Dispersion and Diffusion Influences on Yield in Complex Reaction Networks

Differences in the dispersion and/or catalytic pellet size between laboratory and commercial reactors, operating at the same average residence time, may lead to differences in the yield of a desired product. Bounds are developed for predicting the maximal design uncertainty introduced by these phenomena for a network consisting of an arbitrary number of irreversible first-order reactions. A major advantage of these bounds is that they do not require any knowledge of the rate constants. It is shown that in a packed-bed reactor, the fractional yield loss is smaller than:

$$0.5\,(m-1)\left[\sigma_\theta^2 + \left(1.2 + \frac{2}{Bi_m}\right)p^2\right]$$

where $m - 1$ is the number of reaction steps involved in converting a reactant to the desired product, σ_θ^2 is the dimensionless variance of the residence time density function, Bi_m is the Biot number, $p^2 = [(V_p/S_x)^2(1/(D_e\tau)]$, and τ is the average residence time.

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Introduction

The different impact of nonideal flow and/or catalytic pellet transport limitations on the performance of laboratory or pilot plant reactors and commercial ones leads to uncertainties in the scale-up procedure. These are especially important when a large number of chemical reactions occur simultaneously.

In many tubular and packed-bed reactors, deviations from plug flow may be accounted for by an axial dispersion model. Many papers have examined the influence of axial dispersion or residence time distribution on the conversion or yield in reactors in which first-order reactions occur. Many investigators studied the conditions leading to optimal yield for specific reaction networks and kinetic parameters (Tichacek, 1963; Kipp and Davis, 1968; Chung and Howell, 1970; Glasser et al., 1973; Wan and Ziegler, 1973; Silverstein and Shinnar, 1975; Dang, 1984).

The yield in a short laboratory reactor is affected by axial dispersion more than that of a full-scale industrial reactor operating at the same residence time. To estimate the uncertainty involved in the scale-up it is important to have an *a priori* estimate of the maximal deviation in the yield between a laboratory and a full-scale reactor. This information is essential for predicting the minimal length a laboratory reactor should have for specified operating conditions so that the yield of a desired product will not deviate by more than some specified value from that of a full scale reactor.

Tichacek (1963) developed a rule of thumb that for two consecutive reactions, the maximum fractional reduction in the yield of an intermediate due to axial dispersion is approximately equal to $1/Pe = D_a/vL$, where D_a is the axial disperison coefficient. Glasser et al. (1973) and Silverstein and Shinnar (1975) conjectured that for n isothermal, irreversible, first-order, consecutive reactions,

$$A_1 \rightarrow A_2 \rightarrow A_3 \rightarrow \cdots\cdots A_m \rightarrow \cdots\cdots \rightarrow A_{n+1}$$

the maximal fractional yield loss of the mth species due to axial dispersion occurs when the rate constants of the first m reactions are equal. This led to a prediction that the maximal fractional yield loss of the mth species due to a small deviation from plugflow is

$$\delta_m^* = \max\left(\frac{a_{p,m} - a_{d,m}}{a_{p,m}}\right) = \frac{(m-1)\sigma^2}{2\tau^2} \qquad (1)$$

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where $a_{p,m}$ and $a_{d,m}$ are the exit concentrations of an intermediate species, m, in a plug flow reactor and in a reactor with axial dispersion, respectively. τ is the average contact time in the reactor and σ is the standard deviation of the contact time distribution. They used established correlations about the dependence of σ/τ on the operating conditions to predict the minimal reactor length needed to guarantee that the selectivity loss due to dispersion will not exceed a specified value. This serves as a very useful guide in the *a priori* design of laboratory reactors.

It is well known that transport limitations in catalytic pellets affect the yield of a desired product when many isothermal reactions occur simultaneously. The catalyst pellets in a laboratory reactor are usually smaller than those used in a commercial reactor. Thus, the yield in a laboratory reactor is often higher than that in the commercial unit and it is important to be able to predict the maximal uncertainty that may be introduced by this difference. Wei (1962a, b) and Aris (1975) determined the impact of diffusion on the local yield of a desired product for a system with an arbitrary number of first-order isothermal reactions. That prediction requires knowledge of all the rate constants. It is desirable to develop *a priori* design criteria which do not require the determination and knowledge of all the rate constants.

The goal of this work is to provide rigorous bounds on the maximal loss of yield due to axial dispersion, residence time distribution, and/or intraparticle diffusion in a reaction network of several first-order reactions, the rate constants of which are unknown. The analysis is based on the use of the divided differences of a function. The needed mathematical background is presented in the following section. Discussed in subsequent sections are: a bound on the maximal loss of yield due to axial dispersion for a homogeneous reactor; a similar bound, based on knowledge of the residence time distribution; and a bound on the maximal yield loss due to both catalytic pellet transport limitations and axial dispersion or residence time distribution.

Mathematical Background

Consider an isothermal reactor in which a large number of first-order reactions occur among n species, i.e., the governing kinetic expression is

$$\frac{d\boldsymbol{a}}{dt} = \boldsymbol{K}\boldsymbol{a} \qquad (2)$$

where $\boldsymbol{a}$ is a vector of the n species concentrations and $\boldsymbol{K}$ is the matrix of rate constants. Several linear processes may occur in the reactor, such as dispersion due to axial diffusion or residence time distribution, transport resistances between the fluid and catalyst, etc. Since all the processes are linear, we can always obtain a formal solution of the form

$$\boldsymbol{a}(\tau) = f(\boldsymbol{K}, \boldsymbol{p})\boldsymbol{a}_0 \qquad (3)$$

where $\boldsymbol{a}(\tau)$ and $\boldsymbol{a}_0$ are the outlet and inlet concentration vectors, and $\boldsymbol{p}$ is a vector of parameters such as residence time, τ, dispersion coefficient, etc. For example, for a pseudohomogeneous plug flow reactor,

$$f_p(\boldsymbol{K}, \boldsymbol{p}) = e^{\boldsymbol{K}\tau}. \qquad (4)$$

As a second example, consider a plug flow reactor with axial dispersion. Here the concentrations of the species must satisfy the relations,

$$\frac{1}{Pe}\frac{d^2\boldsymbol{a}}{ds^2} - \frac{d\boldsymbol{a}}{ds} + \boldsymbol{Da}\,\boldsymbol{a} = 0 \qquad (5)$$

$$\frac{1}{Pe}\frac{d\boldsymbol{a}}{ds} = \boldsymbol{a} - \boldsymbol{a}_0 \quad s = 0 \qquad (6)$$

$$\frac{d\boldsymbol{a}}{ds} = 0 \quad s = 1 \qquad (7)$$

where

$$s = \frac{x}{L}, \quad Pe = \frac{vL}{D_a},$$

$$\boldsymbol{Da} = \boldsymbol{K}\tau = \frac{\boldsymbol{K}L}{v}. \qquad (8)$$

In most applications, Pe is much larger than unity and a singular perturbation technique gives the solution,

$$\boldsymbol{a}(\tau) = \left(\boldsymbol{I} + \frac{\boldsymbol{Da}^2}{Pe}\right)e^{\boldsymbol{Da}}\boldsymbol{a}_0 + O\left(\frac{1}{Pe^2}\right). \qquad (9)$$

Thus, in this case,

$$f_d(\boldsymbol{K}, \boldsymbol{p}) = \left(\boldsymbol{I} + \frac{\boldsymbol{Da}^2}{Pe}\right)e^{\boldsymbol{Da}}. \qquad (10)$$

We shall derive here an *a priori* prediction of the maximal impact of the dispersion and/or intraparticle diffusion on the yield of an intermediate species, m, for a case that all the reactions are irreversible. We denote by $k_{j,i}$, the rate constant for the formation of species j from i and enumerate the species so that $j > i$. Thus, all the species which cannot lead to formation of species m have an index, $i > m$. We aggregate all these species with $i > m$ into lump L_{m+1}, as we are interested only in the concentration of species m. Thus, we consider the case

$$\boldsymbol{K} = \begin{pmatrix} \lambda_1 & 0 & \cdot & \cdot & 0 & 0 \\ k_{2,1} & \lambda_2 & \cdot & \cdot & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ k_{m,1} & k_{m,2} & \cdot & \cdot & \lambda_m & 0 \\ k_1^* & k_2^* & \cdot & \cdot & k_m^* & 0 \end{pmatrix}, \quad \boldsymbol{a} = \begin{pmatrix} a_1 \\ a_2 \\ \cdot \\ \cdot \\ a_m \\ L_{m+1} \end{pmatrix} \qquad (11)$$

where

$$k_i^* = \sum_{j=m+1}^{n} k_{j,i}, \quad \lambda_i = -\left(\sum_{j=i+1}^{m} k_{j,i} + k_i^*\right); \quad i = 1, 2, \ldots, m. \qquad (12)$$

Note that $\lambda_0 = 0$ and λ_i; $i = 1, 2, \ldots, m$ are eigenvalues of $\boldsymbol{K}$.

Our goal is to derive a simple bound on the maximal yield loss of species m. As a first step we introduce some mathematical background. Consider a function, $f(x)$, the value of which is specified at n points, $x_1, x_2, \ldots, x_n$. The divided difference of $f(x)$ of order $n-1$ is defined as (Milne-Thomson, 1951)

$$f[x_1, x_2, \ldots, x_n] = \frac{f[x_1, x_3, \ldots, x_n] - f[x_2, x_3, \ldots, x_n]}{x_1 - x_2} = \sum_{i=1}^{n} \frac{f(x_i)}{\prod_{j=1,i}^{n} (x_i - x_j)}. \tag{13}$$

For example, the divided differences of order one and two are

$$f[x_1, x_2] = \frac{f(x_1) - f(x_2)}{x_1 - x_2} \tag{14}$$

$$f[x_1, x_2, x_3] = \frac{f[x_1, x_3] - f[x_2, x_3]}{x_1 - x_2} = \frac{f[x_1, x_2] - f[x_1, x_3]}{x_2 - x_3}. \tag{15}$$

In some cases we shall denote the order of the divided difference function by a subscript.

The divided difference function has several interesting properties. For example, given two divided difference functions, $f(x)$ and $g(x)$ of order $n-1$, it is always possible to find some u satisfying

$$\min(x_1, x_2, \ldots, x_n) \le u \le \max(x_1, x_2, \ldots, x_n) \tag{16}$$

for which

$$f[x_1, x_2, \ldots, x_n] = f_{n-1}[u, u, \ldots, u] = \frac{f^{(n-1)}(u)}{(n-1)!} \tag{17}$$

$$\frac{f[x_1, x_2, \ldots, x_n]}{g[x_1, x_2, \ldots, x_n]} = \frac{f_{n-1}[u, u, \ldots, u]}{g_{n-1}[u, u, \ldots, u]} = \frac{f^{(n-1)}(u)}{g^{(n-1)}(u)} \tag{18}$$

For example, for $n = 2$, the above relations predict that there exists a number, u, in (x_1, x_2) for which

$$f[x_1, x_2] = \frac{f(x_1) - (f(x_2)}{x_1 - x_2} = f'(u) \tag{19}$$

$$\frac{f[x_1, x_2]}{g[x_1, x_2]} = \frac{f(x_1) - f(x_2)}{g(x_1) - g(x_2)} = \frac{f'(u)}{g'(u)}. \tag{20}$$

These are a mean value and a generalized mean value theorem (Cauchy's theorem), respectively. Moreover, the sum of divided differences of various orders

$$\sum_{k=0}^{n} C_k f[x_1, \ldots, x_{k+1}] \tag{21}$$

is also a divided difference of order, n, of an appropriately defined function. For example,

$$F[x_1, x_2, x_3] = C_1 f[x_1, x_2] + C_2 f[x_1, x_2, x_3] \tag{22}$$

is a divided difference of

$$F(x) = f(x)[C_1(x - x_3) + C_2]. \tag{23}$$

Consider now the case that the rate constants matrix $\boldsymbol{K}$ has a set of discrete eigenvalues, i.e., all $\lambda_i (i = 0, \ldots, m)$ are different from each other, so that the eigenvectors of this matrix form a complete set. Liou (1989) has used rather lengthy algebraic manipulations to derive an explicit solution for this case. Consider first the case of a pure feed containing only a_1, i.e.,

$$\mathbf{a}_0 = \mathbf{e}_1 \tag{24}$$

where e_j denotes a vector of $m + 1$ elements with a jth element of unity, and zero for all other m elements. In this case the formal solution of the concentration vector, Eq. 3, can be written for any f as

$$a_1 = f(\lambda_1)$$

$$a_m = k_{m,1} f[\lambda_1, \lambda_m] + \sum_{j=2}^{m-1} N_j(1, m) f_j[\lambda_{n_1}, \ldots, \lambda_{n_t}, \ldots, \lambda_{n_{j+1}}] \cdot \left(\prod_{t=1}^{j} k_{n_{t+1}, n_t}\right); \quad m > 1 \tag{25}$$

where $f_j[\lambda_{n_1}, \ldots, \lambda_{n_t}, \ldots, \lambda_{n_{j+1}}]$ is the divided difference of order j of the formal solution (Eq. 3) defined at the eigenvalues of $\boldsymbol{K}$. $N_j(i, m)$ is an operator which generates all the possible sequences of $j + 1$ indices n_t, subject to the constraint

$$n_1 = i < n_2 < n_3 < \ldots n_{j+1} = m. \tag{26}$$

For example, $N_1(1, 4)$ generates the sequence of indices $(n_1, n_2) = (1, 4)$, while $N_2(1, 4)$ generates the two sequences $(1, 2, 4)$ and 1, 3, 4). The operator $N_j(i, m)$ may be also written as

$$N_j(i, m) = \sum_{n_2 = n_1 + 1}^{m+1-j} \; \sum_{n_3 = n_2 + 1}^{m+2-j} \cdots \sum_{n_j = n_{j-1} + 1}^{m-1} \tag{27}$$

and $n_1 = i, n_{j+1} = m$.

The above expression appears at first to be rather cumbersome, but it is simple to construct, noting that each term represents the concentration of A_m formed from pure A_1 in a reaction route consisting of j steps. For example, consider the reaction network of five species, shown in Figure 1, with A_4 being the desired product. A_4 can be formed from A_1 via four different routes, namely,

$$A_1 \xrightarrow{k_{4,1}} A_4$$

$$A_1 \xrightarrow{k_{2,1}} A_2 \xrightarrow{k_{4,2}} A_4$$

$$A_1 \xrightarrow{k_{3,1}} A_3 \xrightarrow{k_{4,3}} A_4$$

$$A_1 \xrightarrow{k_{2,1}} A_2 \xrightarrow{k_{3,2}} A_3 \xrightarrow{k_{4,3}} A_4.$$

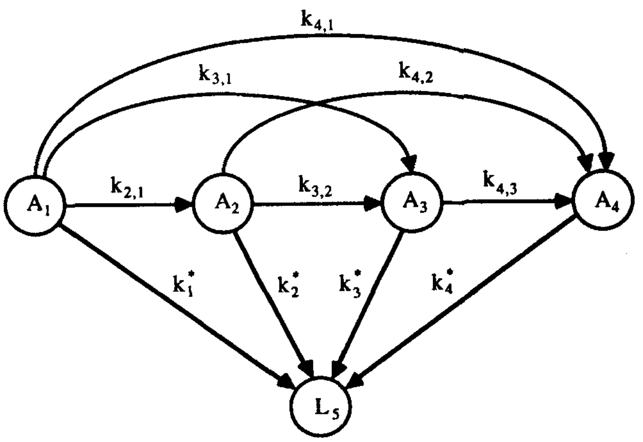

Figure 1. Network of irreversible reactions among five species with A_4 as desired product.

The expression for A_4 consists of four terms, each corresponding to one of these routes, i.e.,

$$a_4 = k_{4,1} f[\lambda_1, \lambda_4] + k_{2,1}k_{4,2} f[\lambda_1, \lambda_2, \lambda_4] + k_{3,1}k_{4,3} f[\lambda_1, \lambda_3, \lambda_4] + k_{2,1}k_{3,2}k_{4,3} f[\lambda_1, \lambda_2, \lambda_3, \lambda_4]. \quad (28)$$

Obviously, if some of these reactions do not occur, i.e., $k_{j,l} = 0$, the expression is reduced to a smaller number of terms.

It is important to note that the expression for a_m, defined by Eq 25, is valid for any $f(\boldsymbol{K},\boldsymbol{p})$. The only restrictions are that $\boldsymbol{K}$ is a lower triangular matrix and that $f(x)$ is finite for all λ_i.

The above expression can be extended to the case of any arbitrary input vector

$$\mathbf{a}_0 = [a_1(0), a_2(0), \ldots, a_m(0), L_{m+1}(0)]^T. \quad (29)$$

The output concentration, a_m, is given by the relation

$$a_m = a_m(0) f(\lambda_m) + \sum_{q=1}^{m-1} a_q(0) k_{m,q} f[\lambda_q, \lambda_m] + \sum_{j=2}^{m-1} \sum_{q=1}^{m-j} a_q(0) N_j(q, m) f_j[\lambda_{n_1}, \ldots, \lambda_{n_l}, \ldots, \lambda_{n_{j+1}}] \cdot \left(\prod_{l=1}^{j} k_{n_{l+1}}, n_l \right) \quad (30)$$

We shall now apply this result to determine the yield loss in a tubular reactor with axial dispersion, in a reactor with a specified residence time distribution (RTD), and in a packed bed reactor in which both catalytic pellet transport limitations and axial dispersion exist.

Maximal Fractional Yield Loss in a Reactor with Axial Dispersion

We define the fractional yield loss of a desired product, a_m, in a reactor, with dispersion relative to that in an ideal plug flow reactor, as

$$\delta_m = \frac{a_{p,m} - a_{d,m}}{a_{p,m}} \quad (31)$$

where $a_{p,m}$ and $a_{d,m}$ are the concentions of mth species in a plug flow reactor and in a reactor with axial dispersion.

Using Eqs. 4 and 10, it can be shown that

$$\delta_m = -\frac{1}{Pe} \frac{e_m^T (\mathbf{K}\tau)^2 e^{\mathbf{K}\tau} \mathbf{a}_0}{e_m^T e^{\mathbf{K}\tau} \mathbf{a}_0} \quad (32)$$

Established correlations about the dependence of the axial dispersion on the operating conditions can be used to predict the effect of reactor length on Pe for operation at a fixed residence time. Note that both the numerator and denominator of the righthand side of Eq. 32 are of the form defined by Eq. 3. It follows from Eq. 30 that they can be expressed as

$$\delta_m = -\frac{1}{Pe} \frac{F[x_1, x_2, \ldots, x_m]}{G[x_1, x_2, \ldots, x_m]} \quad (33)$$

where

$$F[x_1, x_2, \ldots, x_m] = a_m(0) f(x_m) + \sum_{q=1}^{m-1} a_q(0) \tau k_{m,q} f[x_q, x_m] + \sum_{j=2}^{m-1} \sum_{q=1}^{m-j} a_q(0) N_j(q, m) f_j[x_{n_1}, \ldots, x_{n_l}, \ldots, x_{n_{j+1}}] \cdot \left(\prod_{l=1}^{j} \tau k_{n_{l+1}, n_l} \right) \quad (34)$$

with $x_i = \lambda_i \tau$ and $f(x) = x^2 e^x$. $G[x_1, x_2, \ldots, x_m]$ is given by an identical expression but with $f(x) = e^x$. Note that $F[x_1, x_2, \ldots, x_m]$ and $G[x_1, x_2, \ldots, x_m]$ are both divided difference functions of order $m - 1$.

Using Eq. 18, we can rewrite Eq. 33 as

$$\delta_m = -\frac{1}{Pe} \frac{F_{m-1}[u, u, \ldots, u]}{G_{m-1}[u, u, \ldots, u]}. \quad (35)$$

By carrying out the differentiation we get

$$\delta_m = -\frac{1}{Pe} \frac{\sum_{j=0}^{m-1} w_j [u^2 + 2ju + j(j-1)]}{\sum_{j=0}^{m-1} w_j} \quad (36)$$

with

$$w_0 = a_m(0) \quad (37)$$

$$w_1 = \tau \sum_{q=1}^{m-1} a_q(0) k_{m,q} \quad (38)$$

$$w_j = \frac{\tau^j}{j!} \sum_{q=1}^{m-j} a_q(0) N_j(q, m) \left(\prod_{l=1}^{j} k_{n_{l+1}, n_l} \right); \quad j = 2, 3, \ldots, m-1. \quad (39)$$

Equation 36 shows that δ_m is a weighted average value of the function, $u^2 + 2ju + j(j-1)$. The smallest value of this function for all the feasible j values occurs at $u = -j = -(m-1)$. Thus, the largest value of δ_m occurs when

$$w_j = 0; \quad j = 0, 1, \ldots, m-2, \quad (40)$$

$$w_{m-1} \neq 0, \tag{41}$$

$$u = u_{m-1} = \lambda_i \tau = -(m-1); \qquad i = 1, 2, \ldots, m-1. \tag{42}$$

We show in Appendix A that the above conditions imply that

$$a_1(0) \neq 0, a_i(0) = 0; \qquad i > 1 \tag{43}$$

i.e., the maximum deviation is found for a pure feed containing a_1. Moreover,

$$k_{j,i} = 0; \qquad m + 1 > j > i + 1 \tag{44}$$

$$k_{i+1,i} \neq 0; \qquad i = 1, 2, \ldots, m-1. \tag{45}$$

Equations 42, 44, and 45 imply that the maximal dispersion effect occurs in the reaction network shown in Figure 2 with

$$(k_{i+1,i} + k_i^*)\tau = k_m^*\tau = m - 1; \qquad i = 1, 2, \ldots, m-1. \tag{46}$$

The above result shows that the maximal loss of fractional yield occurs at a residence time at which the yield of the desired product attains its maximal value in a plug flow reactor. Note that the rate constant matrix, ***K***, which satisfies Eqs. 44–46 is the most degenerate possible nontrivial rate matrix. It has only one nonzero eigenvalue of multiplicity, m, and one corresponding eigenvector.

We conclude that the maximal fractional yield loss is found for the reaction network shown in Figure 2, and is equal to

$$\delta_m^* = \max(\delta_m) = \frac{m-1}{Pe}. \tag{47}$$

This is a very useful result for *a priori* design calculations, and can be used to determine the minimal reactor length, or equivalently, Pe needed to keep δ_m below a specified bound. The equation predicts that the maximal error is proportional to the number of species from which a_m can be produced directly or via some intermediates.

It is of interest to note that the value of the rate constants for the side reactions, k_i^* $(i = 1, 2, \ldots, m-1)$, has no effect on the magnitude of the fractional yield loss as long as Eq. 46 is satisfied.

The exact solutions of δ_m^* for $m = 2$ and 3, determined by solving Eqs. 5–7, show that the value of u_{m-1} depends on Pe and is exactly equal to $-(m-1)$ only when $Pe = 0$ or $Pe = \infty$. The maximal deviation in the value of u_{m-1} is 10.3 and 8.3 percent for $m = 2$ and 3, respectively. The value of δ_m^* found from the perturbation solution (Eq. 47) always exceeds that of the exact solution. Thus, Eq. 47 is always a conservative estimate of δ_m^*.

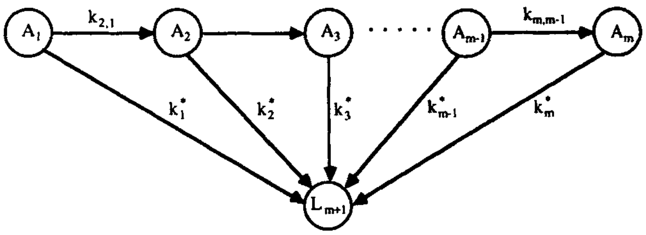

Figure 2. Network of irreversible reactions leading to maximal value of δ_m.

Maximal Fractional Yield Loss for Reactor with Specified RTD

In many commercial reactors the residence time distribution differs significantly from that of a plug flow reactor so that the impact of dispersion cannot be accounted for by axial dispersion, and requires use of the residence time density function, $E(t)$, or $E(\theta)$, where θ is the dimensionless time, t/τ. Thus.

$$\int_0^\infty E(\theta)\, d\theta = \int_0^\infty \theta E(\theta) d\theta = 1. \tag{48}$$

The concentrations vector at the exit of the reactor is

$$\mathbf{a}_E = \left(\int_0^\infty e^{\mathbf{K}\tau\theta} E(\theta) d\theta\right) \mathbf{a}_0 \tag{49}$$

which has the form of the formal solution, Eq. 3. Thus, the outlet concentration of the desired product a_m, is given again by Eq. 30 with

$$f(x) = \int_0^\infty e^{x\theta} E(\theta) d\theta \tag{50}$$

and $x_i = \lambda_i \tau$. The fractional yield loss of the desired product relative to that in an ideal plug flow reactor is given by the relation

$$\delta_m = \frac{a_{p,m} - a_{E,m}}{a_{p,m}} = 1 - \frac{F[x_1, x_2, \ldots, x_m]}{G[x_1, x_2, \ldots, x_m]} \tag{51}$$

where F is defined by Eq. 34 and $f(x)$ defined by Eq. 50 and G is defined by the same expression but with $f(x) = e^x$.

Using again Eq. 18 we can replace Eq. 51 by the relation

$$\delta_m = 1 - \frac{\sum_{j=0}^{m-1} w_j G_j(u)}{\sum_{j=0}^{m-1} w_j} \tag{52}$$

where

$$G_j(u) = e^{-u} \int_0^\infty \theta^j e^{u\theta} E(\theta)\, d\theta \tag{53}$$

and the coefficients, w_j are defined by Eqs. 37–39.

We show in Appendix B that in this case the maximal fractional yield loss is found again for the reaction network described by Figure 2, subject to the restrictions that

$$(k_{i+1,i} + k_i^*)\tau = k_m^*\tau = -u_{m-1}; \quad i = 1, 2, \ldots, m-1 \tag{54}$$

where u_{m-1} is the value of u corresponding to the minimum in the value of $G_{m-1}(u)$. It satisfies the condition,

$$\frac{d^{m-1}}{du^{m-1}} \bar{E}(-u) = \frac{d^m}{du^m} \bar{E}(-u) \tag{55}$$

where $\bar{E}(s)$ is the Laplace transform of $E(\theta)$. Practically, $-u_{m-1}$ can be considered as the dimensionless residence time corresponding to the maximal fractional yield loss. In many applications, but not in all, u_{m-1} is equal to $-(m-1)$. The maximal fractional loss is given by

$$\delta_m^* = 1 - G_{m-1}(u_{m-1}) = 1 - e^{-u_{m-1}} \frac{d^{m-1}}{du^{m-1}} \bar{E}(-u_{m-1}). \qquad (56)$$

The above strong result provides a rapid estimate of the maximal fractional yield loss due to deviations from an ideal plug flow. Moreover, it enables the *a priori* determination of the sensitivity of the fractional yield loss to the functional form of the RTD function and the associated parameters. Two examples will be given to demonstrate how to obtain the upper bound, δ_m^*, from the Laplace transform of the RTD function of a reactor, i.e., from its transfer function.

Example 1

Consider a reactor with a residence time distribution close to that of a plug flow reactor so that its Laplace transform can be represented as (Silverstein and Shinnar, 1975)

$$\bar{E}(s) = \left(1 + \frac{\sigma_\theta^2}{2} s^2\right) e^{-s} \qquad (57)$$

where σ_θ^2 is the dimensionless variance of the RTD function. Using Eqs. 55 and 56, we find that

$$u_{m-1} = -(m-1) \qquad (58)$$

$$\text{and} \qquad \delta_m^* = \frac{\sigma_\theta^2}{2}(m-1) \qquad (59)$$

This exact result agrees with the one obtained by Silverstein and Shinnar (1975) using heuristic arguments. Equation 59 is the same as Eq. 47 since, for a plug flow reactor with small dispersion (Levenspiel, 1972),

$$\frac{1}{Pe} = \frac{\sigma_\theta^2}{2}. \qquad (60)$$

Example 2

Consider a reactor, the residence time density function of which is a Gamma distribution, i.e.,

$$E(\theta) = \frac{b^b}{\Gamma(b)} \theta^{b-1} e^{-b\theta} \qquad (61)$$

where b is the mixing index, equal to unity for a CSTR, and infinity for an ideal plug flow reactor. It is related to the variance of $E(\theta)$ by

$$b = \frac{1}{\sigma_\theta^2}. \qquad (62)$$

The Laplace transform of $E(\theta)$ is

$$\bar{E}(s) = \left[\frac{b}{b+s}\right]^b. \qquad (63)$$

Using Eqs. 55 and 56, we find that Eq. 58 is valid also in this case and that

$$\delta_m^* = 1 - \frac{b^b \Gamma(m+b)}{\Gamma(b)} \left(\frac{1}{m+b-1}\right)^{m+b} e^{m-1} \qquad (64)$$

When $b \gg 1$ or $\sigma_\theta^2 \ll 1$, Eq. 64 can be simplified by Stirling's formula (Abramowitz and Stegun, 1970) to

$$\delta_m^* = \frac{(m-1)}{2b} = \frac{\sigma_\theta^2}{2}(m-1) \qquad (65)$$

which is the same as Eq. 59. When $\sigma_\theta^2 \rightarrow 1$, corresponding to the value in a CSTR, δ_m^* approaches asymptotically the value

$$\delta_m^*(\sigma_\theta^2 \rightarrow 1) = 1 - \frac{m! e^{m-1}}{m^{m+1}}. \qquad (66)$$

Figure 3 describes the dependence of δ_m^* for the Gamma distribution model on σ_θ^2, and the smooth shift from the asymptotic dependence given by Eq. 65 to that defined by Eq. 66. In all the examples considered so far, Eq. 58 is valid, but there are exceptions. For example, consider the generalized Gamma distribution model described by Wen and Fan (1975, chapter 8)

$$E(\theta) = \frac{b^b}{(1-a)^b \mathrm{T}(b)} (\theta - a)^{b-1} e^{-b(\theta-a)/(1-a)};$$

$$\sigma_\theta^2 = \frac{(1-a)^2}{b} \qquad (67)$$

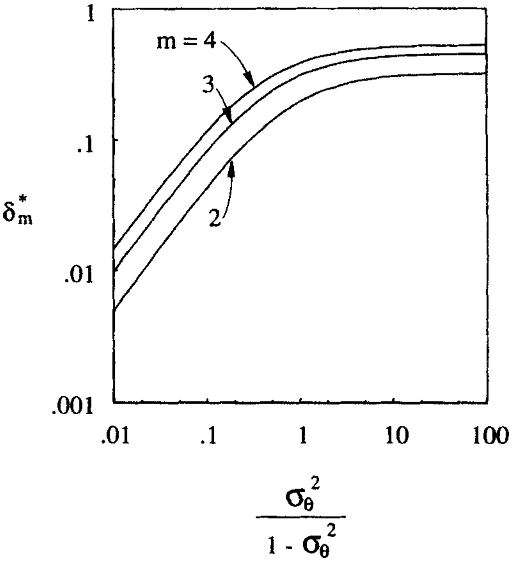

Figure 3. Dependence of fractional yield loss, δ_m^*, on σ_θ^2 for Gamma distribution model.
$m = 2, 3,$ and 4.

where a is dimensionless dead time. Here, u_{m-1} is not equal to $-(m-1)$ if $a \neq 0$ and its exact value has to be computed numerically. Similarly, for the axial dispersion model (with a finite Pe value) and for the recycle model, u_{m-1} is not equal to $-(m-1)$. In all these cases, the maximal fractional yield loss will not always occur for a residence time at which the yield attains its maximum value in a plug flow reactor.

It should be pointed out that even though Figure 3 is constructed for the Gamma distribution model, it is a very close approximation for any system having a unimodal residence time density function. For example, calculations with the axial dispersion model gives curves that are nearly indistinguishable from those shown in Figure 3. Thus the graph shown in Figure 3 can be used to predict δ_m^* for any system which has a unimodal residence time density function.

Maximal Yield Loss Due to Intraparticle Diffusion and Axial Dispersion in a Packed Bed Reactor

The analysis and scale-up of a laboratory packed bed reactor is often complicated by the presence of intraparticle diffusion resistance, which disguises the intrinsic kinetics. The difference in particle size, and hence intraparticle diffusion, introduces an uncertainty in the scale-up procedure. Thus, it is often important to be able to predict *a priori* the maximal impact of both intraparticle diffusion and axial dispersion on reactors in which several reactions occur simultaneously. We derive here an upper bound on the impact of these effects for the case that all the effective diffusion coefficients are equal.

The local reaction rate in a catalytic pellet may be expressed as (Wei, 1962a, b; Aris, 1975)

$$\frac{da}{dt} = K^* a \tag{68}$$

where K^* is a matrix of intraparticle diffusion and external mass-transfer disguised rate constants. When the diffusion and mass transfer coefficients of all the species are the same

$$\mathbf{K}^* = \mathbf{Z}\Lambda\eta\mathbf{Z}^{-1} \tag{69}$$

where Z is a matrix of the eigenvectors of the intrinsic kinetic matrix K, Λ is a diagonal matrix of the eigenvalues, λ_i of K, and η is a diagonal matrix of the effectiveness factor, η_i, which satisfies the relation

$$\eta_i = \frac{3\varphi_i \coth(3\varphi_i) - 1}{3\varphi_i^2\left[1 + \dfrac{3\varphi_i \coth(3\varphi_i) - 1}{3Bi_m}\right]} \tag{70}$$

where

$$\varphi_i^2 = \frac{-\lambda_i}{D_e}\left(\frac{V_p}{S_x}\right)^2, \quad Bi_m = \frac{k_g}{D_e}\left(\frac{V_p}{S_x}\right). \tag{71}$$

While the eigenvectors of K^* are the same as those of K, the eigenvalues of K^* are $\eta_i\lambda_i$, while those of K are λ_i. The previous result, Eq. 9, for the output of a reactor with axial dispersion can be modified directly to predict that when transport limitations exist, the effluent concentration satisfies the relation

$$\mathbf{a}(\tau) = \left(\mathbf{I} + \frac{\mathbf{Da}^{*2}}{Pe}\right)e^{\mathbf{Da}^*}\mathbf{a}_0 + O\left(\frac{1}{Pe^2}\right) \tag{72}$$

where the diffusion disguised Damköhler matrix is defined as

$$\mathbf{Da}^* = \mathbf{K}^*\tau = \mathbf{Z}\Lambda\eta\mathbf{Z}^{-1}\tau \tag{73}$$

The outlet concentration is given by Eq. 30 with

$$f(x) = \left(1 + \frac{x^2\eta(x)^2}{Pe}\right)e^{x\eta(x)} \tag{74}$$

and $x_i = \lambda_i\tau$. Defining the outlet concentration of species m by $a_{dD,m}$, the fractional yield loss relative to that in an ideal plug flow reactor with no diffusion and axial dispersion is

$$\delta_m = \frac{a_{p,m} - a_{dD,m}}{a_{p,m}} = 1 - \frac{F[x_1, x_2, \ldots, x_m]}{G[x_1, x_2, \ldots, x_m]} \tag{75}$$

where F is defined by Eq. 34 with $f(x)$ defined by Eq. 74, and G is defined by the same expression with $f(x) = e^x$. Following the same procedure, δ_m can be computed by Eq. 52 but with

$$G_j(u) = e^{-u}\frac{d^j}{du^j}\left[\left(1 + \frac{1}{Pe}\eta^2u^2\right)e^{\eta u}\right] \tag{76}$$

where

$$\eta = \frac{3\varphi \coth(3\varphi) - 1}{3\varphi^2\left[1 + \dfrac{3\varphi \coth(3\varphi) - 1}{3Bi_m}\right]}, \tag{77}$$

$$\varphi^2 = -up^2, \tag{78}$$

and

$$p = \sqrt{\frac{1}{D_e\tau}\left(\frac{V_p}{S_x}\right)^2}. \tag{79}$$

Note that the value of p, unlike that of φ, can be determined without knowledge of any rate constant. We show in Appendix C that the maximal fractional yield loss due to dispersion and diffusion is given by

$$\delta_m^* = 1 - G_{m-1}(u_{m-1}) = 1 - e^{-u_{m-1}}\frac{d^{m-1}}{du^{m-1}} \cdot \left[\left(1 + \frac{1}{Pe}\eta^2u^2\right)e^{\eta u}\right]\Big|_{u=u_{m-1}} \tag{80}$$

corresponding to the reaction network described by Figure 2, subject to the restrictions defined by Eq. 54. Again, u_{m-1} is the value of u corresponding to the minimum in the value of $G_{m-1}(u)$, found by the solution of

$$\frac{d^{m-1}}{du^{m-1}}\left[\left(1 + \frac{1}{Pe}\eta^2u^2\right)e^{\eta u}\right] - \frac{d^m}{du^m}\left[\left(1 + \frac{1}{Pe}\eta^2u^2\right)e^{\eta u}\right] = 0. \tag{81}$$

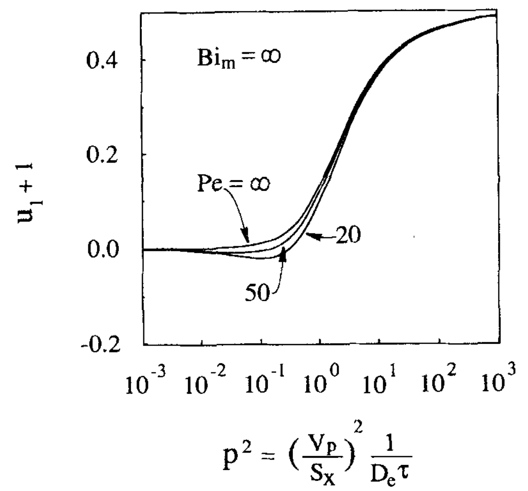

Figure 4. Dependence of $u_1 + 1$ on p for different Pe and for $Bi_m = \infty$.

One may expect that u_{m-1} is not equal to $-(m - 1)$ in this case. However, it can be shown that $u_{m-1} + m - 1$ has the asymptotic value of 0 for very small p. For large p, $u_{m-1} + m - 1$ approaches 0.5 for $Bi_m = \infty$ and -0.5 for finite Bi_m. Figure 4 shows the dependence of $u_1 + 1$ on p for the case of $m = 2$ for three different Peclet numbers and $Bi_m = \infty$. When Pe is very large, i.e., when the axial dispersion is negligible, $u_1 + 1$ is a monotonically increasing function of p. However, for finite values of Peclet number, $u_1 + 1$ attains a local minimum value for some intermediate p values. This implies that for intermediate p values, the maximal value of δ_m occurs for a residence time exceeding that in which the maximum yield is found in an ideal plug flow reactor with no diffusional limitations. However, for larger values of p, the maximal δ_m occurs for a residence time smaller than that corresponding to the maximal yield in an ideal plug flow reactor with no diffusional limitations.

Due to the nonlinear dependence of η on u, Eqs. 80 and 81 can be solved only numerically. When the diffusion parameter is small, i.e., when $p^2 \ll 1$, η may be approximated by

$$\boldsymbol{\eta} = \left[\mathbf{I} + \left(\frac{3}{5} + \frac{1}{Bi_m}\right) p^2 \tau \boldsymbol{\Lambda}\right] + O(p^4). \tag{82}$$

Substituting Eq. 82 into Eq. 73 we have

$$\mathbf{Da}^* = \mathbf{Da} + \left(\frac{3}{5} + \frac{1}{Bi_m}\right) p^2 \mathbf{Da}^2 + O(p^4). \tag{83}$$

Then Eq. 72 becomes

$$\mathbf{a}(\tau) = \left\{\mathbf{I} + \left[\left(\frac{3}{5} + \frac{1}{Bi_m}\right) p^2 + \frac{1}{Pe}\right] \mathbf{Da}^2\right\} e^{\mathbf{Da}} \boldsymbol{a}_0 + h.o.t. \tag{84}$$

Equation 84 is a generalization of Eq. 10, and the results obtained earlier in this paper can be applied directly to obtain the approximate bound

$$\delta_m^* = \frac{m - 1}{2}\left[\frac{2}{Pe} + \left(\frac{6}{5} + \frac{2}{Bi_m}\right) p^2\right]. \tag{85}$$

Thus, the perturbation solution predicts that the loss in yield is the sum of losses due to three effects, one due to intraparticle diffusion, one to external mass transfer, and one to dispersion. All these losses increase with m. Practically, $Bi_m \gg 1$. Therefore, the contribution from external mass transfer is negligible.

The approximate bound defined by Eq. 85 is similar to that obtained by Silverstein and Shinnar (1975) for a system of m consecutive irreversible reactions using some intuitive arguments. The analysis here shows that this bound is applicable to a much larger class of irreversible reactions. It points out the approximations on which it is based, and shows how to obtain a more general result when any of these assumptions is invalid.

Figure 5 describes the influence of diffusion on the bound of fractional yield loss for $m = 2$, 3, and 4 in a plug flow reactor with no axial dispersion, i.e., $Pe = \infty$, and $Bi_m = \infty$. For small p^2, δ_m^* approaches asymptotically the value of $0.6(m - 1)p^2$ predicted by Eq. 85. The graphs indicate that for p^2 values smaller than about 0.01, δ_m^* is rather small. However, the value of δ_m^* increases rapidly and for p^2 larger than 0.2, the yield uncertainty introduced by not accounting for intraparticle diffusional limitations reaches unacceptable levels.

Figure 6 describes the dependence of δ_m^* on the diffusional parameter p for three Peclet numbers, 20, 50, ∞, and $m = 2$ when $Bi_m = \infty$. For small values of p, δ_m^* has the asymptotic value predicted by Eq. 85. The graphs indicate that for p^2 values smaller than about 0.01, the axial dispersion is the main cause of yield loss or design uncertainty. However, for p^2 values larger than 0.2, the intraparticle diffusion becomes the main contributor to δ_m^*, and the uncertainty in the value of the yield becomes exceedingly high.

In the design of a laboratory scale reactor, one needs to know the minimum length of a reactor or/and the maximum size of the catalyst needed to keep the scale-up uncertainty below a specified level. Figure 7 shows such boundaries. The solid line represents values computed by Eqs. 80 and 81, while the dashed line represents the approximate bound computed by Eq. 85. For all p and Pe values below the curve, the maximal fractional yield loss due to axial dispersion and intraparticle diffusion is below the specified level. When $\delta_m^* = 0.02$, Eq. 85 approx-

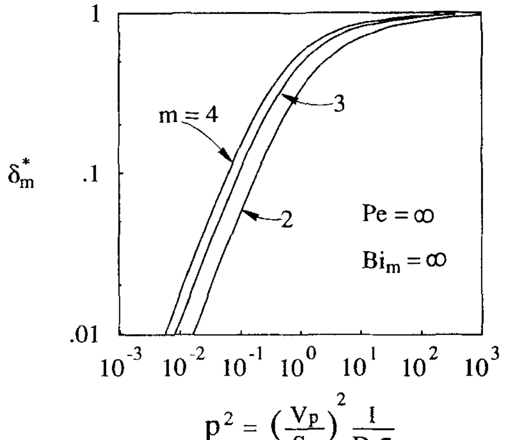

Figure 5. Dependence of fractional yield loss, δ_m^*, on p for $m = 2, 3, 4$.

Axial dispersion and external mass transfer resistance are negligible.

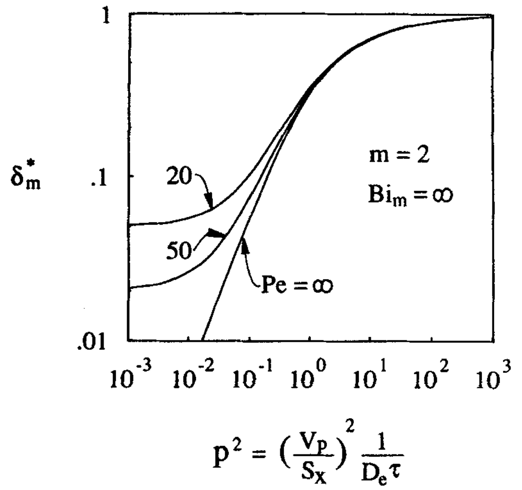

Figure 6. Dependence of fractional yield loss, δ_m^*, on p for $m = 2$ and for different Pe when $Bi_m = \infty$.

imates the bound very closely. The bound computed by Eq. 85 deviates from that calculated by Eqs. 80 and 81 when δ_m^* increases. This deviation increases as δ_m^* increases. Surprisingly, the boundaries calculated from Eq. 80 and 81 are very close to a straight line for δ_m^*, up to 0.1. The approximate bound calculated by Eq. 85 is always more conservative than that from Eqs. 80 and 81. Therefore, Eq. 85 can be used as a conservative rapid estimate of the maximal fractional yield loss due to the diffusion limitations and dispersion. The result can be extended to a reactor with any RTD function having variance $\sigma_\theta^2 \ll 1$, by using Eq. 60. Although the curves shown in Figure 7 are valid only for $m = 2$, similar results may be obtained for any value of m. Figures such as Figure 7 are most useful for *a priori* design of laboratory reactor length and of the catalyst pellet size.

When the axial dispersion model does not adequately describe the deviation from plug flow, the impact of dispersion can be accounted for by use of the RTD function, $E(\theta)$. In this case, the effluent concentration vector becomes

$$\mathbf{a}_{ED} = \left(\int_0^\infty e^{\mathbf{K}^*\tau\theta} E(\theta)\, d\theta\right) \mathbf{a}_0. \tag{86}$$

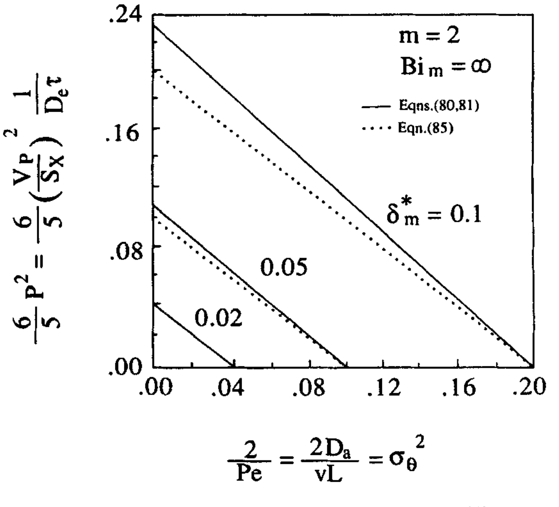

Figure 7. Boundaries of p and Pe with specific level of fractional yield loss for $m = 2$ and $Bi_m = \infty$.

Eq. 30 gives the explicit expression for $a_{ED,m}$ with

$$f(x) = \int_0^\infty e^{x\eta(x)\theta} E(\theta)\, d\theta \tag{87}$$

and $x_i = \lambda_i \tau$. The fractional yield loss for a_m, relative to that in an ideal plug flow reactor without intraparticle diffusion is given by

$$\delta_m = \frac{a_{p,m} - a_{ED,m}}{a_{p,m}} = 1 - \frac{F[x_1, x_2, \ldots, x_m]}{G[x_1, x_2, \ldots, x_m]} \tag{88}$$

where F is defined by Eq. 34 with $f(x)$ defined by Eq. 87. Again, δ_m can be expressed as Eq. 52 but with

$$G_j(u) = e^{-u} \frac{d^j}{du^j} \int_0^\infty e^{\eta u\theta} E(\theta)\, d\theta. \tag{89}$$

We show in Appendix D that the maximal fractional yield loss is

$$\delta_m^* = 1 - G_{m-1}(u_{m-1}) = 1 - e^{-u_{m-1}} \frac{d^{m-1}}{du^{m-1}} [\bar{E}(-u\eta)]|_{u=u_{m-1}} \tag{90}$$

where u_{m-1} is the solution of

$$\frac{d^{m-1}}{du^{m-1}} \bar{E}(-u\eta) - \frac{d^m}{du^m} \bar{E}(-u\eta) = 0. \tag{91}$$

Recall that η is related to u by Eqs. 77–79. The reaction network for this maximal impact is, as shown in Figure 2, subject to the restriction defined by Eq. 54.

Concluding Remarks

This work presents rigorous upper bounds on the maximal fractional yield loss, which may be caused by deviation from ideal plug flow and/or intraparticle diffusional limitations. A major advantage of these bounds is that they do not require knowledge of the kinetic parameters and may be used even when the exact structure of the reaction network is unknown. The only needed information is the maximal number of irreversible reactions needed to form the desired product from the reactants.

The analysis predicts that for small deviations from plug flow the uncertainty introduced by the dispersion is a linear function of the number of reactions needed to transform a reactant to the desired product. A more complex relation exists for large deviations from plug flow. The analysis provides a rigorous basis to the common rule of thumb that the impact of mass dispersion is more important in complex reacting networks than in the case of a single reaction. The analysis proves that the intuitive rule proposed by Silverstein and Shinnar (1975) for predicting the impact of dispersion for a system of consecutive reactions can be used for a much wider class of reactions.

The analysis provides a very useful criteria for *a priori* estimation of diffusional limitations may affect the yield based on knowledge of observable quantities. The analysis shows that use of different particle sizes in laboratory and full scale reactors may lead to a very high level of uncertainty in the design when p is large. This uncertainty can be reduced by decreasing the size difference between the particles used in the two types of reactors and/or by using mathematical models to predict the impact of diffusion once a kinetic model and the associated parameters are available.

A remaining open question is whether the bounds derived here are applicable when the reactions are reversible. Analysis of the impact of dispersion on several rather simple reaction networks suggests that the results for the irreversible systems hold also for the reversible case if one selects $(m - 1)$ to be the number of reactions on the longest noncircular path needed to transform a reactant to the product. For example, in the case of consecutive reactions, the number of reactions in the bound does not change by assuming that some or all the reactions are reversible. Thus, we conjecture that the analysis of the irreversible case provides an upper bound on the value of δ_m for the more general reversible case.

Acknowledgment

We are thankful to the NSF for partial support of this work.

Notation

a = dimensionless dead time in Gamma distribution model
$\mathbf{a}$ = outlet concentration vector
a_i = concentration of ith species
$\mathbf{a}_0$ = feed concentration
b = mixing index in Gamma distribution model
Bi_m = Biot number of mass transfer
D_a = axial dispersion coefficient
$\mathbf{Da}$ = matrix of Domköhler numbers
$\mathbf{Da}^*$ = diffusion disguised matrix of Damköhler numbers
D_e = effective diffusion coefficient
$E(\theta)$ = residence time distribution function
$\bar{E}(s)$ = Laplace transform of $E(\theta)$
$\mathbf{K}$ = matrix of rate constants
$\mathbf{K}^*$ = matrix of diffusion disguised rate constants
k_g = external mass transfer coefficient
k_i^* = lumped rate constant, Eq. 12
k_{ij} = rate constant for transformation of jth to ith species
L = reactor length
Pe = Peclet number
p = dimensionless parameter, Eq. 76
S_x = external surface area of catalyst pellet
v = average velocity in reactor
V_p = volume of catalyst pellet
$\mathbf{Z}$ = matrix of eigenvectors of $\mathbf{K}$

Greek letters

δ_m = fractional yield loss of species m
δ_m^* = maximal value of δ_m
η_i = effectiveness factor
$\boldsymbol{\eta}$ = diagonal matrix of effectiveness factors
φ_i = Thiele modulus
λ_i = eigenvalue of $\mathbf{K}$
$\boldsymbol{\Lambda}$ = diagonal matrix of $\mathbf{K}$ eigenvalues
θ = dimensionless time
σ^2 = variance of residence (contact) time distribution function
σ_θ^2 = normalized variance of residence time distribution function
τ = residence time

Subscripts

d = corresponding to a reactor with dispersion
D = corresponding to a reactor with intraparticle diffusion resistence
E = corresponding to a reactor with residence time distribution, $E(\theta)$
p = corresponding to a plug flow reactor

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Appendix A: Derivation of Eqs. 43–45.

Using the definition of w_j, Eq. 39, we get

$$w_{m-1} = \frac{\tau^{m-1} a_1(0)}{(m-1)!} \prod_{i=1}^{m-1} k_{i+1,i} \,. \tag{A1}$$

Thus, Eq. 41 can be satisfied only if

$$a_1(0) \neq 0 \tag{A2}$$

$$k_{i+1,i} \neq 0; \qquad i = 1, 2, \ldots, m-1. \tag{A3}$$

According to Eq. 40, $w_0 = 0$, hence Eq. 37 implies that

$$a_m(0) = 0. \tag{A4}$$

w_j may be expressed for all j in $(2, m-2)$ as

$$w_j = \frac{\tau^j}{j!}\left[\sum_{q=1}^{m-j-1} a_q(0) N_j(q, m) \left(\prod_{l=1}^{j} k_{n_{l+1},n_l}\right) + a_{m-j}(0) \prod_{i=m-j}^{m-1} k_{i+1,i}\right] \tag{A5}$$

We note that each term in w_j is nonnegative. All the rate constants multiplying $a_{m-j}(0)$ are positive, according to Eq. A3. Thus, w_j $(j = 2, 3, \ldots, m-2)$ can zero only if $a_{m-j}(0) = 0$, and

Eq. 40 can be satisfied only if

$$a_i(0) = 0; \qquad i = 2, 3, \dots, m - 2. \tag{A6}$$

From Eqs. (A3, A6, and 38), Eq. 40 implies

$$a_{m-1}(0) = 0 \tag{A7}$$

and

$$k_{m,1} = 0 \tag{A8}$$

Substitution of Eqs. A6 and A7 in Eq. 39, we get

$$wj = \frac{\tau^j}{j!} a_1(0) N_j(q,m) \prod_{t=1}^{j} k_{n_{t+1},n_t}. \tag{A9}$$

w_j can vanish only if the product of rate constants in Eq. A9 vanishes. This requires that any rate constant among nonconsecutive species, i.e., $k_{p,i}$, with $m \geq p > i + 1$, must be zero.

Appendix B: Derivation of Eqs. 54–56

It follows from the definition of $G_j(u)$, Eq. 53, that

$$G_j(u) > 0 \tag{B1}$$

and

$$\frac{d^2G_j(u)}{du^2} = G_{j+2}(u) - 2G_{j+1}(u) + G_j(u)$$

$$= e^{-u} \int_0^\infty \theta^j(\theta - 1)^2 e^{u\theta} E(\theta) d\theta > 0 \tag{B2}$$

Eq. B2 implies that $dG_j(u)/du$ is a monotonically increasing function. Recall that

$$\frac{dG_j(u)}{du} = G_{j+1}(u) - G_j(u)$$

$$= e^{-u} \int_0^\infty \theta^j(\theta - 1) E(\theta) e^{u\theta} d\theta. \tag{B3}$$

The term $e^{u\theta}$ is equal to unity when $\theta = 0$ and is rapidly decreasing to zero for $\theta > 0$ when $u \longrightarrow -\infty$. Since $\theta^j(\theta - 1)E(\theta)$ is negative when $\theta < 1$, it follows from Eq. B3 that

$$\frac{dG_j(u)}{du} < 0 \text{ for } u \longrightarrow -\infty. \tag{B4}$$

Therefore, from Eqs. B3, B4, we have

$$G_j(u) \longrightarrow \infty, \text{ when } u \longrightarrow -\infty. \tag{B5}$$

According to the definition of $G_j(u)$,

$$G_0(0) = G_1(0) = 1 \tag{B6}$$

Using Eq. B2 we get

$$G_k(0) - 2G_{k-1}(0) + G_{k-2}(0) > 0,$$

which can be written as

$$G_k(0) - G_{k-1}(0) > G_{k-1}(0) - G_{k-2}(0). \tag{B7}$$

It follows by induction that

$$G_{k+1}(0) > G_k(0); \qquad k > 1. \tag{B8}$$

By differentiation of $G_j(u)$ one finds that

$$\frac{dG_1(0)}{du} = 0 \tag{B9}$$

$$\frac{dG_j(0)}{du} = G_{j+1}(0) - G_j(0) > 0; \qquad j > 1 \tag{B10}$$

where the inequality in Eq. B10 follows from Eq. B8. The minimum of $G_j(u)$ is obtained at $u = u_j$, where

$$\frac{dG_j(u)}{du} = 0. \tag{B11}$$

From the definition of $G_j(u)$, we find that Eq. B11 is equivalent to

$$G_j(u_j) = G_{j+1}(u_j). \tag{B12}$$

The above properties of $G_j(u)$ Eqs. B2, B5, and B10 indicate that any $G_j(u)$ has one minimum for $u \leq 0$. Moreover, Eq. B12 implies that $G_{j+1}(u)$ and $G_j(u)$ intersect at the minimum point, u_j, of $G_j(u)$, and Eq. B8 implies that

$$G_j(u_j) > G_{j+1}(u_{j+1}) \tag{B13}$$

and

$$u_j > u_{j+1}. \tag{B14}$$

Thus, the smallest value of $G_j(u)$ for all feasible j and negative u is $G_{m-1}(u_{m-1})$. Thus, the largest value for δ_m defined by Eq. 52 is obtained by the choice of w_i, defined by Eqs. 40 and 41. This implies that the largest value of δ_m is given by Eq. 56. It was proven in Appendix A that the above conditions imply a reaction network for which Eqs. 43–45 are satisfied, i.e., the reaction network shown in Figure 2, subject to restrictions shown in Eq. 54.

Appendix C: Derivation of Eqs. 80 and 81

From the definition of $G_j(u)$, it is obvious that

$$\frac{dG_j(u)}{du} = G_{j+1}(u) - G_j(u) \tag{C1}$$

From Faa di Bruno's theorem (Abramowitz and Stegun, 1970), we have

$$G_1(0) = 1 \tag{C2}$$

$$G_j(0) = \frac{d^j}{du^j}\left[\left(1 + \frac{1}{Pe}\eta^2u^2\right)e^{\eta u}\right]\Bigg|_{u=0}$$

$$= j!C_j + j!\sum_{t_1,t_2,\ldots,t_{j-1}}\left\{\left[1 + \frac{1}{Pe}t(t-1)\right]\left(\prod_{p=1}^{j-1}\frac{C_p^{t_p}}{t_p!}\right)\right\}; \quad \text{for } j \geq 2 \qquad \text{(C3)}$$

where $t = \Sigma_{p=1}^{j-1} t_p$, and the sum is taken over all the nonnegative integer sets of $(t_1, t_2, \ldots, t_{j-1})$ such that $\Sigma_{p=1}^{j-1} p t_p = j$. C_i's are the coefficients of the Taylor's expansion of η at $u = 0$, i.e.,

$$\eta = \sum_{i=1}^{\infty} C_i u^{i-1} \qquad \text{(C4)}$$

or

$$C_i = \frac{1}{(i-1)!}\frac{d^{i-1}\eta}{du^{i-1}}\Bigg|_{u=0} \qquad \text{(C5)}$$

In any case, $C_1 = 1$ and $C_i > 0$. The coefficient of the term $\Pi_{p=1}^{j-1} C_p{}^{t_p}$) in $G_j(0)$ is

$$\left[1 + \frac{1}{Pe}t(t-1)\right]\frac{j!}{\prod\limits_{p=1}^{j-1} t_p!} \qquad \text{(C6)}$$

Thus, the coefficient of the term $(\Pi_{p=1}^{j-1} C_p{}^{t_p})$ in $G_{j+1}(0) - G_j(0)$ is

$$\left\{\frac{(j+1)\left[1 + \frac{1}{Pe}t(t+1)\right]}{(t_1+1)} - \left[1 + \frac{1}{Pe}t(t-1)\right]\right\}\frac{j!}{\prod\limits_{p=1}^{j-1} t_p!} > 0 \qquad \text{(C7)}$$

because $2 \leq t_1 \leq t \leq j$. Therefore,

$$G_{j+1}(0) > G_j(0) \qquad \text{(C8)}$$

and

$$\frac{dG_j(0)}{du} > 0 \qquad \text{(C9)}$$

which is followed directly from Eq. C1. Using the Faa di Bruno's theorem, we can show that

$$G_j(u)\big|_{|u|\to\infty} \sim O(|u|^{1-j/2}\mathrm{e}^{|u|^{1/2}})$$

So that

$$G_j(u)\big|_{|u|\to\infty} \to \infty \text{ for finite } j. \qquad \text{(C10)}$$

If $G_j(u)$ has a minimum at $u = u_j$, then Eq. C1 implies

$$G_j(u_j) = G_{j+1}(u_j). \qquad \text{(C11)}$$

Eqs. C9, C10 imply that $G_j(u)$ has at least one minimum for $u \leq 0$ and Eqs C1, C8, C9, and C11 imply that Eqs B11 and B12 are also true for $G_j(u)$, defined by Eq. 76. By following the same argument as in Appendix B, Eqs. 80 and 81 can then be obtained.

Appendix D: Derivation of Eqs. 90 and 91

We shall show that $G_j(u)$, defined by Eq. 89, satisfies Eqs. C1, C8, C9, C10 and C11. Thus, Eqs. 90 and 91 can be obtained by the same argument.

$G_j(u)$, defined in Eq. 89, clearly satisfies Eqs. C1 and C11. Faa di Bruno's theorem gives that

$$G_1(0) = M_1 \qquad \text{(D1)}$$

$$G_j(0) = \frac{d^j}{du^j}\left(\int_0^\infty e^{\eta u\theta}E(\theta)\,d\theta\right)\Bigg|_{u=0}$$

$$= j!M_1C_j + j!\sum_{t_1,t_2,\ldots,t_{j-1}} M_t\left(\prod_{p=1}^{j-1}\frac{C_p^{t_p}}{t_p!}\right); \quad \text{for } j \geq 2 \qquad \text{(D2)}$$

where M_i is the ith moment of $E(\theta)$, i.e.,

$$M_i = \int_0^\infty \theta^i E(\theta)\,\mathrm{d}\theta$$

The coefficient of the term $(\Pi_{p=1}^{j-1} C_p^{t_p})$ in $G_j(0)$ is

$$\frac{M_t j!}{\prod\limits_{p=1}^{j-1} t_p!} \qquad \text{(D3)}$$

Thus, the coefficient of the term $(\Pi_{p=1}^{j-1} C_p^{t_p})$ in $G_{j+1}(0) - G_j(0)$ is

$$\left\{\frac{(j+1)M_{t+1}}{(t_1+1)} - M_t\right\}\frac{j!}{\prod\limits_{p=1}^{j-1} t_p!} > 0 \qquad \text{(D4)}$$

because $2 \leq t_1 \leq t \leq j$, and $M_{t+1} > M_t$. Therefore, Eqs. C8 and C9 are satisfied. It also follows from the Faa di Bruno's theorem that

$$G_j(u)\big|_{|u|\to\infty} \sim O(|u|^{-1/2-j}e^{|u|^{1/2}}) \qquad \text{(D5)}$$

Thus, Eq. C10 is valid in this case.

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