bessel's function
k^*	= first-order rate constant, $\text{m}^3/\text{kg (cat.) hr}$
k_1	= Arrhenius function in rate expression, $[\text{kg (cat.) hr}/\text{kg-mole}]^{1/2}$
k_2	= Arrhenius function in rate expression, $[\text{kg (cat.) hr}/\text{kg-mole}]^{1/2}$
K_{eq}	= equilibrium constant
k_r	= radial effective thermal conductivity, $\text{kcal}/\text{m hr } ^{\circ}\text{C}$
k_z	= axial effective thermal conductivity, $\text{kcal}/\text{m hr } ^{\circ}\text{C}$
L	= reactor length, m

M = number of interior collocation points in axial direction
 N = number of interior collocation points in radial direction
 $Pe_{h,r}$ = radial Peclet number for heat, $d_p GC_p / k_r$
 $Pe_{h,z}$ = axial Peclet number for heat, $d_p GC_p / k_z$
 $Pe_{m,r}$ = radial mass Peclet number, $d_p G / (\rho D_r)$
 $Pe_{m,z}$ = axial mass Peclet number, $d_p G / (\rho D_z)$
 r = radial position, r'/r_0
 r' = radial position, m
 $R(X, T)$ = apparent reaction rate, kg-mole/kg (cat.) hr
 T = dimensionless temperature, $(T' - T_w)/(T_0 - T_w)$
 T' = temperature, °C or °K
 U = overall heat transfer coefficient, kcal/m² hr °C
 X = fractional conversion, $1 - C/C_0$
 z = axial position, z'/L
 z' = axial position, m

GREEK LETTERS

α = $\rho D_r L / (Gr_0^2)$ or $d_p L / (r_0^2 Pe_{m,r})$
 α' = $k_r L / (GC_p r_0^2)$ or $d_p L / (r_0^2 Pe_{h,r})$
 β = $\rho \rho_B L / (GC_0)$
 β' = $-\Delta H \rho_B L / [(T_0 - T_w) GC_p]$
 γ = $\rho D_z / (GL)$ or $d_p / (L Pe_{m,z})$
 γ' = $k_z / (L GC_p)$ or $d_p / (L Pe_{h,z})$
 λ_n = eigenvalues
 ρ = density, kg/m³
 ρ_B = mass of catalyst per unit volume of bed, kg (cat.) / m³

SUBSCRIPTS

A = value for inlet region
 C = value for outlet region
 0 = inlet or reference value
 P = value assuming no axial dispersion
 r = value for radial direction
 s = value on catalyst surface
 w = value at tube wall
 z = value for axial direction

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