Two-Mode Models for Describing Mixing Effects in Homogeneous Reactors

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The Liapunov–Schmidt technique of bifurcation theory is used to spatially average the convection–diffusion–reaction equation over smaller time/length scales to obtain two-mode models (TMMs) for describing mixing effects in homogeneous tubular, loop/recycle and tank reactors. For the isothermal case, these TMMs are described by a pair of coupled balance equations involving the mixing-cup (C_m) and the spatially averaged ($\langle C \rangle$) concentrations. One equation traces the evolution of C_m with (residence) time, while the other is a local equation that describes mixing resulting from coupling between diffusion, velocity gradients, and reaction at the local scales, in terms of an exchange between the two modes, C_m and $\langle C \rangle$. The TMMs have many similarities with the two-phase models of catalytic reactors, with concept of transfer between phases being replaced by that of exchange between the two modes. Examples are presented to illustrate the usefulness of these TMMs in predicting micromixing effects on homogeneous reactions.

Introduction

The study of mixing effects on chemical reactions has been an active area of research since the pioneering papers of Danckwerts (1958) and Zweitering (1959). The topic has become a part of classic chemical reaction engineering and has been discussed in textbooks (Levenspiel, 1999; Froment and Bishchoff, 1990; Westerterp et al., 1984) and review articles (Villermaux, 1991). Historically, this study has progressed in two parallel branches, based on the Lagrangian and Eulerian frameworks of description, respectively.

The mechanistic models based on the Lagrangian description were initiated by the studies of Danckwerts (1958) and Zweitering (1959), using the residence-time distribution (RTD) theory and the ideas of "complete segregation" and "maximum mixedness." The two- and the three-environment models (Ng and Rippin, 1965; Miyawaki et al., 1975) that followed, described *micromixing* (that is, mixing caused by local diffusion, local velocity gradients, and reaction at the small scales) as an exchange between the environments of "complete segregation" and "maximum mixedness." Other mechanistic models that have been formulated in the last forty years include the coalescence–redispersion model (Harada, 1962), the interaction by exchange with mean (IEM) model (Villermaux and Devillon, 1972), models that assume diffusion with chemical reaction in deforming fluid lamellae (Ottino et al., 1979), and the engulfment–deformation–diffusion (EDD) models (Baldyga and Bourne, 1984). Although many of these models were low-dimensional (and, therefore, are inexpensive to compute) and could relate the global to the local interactions quite effectively, they are phenomenological in nature and are derived based on a top-down approach involving simplifying assumptions on the diffferent time and length scales of the system.

The Eulerian (bottom-up) approach is to start with the convective–diffusion equation and through Reynolds averaging, obtain time-smoothed transport equations that describe micromixing effectively. Several schemes have been proposed to close the two terms in the time-smoothed equations, namely, scalar turbulent flux in reactive mixing and the mean reaction rate (Bourne and Toor, 1977; Dutta and Tarbell, 1989; Fox, 1992). However, numerical solutions of the three-dimensional transport equations for reacting flows using CFD codes are prohibitive in terms of the numerical effort required. For example, the minimum number of mesh points (N_{xyz}) necessary to perform the direct numerical simulation (DNS) of the convective–diffusion equation for nonreacting turbulent flow is given by $N_{xyz} \approx Re^{9/4}Sc^{3/2}$, where Re and Sc

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are the Reynolds and turbulent Schmidt numbers, respectively. Moreover, due to strong coupling between transport and reaction-rate processes, the model equations for reacting flows are highly nonlinear and are known to exhibit a variety of spatiotemporal behaviors. For cases of practical interest, even with the present-day computational power, it is impractical to explore the different types of solutions and bifurcation behaviors that exist in the multidimensional parameter space, using CFD codes.

In this article, we present an alternate bottom-up approach of describing mixing effects in chemical reactions. This approach is based on rigorous spatial averaging of the three-dimensional convection–diffusion–reaction (CDR) equations over the local scales to obtain low-dimensional mixing models, which combine the rigor of the Eulerian models with the simplicity of the Lagrangian ones. This averaging, which is performed by using the Liapunov–Schmidt (L–S) technique of classical bifurcation theory, retains *all* the parameters of the CDR equations in the low-dimensional models, and, therefore, *all* the qualitative features of the latter. We show that in order to describe mixing through low-dimensional models effectively, we require *two* concentration variables for each species (instead of one variable, as in many traditional mixing models) and a local balance equation that captures micromixing as a difference between the two concentrations. The two concentration variables are called the *two modes* of the system, and these models are called *two-mode models* (TMMs). In this work, we present the two-mode models for various reactors and illustrate their applications with examples.

Formulation of Two-Mode Models

Spatial averaging by the L – S technique

In this section, we introduce the L–S technique as a tool for spatial averaging of different types of reactors and reacting flows. We illustrate this averaging technique by first considering the classical example of a laminar-flow tubular reactor. Extensions to other flow fields and reactor types then follow.

We start with the three-dimensional partial differential equations that describe the convection, diffusion, and reaction in the system and average them over the local (transverse) dimensions using the L–S technique to obtain low-dimensional models. Such spatial averaging (dimension reduction) is possible if there exists a time/length-scale separation in the system, that is, the local diffusion time is small (but finite) as compared to the convection time of the system. Under such conditions, local equilibrium exists at the short time scales, and the transverse diffusion operator of the CDR equation at equilibrium has a zero eigenvalue with a constant eigenfunction. For small deviations from the equilibrium, the L–S method projects the CDR equation on two orthogonal function spaces, such that one contains the equilibrium solution (that is, the constant eigenfunction) and the other contains the fluctuation about the equilibrium. The fluctuation could then be solved perturbatively to any order in p (where p is the ratio of local diffusion time to convection time of the system). As mentioned earlier, irrespective of the flow or reactor type, the spatially averaged equations obtained retain all the parameters present in the CDR equations, and, therefore, all the qualitative features of the latter. A detailed illustration of the preceding methodology follows.

We assume that the scalar concentration $C(\xi', \theta, x, t)$ in a tubular reactor of uniform cross section Ω with unidirectional laminar flow obeys the CDR equation

$$\frac{\partial C}{\partial t'} + u_x(\xi')\frac{\partial C}{\partial x} + R(C) = D_m\left[\frac{1}{\xi'}\frac{\partial}{\partial \xi'}\left(\xi'\frac{\partial C}{\partial \xi'}\right) + \frac{1}{\xi'^2}\frac{\partial^2 C}{\partial \theta^2} + \frac{\partial^2 C}{\partial x^2}\right] \quad (1)$$

where $u_x(\xi')$ is the fully developed velocity field, D_m is the molecular diffusivity, $R(C)$ is the sink term due to the presence of chemical reaction, and x, θ, and ξ' are the axial, azimuthal, and radial coordinates, respectively. In the transverse direction, Eq. 1 is subject to the no-flux boundary condition at the wall, $\nabla_* C \cdot \boldsymbol{n} = 0$, where $\boldsymbol{n}$ is the unit normal to the boundary $\partial\Omega$ and ∇_* is the gradient operator in Ω, while the inlet condition at $x = 0$ is of Danckwerts' type: $(\partial C/\partial x) = u_x(\xi')[C(\xi', x) - C_{\text{in}}(\xi')]$. Using a (radius of the pipe) and L (length of the pipe) as the characteristic lengths in the transverse and axial directions, respectively, and C_R as the reference concentration, we obtain four time-scales in the system associated with convection (τ_C), local/transverse diffusion (t_D), axial diffusion (t_Z), and reaction (t_R)

$$\tau_C = \frac{V}{q_{\text{in}}} = \frac{L}{\langle u_x\rangle}, \quad t_D = \frac{a^2}{D_m}, \quad t_Z = \frac{L^2}{D_m}, \quad t_R = \frac{C_R}{R(C_R)} \quad (2)$$

where V and q_{in} are the volume of the reactor and the volumetric flow rate of the reactants, respectively. The ratios of these time scales give rise to the dimensionless parameters: p (transverse Peclet number), Pe (axial Peclet number), Da (Damköhler number), and ϕ^2 (local Damköhler number), given by

$$p = \frac{a^2\langle u_x\rangle}{LD_m} = \frac{t_D}{\tau_C}, \quad Pe = \frac{\langle u_x\rangle L}{D_m} = \frac{t_Z}{\tau_C},$$
$$Da = \frac{LR(C_R)}{\langle u_x\rangle C_R} = \frac{\tau_C}{t_R}, \quad \phi^2 = pDa = \frac{a^2R(C_R)}{D_mC_R} = \frac{t_D}{t_R} \quad (3)$$

Using the following dimensionless variables,

$$t = \frac{t'}{\tau_C}, \quad \xi = \frac{\xi'}{a}, \quad z = \frac{x}{L}, \quad u = \frac{u_x}{\langle u_x\rangle}, \quad c = \frac{C}{C_R}, \quad r(c) = \frac{R(C)}{R(C_R)}$$

we rewrite Eq. 1 in dimensionless form as

$$\frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi\frac{\partial c}{\partial \xi}\right) + \frac{1}{\xi^2}\left(\frac{\partial^2 c}{\partial \theta^2}\right) = p\left[\frac{\partial c}{\partial t} - \frac{1}{Pe}\frac{\partial^2 c}{\partial z^2} + u(\xi)\frac{\partial c}{\partial z} + Da \quad r(c)\right], \triangleq pg(c) \quad (4)$$

with boundary and initial conditions being given by

$$\frac{1}{Pe}\frac{\partial c}{\partial z} = u(\xi)[c - c_{\text{in}}] \quad @ \quad z = 0 \tag{5}$$

$$\frac{\partial c}{\partial z} = 0 \quad @ \quad z = 1 \tag{6}$$

$$\frac{\partial c}{\partial \xi} = 0 \quad @ \quad \xi = 0,1 \tag{7}$$

$$c(\xi,\theta,z,t) = c(\xi,\theta + 2\pi,z,t) \tag{8}$$

$$c(\xi,\theta,z,t = 0) = c_o \tag{9}$$

We may note that for $p = 0$, the transverse diffusion operator in Eq. 4 has a zero eigenvalue, with the equilibrium solution being given by a constant eigenfunction $\langle c\rangle$, where $\langle c\rangle$ is the transverse averaged concentration defined as

$$\langle c\rangle = \frac{1}{2\pi}\int_{\xi=0}^{\xi=1}\int_{\theta=0}^{\theta=2\pi} c\,2\xi\,d\theta\,d\xi \tag{10}$$

For small deviations from the equilibrium, or in other words, if local (transverse) diffusion time is small (but finite) as compared to convection time (that is, p is small), the scalar concentration c in Eq. 4 could be written as

$$c(\xi,\theta,z,t) = \langle c\rangle(z,t) + c'(\xi,\theta,z,t) \tag{11}$$

where c' is the deviation of the concentration from the equilibrium, and goes to zero as $p \to 0$.

Spatial averaging by the L–S technique consists in projecting the CDR equation (Eq. 4) on two orthogonal function spaces, such that one contains the equilibrium solution and the other contains the deviation from the equilibrium. We refer to the former as "the global equation" and the latter as "the local equation." [For details of the L–S technique and its application as an averaging tool, refer to Golubitsky and Schaeffer (1984) and Balakotaiah and Chang (2002), respectively.]

The *global equation* for the case of laminar-flow tubular reactors is obtained by projecting Eq. 4 on the space containing the equilibrium solution, which in this case is acheived by simply integrating Eq. 4 over the transverse dimensions, and is given by

$$\frac{\partial\langle c\rangle}{\partial t} + \frac{\partial c_m}{\partial z} - \frac{1}{Pe}\frac{\partial^2\langle c\rangle}{\partial z^2} + Da\left[r(\langle c\rangle) + \frac{r''(\langle c\rangle)}{2!}\langle c'c'\rangle + \cdots\right] = 0 \tag{12}$$

where the spatially averaged concentration $\langle c\rangle$ is given by Eq. 10, and the mixing-cup concentration c_m is given by

$$c_m = \frac{\int_{\xi=0}^{\xi=1}\int_{\theta=0}^{\theta=2\pi} cu(\xi)2\xi\,d\theta\,d\xi}{2\pi\int_0^1 u(\xi)2\xi\,d\xi} \tag{13}$$

Here, c_m and $\langle c\rangle$ are the two modes of the system, each of which is representative of a physical scale of the system—c_m of the convection scale and $\langle c\rangle$ of the reaction–diffusion scale. The local equation is obtained by multiplying Eq. 11 by $u(\xi) = \langle u\rangle + u'(\xi)$ (where $\langle u\rangle$ is the dimensionless average velocity and u' is the transverse variation about the average), integrating it over the transverse cross section, and is given by

$$c_m = \langle c\rangle + \langle u'c'\rangle \tag{14}$$

It can be readily observed from Eq. 14 that the difference between c_m and $\langle c\rangle$ depends on the local velocity gradients u' and the local concentration gradients c' caused by molecular diffusion and reaction at the local scales. *Micromixing* is, thus, captured by the local equation as an *exchange* between the two modes (scales), c_m and $\langle c\rangle$. Needless to mention that *macromixing*, or large-scale mixing, is captured by the axial Peclet number, *Pe*, in Eq. 12, as in the traditional axial-dispersion model. Other traditional macromixing models, such as the recycle model or the tanks-in-series model, use the recycle ratio Λ or the number of tanks N, respectively, to account for macromixing.

In order to determine c', and, hence, the term $\langle u'c'\rangle$, we substitute Eq. 11 in Eq. 4 to obtain

$$\frac{1}{\xi}\frac{\partial}{\partial\xi}\left(\xi\frac{\partial c'}{\partial\xi}\right) + \frac{1}{\xi^2}\left(\frac{\partial^2 c'}{\partial\theta^2}\right) = pg(\langle c\rangle + c') \tag{15}$$

The L–S technique solves Eq. 15 for c' perturbatively by expanding it as an infinite series in p as

$$c' = \sum_{i=1}^{\infty} p^i c_i \tag{16}$$

Since the transverse operator of the CDR equation is self-adjoint, orthogonality of $\langle c\rangle$ and c' is ensured by simply employing $\langle c'\rangle = 0$, that is, $\langle c_i\rangle = 0$, $i \geq 1$.

For the case of laminar flow in a tube, that is, $u(\xi) = 2(1 - \xi^2)$, with azimuthally symmetric feeding, c' is obtained to $O(p)$ as

$$c' = -p\frac{\partial\langle c\rangle}{\partial z}\left[\frac{1}{12} - \frac{\xi^2}{4} + \frac{\xi^4}{8}\right] \tag{17}$$

and $\langle u'c' \rangle$ and $\langle c'c' \rangle$ are obtained as

$$\langle u'c' \rangle = -\beta_1 p \frac{\partial \langle c \rangle}{\partial z} \tag{18}$$

$$\langle c'c' \rangle = \gamma_1 p^2 \left(\frac{\partial \langle c \rangle}{\partial z} \right)^2 \tag{19}$$

where $\beta_1 = 1/48$ and $\gamma_1 = 1/1{,}440$ for laminar flow in tubes. The local equation (Eq. 14) to $O(p)$ is given as

$$c_m = \langle c \rangle - \beta_1 p \frac{\partial \langle c \rangle}{\partial z} \tag{20}$$

While c' has been derived to higher orders in p elsewhere (Chakraborty and Balakotaiah, 2002), it has been shown that the first-order term is sufficient to retain all the qualitative features of the full CDR equations. Inclusion of higher-order terms in the local equation only ensured greater quantitative accuracy when the solution of the low-dimensional model was compared with the exact solution of the full CDR equation. Spatial averaging of the CDR equations using the L–S technique for wall-catalyzed (surface) reactions shows a similar feature. As a result, the two-phase models for catalytic reactors, which are obtained by truncation of the spatially averaged model at $O(p)$, are known to be qualitatively correct for all values of the local Damköhler number, though they are derived under the assumption of small transverse concentration gradients ($p \ll 1$). A mathematical justification for this behavior of the two-mode/two-phase models is provided in the section on the similarity between two-mode and two-phase models.

The transverse averaged CDR equation to $O(p)$, capable of capturing both macro- and micromixing effects, is given by

$$\frac{\partial \langle c \rangle}{\partial t} + \frac{\partial c_m}{\partial z} - \frac{1}{Pe} \frac{\partial^2 \langle c \rangle}{\partial z^2} + Dar(\langle c \rangle) = 0 \tag{21}$$

$$\langle c \rangle - c_m = \beta_1 p \frac{\partial \langle c \rangle}{\partial z} \tag{22}$$

with boundary and initial conditions given by

$$\frac{1}{Pe} \frac{\partial \langle c \rangle}{\partial z} = c_m - c_{m,\text{in}}, \quad @ \quad z = 0 \tag{23}$$

$$\frac{\partial c_m}{\partial z} = 0, \quad @ \quad z = 1 \tag{24}$$

$$\langle c \rangle = \langle c_0 \rangle, \quad @ \quad t = 0 \tag{25}$$

We shall refer to this model (Eqs. 21–25) as the *two-mode axial dispersion model*.

Tubular reactors

Equations 21–25 give the two-mode model for tubular reactors. In the limit of no macromixing present in the reactor, that is, $Pe \to \infty$, the two-mode models under steady-state conditions simplify to

$$\frac{dc_m}{dz} = -Dar(\langle c \rangle), \quad \text{with } c_m(z = 0) = c_{m,\text{in}} \tag{26}$$

$$c_m - \langle c \rangle = -\beta_1 p \frac{\partial \langle c \rangle}{\partial z} = -\beta_1 p \frac{\partial c_m}{\partial z} + O(p^2) = \beta_1 \phi^2 r(\langle c \rangle) + O(p^2) \tag{27}$$

We shall refer to this model as the *two-mode convection model*. In dimensional form, it is given by

$$\frac{dC_m}{d\tau} = -R(\langle C \rangle), \quad \text{with } C_m(\tau = 0) = C_{m,\text{in}} \tag{28}$$

$$C_m - \langle C \rangle = t_{\text{mix}} R(\langle C \rangle) \tag{29}$$

where τ is the residence time in the reactor ($= x/\langle u_x \rangle$) and t_{mix} is the local mixing time of the system, and is given by

$$t_{\text{mix}} = \beta_1 t_D = \beta_1 \frac{a^2}{D_m} \tag{30}$$

The local mixing time t_{mix} depends on local variables, such as the local diffusion time t_D (which in turn depends on the local diffusional length scale, a, and the species molecular diffusivity, D_m) and the local velocity fluctuations u' (which determines β_1). The coefficient β_1 could be analytically evaluated using the L–S technique for the case of any well-defined flow fields; for example β_1 is 1/48 for fully developed laminar flow in pipes, while for plain Poiseuille and Couette flows, β_1 is 2/105 and 1/30, respectively. For the case of developing flow fields, these local quantities (β_1 and t_D) vary along the length of the reactor, and t_{mix} is, therefore, a function of the residence time τ as well as fluid viscosity. It can be noted that in the limit of complete micromixing, that is, $t_{\text{mix}} \to 0$, the two-mode convection model reduces to the ideal plug-flow reactor model.

The extension of the two-mode axial dispersion model to the case of fully developed turbulent flow in a pipe could be achieved by starting with the time-smoothed (Reynolds-averaged) CDR equation, given by Eq. 4, where the reaction-rate term $R(C)$ in Eq. 4 is replaced by the Reynolds-averaged reaction-rate term, $R_{\text{av}}(C)$, and the molecular diffusivity, D_m, is replaced by the effective diffusivity, D_e, in turbulent flows given by

$$D_e = D_m + D_T \tag{31}$$

where D_T is the turbulent diffusivity, which can be obtained on the basis of turbulent shear stress and expressed in terms of Reynolds number, using a formula similar to that presented by Wen and Fan (1975). Also, the Reynolds-averaged reaction rate, $R_{\text{av}}(c)$, could be evaluated by using the simple closure models of Bourne and Toor (1977), Brodkey and Lewalle (1985), Li and Toor (1986), Dutta and Tarbell (1989), and so on. We skip the details of these methods, since the closure of the Reynolds-averaged transport equation is not the focus of this article. It should also be pointed out that the

spatial averaging presented here is independent of the methodology by which $R_{av}(c)$ and D_T are evaluated, or in other words, *spatial averaging follows time averaging.*

We use a universal velocity distribution obtained by Churchill (2001) to approximate the fully developed velocity profile $u(\xi)$ across the turbulent core, given by

$$u(\xi)=\sqrt{\frac{f}{2}}\left(5.5+2.5\ln\left[(1-\xi)Re\sqrt{\frac{f}{8}}\right]+\frac{15}{4}(1-\xi)^2-\frac{10}{3}(1-\xi)^3\right) \quad (32)$$

where f is the Fanning friction factor and Re is the Reynolds number. The important result is that the two-mode models for a turbulent-flow tubular reactor are the same as those for laminar-flow tubular reactors. The two-mode axial-dispersion model for turbulent-flow tubular reactors is again given by Eqs. 21–25, while the two-mode convection model for the same reactors is given by Eqs. 28–29, where the reaction-rate term $r(\langle c\rangle)$ is replaced by the Reynolds-averaged reaction-rate term, $r_{av}(\langle c\rangle)$. The local mixing time t_{mix} for turbulent flows is given by

$$t_{mix}=\beta_1\frac{a^2}{D_m+D_T} \quad (33)$$

where β_1 is given by

$$\beta_1=0.1f\left(2.05+2.5\ln\left[Re\sqrt{\frac{f}{8}}\right]-\sqrt{\frac{2}{f}}\right) \quad (34)$$

We note that in turbulent flows, typically $D_m \ll D_T$, as a result of which the local mixing time, t_{mix} is *practically* independent of the molecular diffusivity or the molecular Schmidt number.

Loop and recycle reactors

In this section, we present the two-mode models for loop and recycle reactors. In a steady-state loop reactor of loop length, L, a flow rate of q_{in} with an average velocity of $\langle u_{in}\rangle$ enters and leaves the reactor at points $x=0$ and $x=l$, respectively (where x is the length coordinate along the loop), and the total flow rate in the loop is $Q+q_{in}$ between points $x=0$ and $x=l$, and is Q between points $x=l$ and $x=L$, due to a recycle rate of Q. The recycle ratio Λ is the ratio of the volume of fluid returned to the reactor entrance per unit time to the volume of fluid leaving the system per unit time, and is given by $\Lambda=Q/q_{in}$. The two-mode model for a loop reactor is

$$\langle u_{in}\rangle\frac{dC_m}{dx}=\begin{cases}-\dfrac{1}{1+\Lambda}R(\langle C\rangle), & 0\le x<l\\ -\dfrac{1}{\Lambda}R(\langle C\rangle), & l\le x\le L\end{cases} \quad (35)$$

$$C_m-\langle C\rangle=t_{mix}R(\langle C\rangle), \qquad 0\le x<L \quad (36)$$

with the boundary conditions

$$C_m(x=0)=\frac{C_{m,in}+\Lambda C_m(x=L)}{1+\Lambda} \quad (37)$$

$$\langle C\rangle(x=l^-)=\langle C\rangle(x=l^+) \quad (38)$$

For the special case when no reaction occurs between $x=l$ and $x=L$, that is, $C_m(x=l)=C_m(x=L)$, the loop reactor reduces to a recycle reactor of length l, the two-mode model for which is given by

$$\langle u_{in}\rangle\frac{dC_m}{dx}=-\frac{1}{1+\Lambda}R(\langle C\rangle) \quad (39)$$

$$C_m-\langle C\rangle=t_{mix}R(\langle C\rangle), \quad 0\le x<l \quad (40)$$

with the boundary condition

$$C_m(x=0)=\frac{C_{m,in}+\Lambda C_m(x=l)}{1+\Lambda} \quad (41)$$

The two-mode loop and recycle-reactor models, like the two-mode axial-dispersion model, are two-parameter, two-mode models. Here, the two parameters are the recycle ratio, Λ, and the local mixing time, t_{mix}, which describe macro- and micromixing effects in the system, respectively.

Tank reactors (CSTRs)

It is well known that as the recycle ratio Λ of a recycle reactor is increased, the behavior shifts from a PFR at $\Lambda=0$ (no macromixing) to a CSTR at $\Lambda=\infty$ (perfect macromixing). We use this idea to obtain the two-mode model for a perfectly macromixed CSTR, by integrating Eq. 39 along the length of the reactor x and simplifying the resulting equation for $\Lambda\gg1$. This gives the two-mode model for a CSTR as

$$\frac{C_m-\langle C\rangle}{t_{mix}}=\frac{C_{m,in}-C_m}{\tau_C} \quad (42)$$

$$C_m-\langle C\rangle=t_{mix}R(\langle C\rangle) \quad (43)$$

where τ_C $(=V/q_{in})$ is the total residence time in the reactor and t_{mix} is the characteristic local mixing time. Equations 42 and 43, which are the global and local equations, respectively, constitute a two-mode one-parameter model for a perfectly macromixed CSTR. Micromixing effects are captured through the local mixing time, t_{mix}, and in the limit of complete micromixing (that is, $t_{mix}\to0$), it reduces to the ideal one-mode zero-parameter CSTR model. The unsteady-state form of Eqs. 42 and 43 is given by

$$\frac{d\langle C\rangle}{dt'}=\frac{C_m-\langle C\rangle}{t_{mix}}-R(\langle C\rangle), \text{ with } \langle C\rangle(t'=0)=C_0 \quad (44)$$

$$\frac{C_m-\langle C\rangle}{t_{mix}}=\frac{C_{m,in}-C_m}{\tau_C} \quad (45)$$

Physical Interpretation of Two-Mode Models. Using the example of a tank reactor, we present a physical interpretation of the two-mode models. The physical system equivalent to the two-mode model of a CSTR is a tank reactor consisting of two zones, each of size V, namely, a nonreacting steady convection zone (A), represented by C_m, and a reaction zone (B), represented by $\langle C \rangle$. The interaction between zones A and B is quantified by an exchange of reactants and products at a rate of q_E from the convection scale (zone A) to the reaction–diffusion scale (zone B). This exchange of material between zones A and B occurs only through local diffusion, and $t_{\text{mix}}(=V/q_E)$, which is the characteristic time scale for this exchange, therefore, depends on the local diffusion time of the system. Equations 44 and 45 represent the material balances for zone B and zone A, respectively.

In general, any infinitesimal volume dV inside the tank could be so imagined to consist of two zones/scales, and a corresponding two-mode model could be written (Eqs. 42 and 43) for a CSTR of volume dV. If macromixing in the CSTR is complete, the two-mode model for any control volume dV could be integrated over the entire volume of the tank V to generate a single two-mode model (Eqs. 42 and 43) for the whole tank.

However, macromixing effects often are not negligible in real tanks, and are influenced by several factors, including the type and speed of impellers (turbines) and the manner of feed distribution. Macromixing effects in tanks often have been modeled by using compartment models in the mixing literature (Baldyga and Bourne, 1992). The two-compartment model, for example, divides the tank into two compartments, namely, the circulation zone and the impeller zone, which are then modeled as two interacting CSTRs, with macromixing being described as an exchange of material at rate Q_E between the compartments. We can use this two-compartment model (or n-compartment model) to describe macromixing, with each compartment itself being described by a two-mode model that accounts for micromixing. The resulting model is a two-mode, two-compartment model that describes both macro- and micromixing effects in tanks. Similarly, any other traditional macromixing model (such as, recycle model, tanks-in-series model, exchange-with-stagnant-zone model) for tank reactors could be suitably coupled with the two-mode model to describe both macro- and micromixing in tanks. However, if micromixing effects are dominant as compared to macromixing ones, it could be shown that by using L–S reduction in finite dimensions, the two-mode two-compartment model is reducible to a two-mode model for tanks (Eqs. 44 and 45), where the local mixing time t_{mix} is replaced by an effective mixing time t_M, which captures both macro- and micromixing effects. This effective mixing time, t_M, now not only depends on the local diffusion time and local shear rates but also intricately on the tank geometry, type, and number of impellers, baffle positions, and power dissipation in the system. Therefore, only an experimental estimation of t_M is possible. This issue has been addressed in detail elsewhere.

Extension to multiple reactions

The two-mode models for different types of homogeneous reactors for the case of multiple reactions could also be obtained by averaging the vectorial form of the convective–diffusion equation (Eq. 1) using the L–S technique. The dimensional forms of the global evolution equations for multiple reactions are summarized below:

for tubular reactors

$$\frac{d\boldsymbol{C}_m}{d\tau} = -\boldsymbol{R}(\langle \boldsymbol{C} \rangle) \text{ with } \boldsymbol{C}_m(\tau = 0) = \boldsymbol{C}_{m,\text{in}} \tag{46}$$

for tubular reactors with recycle

$$(1+\Lambda)\frac{d\boldsymbol{C}_m}{d\tau} = -\boldsymbol{R}(\langle \boldsymbol{C} \rangle) \text{ with } \boldsymbol{C}_m(\tau = 0) = \frac{\boldsymbol{C}_{m,\text{in}} + \Lambda \boldsymbol{C}_{m,e}}{1+\Lambda} \tag{47}$$

for CSTRs

$$\frac{\boldsymbol{C}_m - \boldsymbol{C}_{m,\text{in}}}{\tau_C} = -\boldsymbol{R}(\langle \boldsymbol{C} \rangle) \tag{48}$$

where Λ is the recycle ratio and τ is the residence time in the reactor ($= x/\langle u_x \rangle$).

The dimensional form of the local equation, which is the same in form for all the four reactor types, is

$$\boldsymbol{C}_m - \langle \boldsymbol{C} \rangle = \boldsymbol{T}_{\text{mix}} \boldsymbol{R}(\langle \boldsymbol{C} \rangle) \tag{49}$$

where $\boldsymbol{T}_{\text{mix}}$ is an $n \times n$ matrix of characteristic local mixing times given by $\boldsymbol{T}_{\text{mix}} = t_{\text{mix}}[\mathbb{D}(\langle \boldsymbol{c} \rangle)]^{-1}$, $\mathbb{D}(\langle \boldsymbol{c} \rangle)$ is the matrix of relative molecular/effective diffusivities (which could depend on the species concentrations), and n is the number of species involved. For turbulent flows, where the local mixing times are practically independent of molecular Schmidt numbers, $\mathbb{D} = \mathbb{I}$ (identity matrix).

Similarity Between Two-Mode Models and Two-Phase Models

A striking structural similarity exists between the two-mode models for homogeneous reactors and two-phase models for heterogeneous catalytic reactors. This can be seen more clearly when Eqs. 28 and 29 are rewritten as

$$\langle u_x \rangle \frac{dC_m}{dx} = -\frac{C_m - \langle C \rangle}{t_{\text{mix}}} = -R(\langle C \rangle), \quad \text{with } C_m = C_{m,\text{in}} \quad @ \quad x = 0 \tag{50}$$

The two-phase model for a heterogeneous wall-catalyzed reaction in a tubular reactor is given by

$$\langle u_x \rangle \frac{dC_m}{dx} = -\frac{C_m - C_S}{t_{TP}} = -R(C_s), \quad \text{with } C_m = C_{m,\text{in}} \quad @ \quad x = 0 \tag{51}$$

It can be noticed that the spatially averaged concentration $\langle C \rangle$ of the TMM (in Eq. 50) is replaced by the surface (wall) concentration C_S in the two-phase model (Eq. 51), while the local mixing time t_{mix} of the TMM is replaced in the two-phase model by a characteristic mass transfer time between

the two phases, t_{TP}, which is given by

$$t_{TP} = \beta_{TP} t_D = \frac{1}{Sh_\infty} \frac{a^2}{D_m} \tag{52}$$

where t_D is the transverse diffusion time scale, and β_{TP} and Sh_∞ are the two-phase transfer coefficient and the asymptotic Sherwood number, respectively, that depend on the velocity profile and tube geometry. For the case of fully developed laminar flow in a circular tube, $Sh_\infty = 1/\beta_{TP} = 48/11 = 4.36$ while its analog in the TMM (comparing Eqs. 30 and 52) is $1/\beta_1 = 48$, where β_1 is the exchange coefficient in the TMMs.

The L–S technique not only gives us the low-dimenisonal models but also allows us to specify the region of validity of these reduced models in the parameter space. This is achieved by solving for the local equation (Eq. 14) to higher orders in p by using Eqs. 15 and 16 and examining the radius of convergence of the local equation, which is now an infinite series in p. The radius of convergence of the local equation specifies the region of applicability of the two-mode models. This methodology has been illustrated elsewhere (Chakraborty and Balakotaiah, 2002) using the example of the two-mode convection model (that is, $Pe \to \infty$) for a laminar-flow tubular reactor with a first-order reaction, the region of validity of which was obtained as

$$kt_{\text{mix}} = Da_{\text{loc}} < 0.858 \tag{53}$$

where k is the first-order rate constant, t_{mix} is the local mixing time, and their product Da_{loc} is the local Damköhler number, the ratio of local mixing time to reaction time. A similar convergence test for the case of tank reactors ($Pe = 0$) shows that the terms in the local equation, when arranged in ascending order of p, change sign alternately (with a finite ratio), thus, guaranteeing convergence for all values of p. As a result, the TMM for a tank reactor remains qualitatively correct for all values of the local Damköhler number, Da_{loc}, and local mixing time, t_{mix}. The same is true for the case of TMMs with any finite Peclet number ($0 \le Pe < \infty$) or recycle ratio ($0 \le (1/\Lambda) < \infty$).

This characteristic of the two-mode models finds an exact analogy in the two-phase models. It has been shown (Gupta and Balakotaiah, 2001) that while for the case of $Pe \to \infty$, the Sherwood number (Sh) obtained using a two-phase convection model diverges as $p \to \infty$ (entry region), it remains finite and bounded for all values of p if the Peclet number is finite ($0 \le Pe < \infty$). A justification of such behavior may be provided by examining the two-dimensional two-phase model with a flat velocity profile and first-order reaction, for the limiting case of $Pe = 0$. An analytical expression of the Sherwood number could be obtained for this case in terms of the transverse Peclet number p, and is given by

$$\frac{1}{Sh} = \beta_{TP} = \frac{I_0\left(\sqrt{p}\right)}{2\sqrt{p}\, I_1\left(\sqrt{p}\right)} - \frac{1}{p} \tag{54}$$

The two-phase transfer coefficient β_{TP} in Eq. 54, when expanded in a series in p, consists of alternate positive and negative terms as

$$\beta_{TP} = \frac{1}{8} - \frac{p}{192} + \frac{p^2}{3{,}072} - \frac{p^3}{46{,}080} + \frac{13}{8{,}847{,}360} p^4 - \ldots,$$

and is convergent for all values of p. As mentioned before, this was also observed to be the case when the convergence of the TMM for $Pe = 0$ was examined using the L–S technique. Thus, for the case of any finite Peclet number ($0 \le Pe < \infty$) or recycled ratio ($0 \le (1/\Lambda) < \infty$), the two-mode models, like the two-phase models, remain qualitatively correct for all values of local Damköhler number and local mixing time.

It will be illustrated with examples in the following section, that just as the two-phase models can capture the mass-transfer-limited asymptote in heterogeneous reactions (which is missed by the pseudohomogeneous models), so can the two-mode models capture the mixing-limited asymptote in homogeneous reactions, which is rendered inaccessible by the traditional one-mode models. Thus, there exists the following one-to-one correspondence between two-phase models of catalytic reactors and two-mode models of homogeneous reactors: two-phase transfer time (t_{TP}) → local mixing time (t_{mix}); two-phase transfer coefficeint (β_{TP}) → exchange coefficient (β_1); surface (wall) concentration C_S → spatially averaged concentration $\langle C \rangle$; mass-transfer-limited reaction → mixing-limited reaction. Also, the two-mode models have a range of applicability similar to that of the two-phase models.

Applications of Two-Mode Models

Single nth order reaction

For the case of an nth order reaction of the type

$$A \xrightarrow{k} B, \quad \text{with rate} = k(C_A)^n, \quad n > 0$$

the steady-state global evolution equations for two-mode convection model and two-mode CSTR model are given by

$$\frac{dC_{A,m}}{d\tau} = -k\langle C_A \rangle^n$$

$$\frac{C_{A,m} - C_{A,m,\text{in}}}{\tau_C} = -k\langle C_A \rangle^n$$

respectively, while the local equation is given by

$$C_{A,m} - \langle C_A \rangle = t_{\text{mix}} k \langle C_A \rangle^n$$

For the case of $n = 1$, the exit conversion

$$X\left(= \frac{C_{A,m,\text{in}} - C_{A,m}}{C_{A,m,\text{in}}} \right)$$

is given by:

for tubular reactors

$$X = 1 - \exp\left[\frac{-k\tau_C}{1 + kt_{\text{mix}}}\right] = 1 - \exp\left[\frac{-Da}{1 + \eta Da}\right] \tag{55}$$

for CSTRs

$$X = \frac{k\tau_C}{(1 + kt_{\text{mix}}) + k\tau_C} = \frac{Da}{1 + (1+\eta)Da} \tag{56}$$

where Da $(= k\tau_C)$ is the Damköhler number and η $(= t_{\text{mix}}/\tau_C)$ is the dimensionless mixing time.

For the case of $n = 2$ (in a CSTR), the exit conversion X is given by

$$X = 1 - \left\{ \frac{\sqrt{4Da(1+\eta)+1} + 2Da\eta(1+\eta) - 1}{2Da(1+\eta)^2} \right\} \tag{57}$$

where Da $(= k\tau_C C_{A,\text{in}})$.

For the case of $n = 1/2$ (in a CSTR), the exit conversion X is given by

$$X = 0.5Da\left[\sqrt{Da^2(1+\eta)^2 + 4} - Da(1+\eta)\right] \tag{58}$$

It should be mentioned that all single nth-order reactions attain the same mixing limited asymptote for $\eta > 0$ and $Da \to \infty$. For the case of a tubular reactor, this asymptote is given by

$$X = 1 - \exp\left[-\frac{1}{\eta}\right] \tag{59}$$

while for the case of a CSTR, it is given by

$$X = \frac{1}{1+\eta} \tag{60}$$

Figure 1 shows the conversion (X) for a single reaction with first-, second- and half-order kinetics in a CSTR for two different cases of $\eta = 0$ (complete local mixing) and $\eta = 1$. For all cases, the conversions attain the mixing-limited asymptote just given (Eq. 60) irrespective of the reaction kinetics.

In the limit of complete local mixing ($t_{\text{mix}} \to 0$), the TMMs for tubular reactors and CSTRs reduce to classic ideal reactor models and the exit conversions predicted by Eqs. 55 and 56 in the asymptotic limit of $\eta \to 0$ are the same as those predicted by the ideal PFR and the ideal CSTR models, respectively (and are independent of η), that is:

for tubular reactors

$$\eta \to 0, \quad X = 1 - \exp\left[-Da\right]$$

for CSTRs

$$\eta \to 0, \quad X = \frac{Da}{1+Da}$$

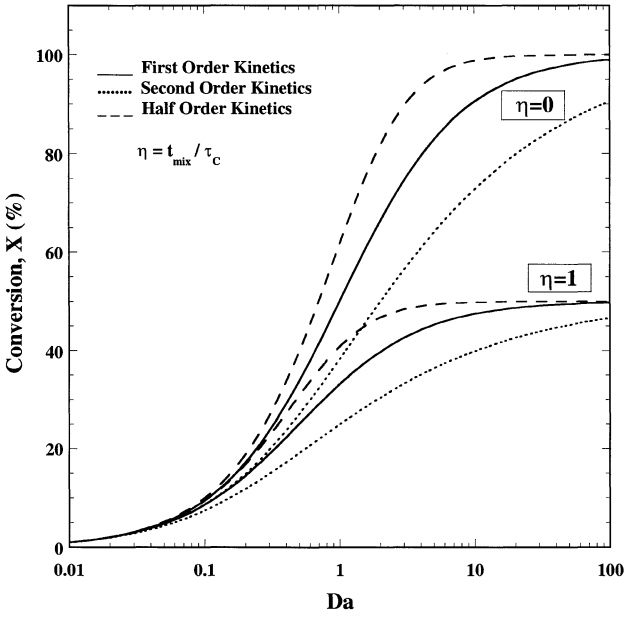

Figure 1. Variation of exit conversion with Damköhler number, *Da*, for a single *n*th-order reaction in a CSTR, for $\eta = 0$ (perfect micromixing) and $\eta = 1$.

In the other asymptotic limit of $t_{\text{mix}} \to \infty$, the TMMs for both the tubular reactor (Eq. 55) and the CSTR (Eq. 56) predict the same exit conversion, as

$$\eta \to \infty, \quad X \to \frac{1}{\eta}$$

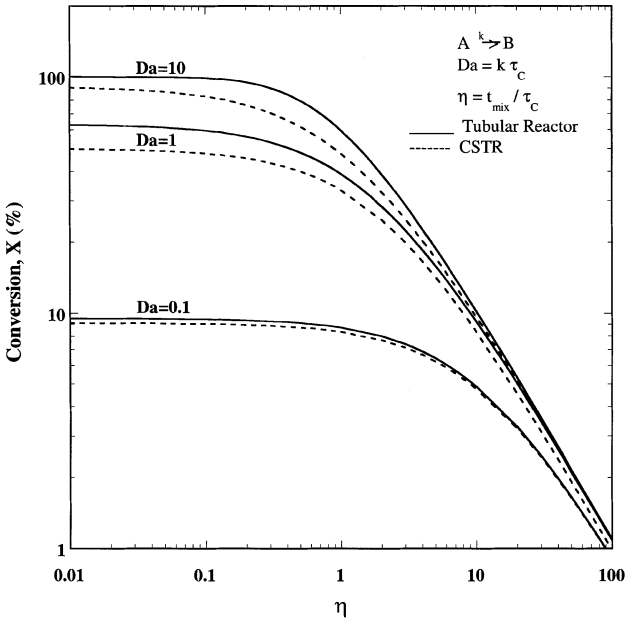

Figure 2. Variation of conversion with dimensionless local mixing time, η, for single first-order reaction in a CSTR.

Figure 2 shows the variation of the exit conversion for a first-order reaction in a tubular reactor and a CSTR, with the dimensionless mixing time η, and the attainment of the two asymptotes for $\eta \to 0$ and $\eta \to \infty$.

First-order reactions in series

It is well known that mixing affects the yields of intermediate products in series reactions, even if the kinetics is linear. We illustrate this with the example of first-order reactions in series of the type

$$A \xrightarrow{k_1} P \xrightarrow{k_2} X$$

occurring in a CSTR, and the reaction rates of A and P being given by

$$R_A = k_1\langle C_A\rangle$$
$$R_P = -k_1\langle C_A\rangle + k_2\langle C_P\rangle$$

The two-mode model equations for this system are given by

$$C_{A,m} - C_{A,\text{in}} = -Da\langle C_A\rangle \tag{61}$$
$$C_{A,m} - \langle C_A\rangle = \eta Da\langle C_A\rangle \tag{62}$$
$$C_{P,m} - C_{P,\text{in}} = -Da\left[-\langle C_A\rangle + \frac{k_2}{k_1}\langle C_P\rangle\right] \tag{63}$$
$$C_{P,m} - \langle C_P\rangle = \eta Da\left[-\langle C_A\rangle + \frac{k_2}{k_1}\langle C_P\rangle\right] \tag{64}$$

where $Da(=k_1\tau_C)$ is the Damköhler number and $\eta(=t_{\text{mix}}/\tau_C)$ is the dimensionless mixing time. The yield of P (for the case of $C_{P,\text{in}}=0$) is given by

$$\frac{C_{P,m}}{C_{A,\text{in}}} = \frac{Da}{\left[1+Da\frac{k_2}{k_1}(1+\eta)\right]\left[1+Da(1+\eta)\right]}$$

Figure 3 shows (for the case of $k_1 = 10k_2$) how the TMM (Eqs. 61–64) predicts the decreasing yield of the intermediate product, P, with increasing local mixing limitations (that is, increasing values of η) in the system.

As seen in Figure 3, the optimal yield of P occurs at a Da given by

$$Da|_{\text{opt}} = \frac{1}{(1+\eta)\sqrt{k_2/k_1}}$$

and the optimal yield of P is

$$\left.\frac{C_{P,m}}{C_{A,\text{in}}}\right|_{\text{opt}} = \frac{1}{1+\eta}\cdot\frac{1}{\left(1+\sqrt{k_2/k_1}\right)^2}$$

Figure 4 shows how the optimum yield of P varies with micromixing limitations in the system, for different values of k_2/k_1.

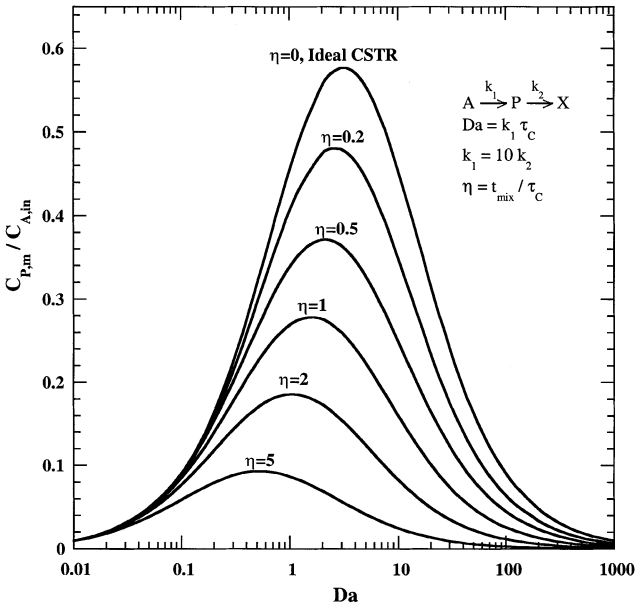

Figure 3. Variation of yield of intermediate product with dimensionless local mixing time, η, for the case of first-order reactions occurring in series.

The preceding analysis could be generalized very easily to the case of an arbitrary number of first-order reactions. For the case of a CSTR, the exit concentration vector is then given by

$$\boldsymbol{C}_m = \left[\boldsymbol{I} + \tau_C \boldsymbol{K}_m\right]^{-1}\boldsymbol{C}_{m,\text{in}} \tag{65}$$

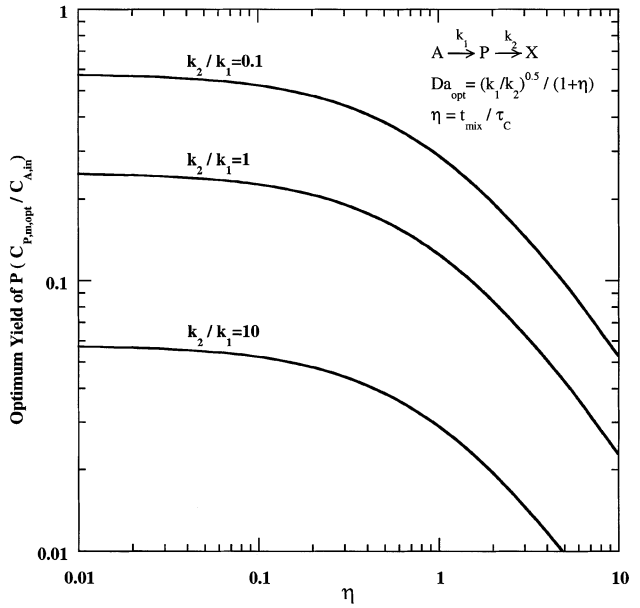

Figure 4. Variation of optimum yield of intermediate product with dimensionless local mixing time, η, for the case of first-order reactions occurring in series, for different values of reaction rate constants.

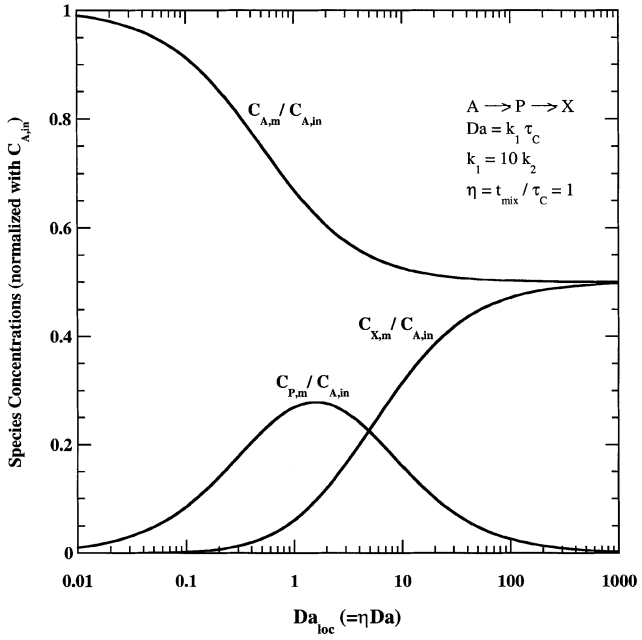

Figure 5. Variation of reactant and product concentration with local Damköhler number, Da_{loc} ($=\eta Da$), for the case of first-order reactions occurring in series.

while for the case of a tubular reactor, the same is given by

$$\boldsymbol{C}_m = \exp\left[-\tau_C \boldsymbol{K}_m\right]\boldsymbol{C}_{m,\text{in}}, \tag{66}$$

where $\boldsymbol{K}_m$ is the mixing-disguised rate-constant matrix, and is given by

$$\boldsymbol{K}_m = \boldsymbol{K}\left(\boldsymbol{I} + t_{\text{mix}}\mathbb{D}^{-1}\boldsymbol{K}\right)^{-1} \tag{67}$$

where $\boldsymbol{K}$ is the matrix of true rate constants and $\mathbb{D}$ is the matrix of relative diffusivities. It can be noted from the preceding equations that in the limit of local mixing control, only a very small percentage of the initial reactant is converted to the final product, and no intermediates are left unreacted. Figure 5 illustrates this well.

Bimolecular second-order reactions

Second-order reactions provide the simplest example of nonlinear kinetics where micromixing limitations have significant effects on reactant conversion. We use the TMM to determine the same for a typical bimolecular second-order reaction of the type

$$A + B \xrightarrow{k} P, \quad \text{with rate} = kC_AC_B$$

occurring in a CSTR. In terms of the Damköhler number $Da(=kC_{A,\text{in}}\tau_C)$ and the dimensionless mixing times $\eta_A(=t_{A,\text{mix}}/\tau_C)$ and $\eta_B(=t_{B,\text{mix}}/\tau_C)$, the balance equations obtained by using the TMM for a CSTR are

$$C_{A,m} - C_{A,\text{in}} = -\frac{Da}{C_{A,\text{in}}}\langle C_A\rangle\langle C_B\rangle \tag{68}$$

$$C_{A,m} - \langle C_A\rangle = \eta_A\frac{Da}{C_{A,\text{in}}}\langle C_A\rangle\langle C_B\rangle \tag{69}$$

$$C_{B,m} - C_{B,\text{in}} = -\frac{Da}{C_{A,\text{in}}}\langle C_A\rangle\langle C_B\rangle \tag{70}$$

$$C_{B,m} - \langle C_B\rangle = \eta_B\frac{Da}{C_{A,\text{in}}}\langle C_A\rangle\langle C_B\rangle \tag{71}$$

For the case of stoichiometric feed ($C_{A,\text{in}} = C_{B,\text{in}} = C_{\text{in}}$) and equal mixing times ($\eta_A = \eta_B$), the conversion (X) is given by Eq. 57. In the limiting case of "maximum mixedness" ($\eta = 0$), it reduces to the ideal CSTR limit given by

$$X = 1 - \left\{\frac{\sqrt{4Da+1}-1}{2Da}\right\} \tag{72}$$

In the limit of "total segregation," that is, $\eta > 0$ and $Da \to \infty$, such that $\eta Da = Da_{\text{loc}} \to \infty$ (infinitely fast reaction), the local concentrations approach zero ($\langle C_A\rangle = \langle C_B\rangle = 0$), while the mixing-cup concentrations approach the mixing-limited asymptote of

$$\frac{C_{Am}}{C_{\text{in}}} = \frac{\eta}{1+\eta}; \quad \frac{C_{Bm}}{C_{\text{in}}} = \frac{\eta}{1+\eta}; \quad X = \frac{C_{Pm}}{C_{\text{in}}} = \frac{1}{1+\eta} \tag{73}$$

Figure 6 illustrates how the conversion (X) varies with the Damköhler number Da for different values of the dimensionless mixing time, η, for the case of stoichiometric feeding of reactants. The attainment of the mixing-limited asymptote is also shown.

As mentioned in the section on the similarity between the two-mode and two-phase models, this mixing-limited asymptote for homogeneous reactions is analogous to the mass-transfer limited asymptote for wall-catalyzed reactions. Just as the wall (surface) concentrations approach zero for the case of infinitely fast surface reactions (while the bulk/mixing-cup concentrations remain finite), so do the local concentrations $\langle C_i\rangle$ for infinitely fast homogeneous reactions ($i = A,B$). Unlike in catalytic reactors, where the exchange between the phases occurs at the solid–fluid boundary, the exchange between modes (scales) in homogeneous reactors occurs in the entire domain.

The case of nonidentical mixing times ($\eta_A \neq \eta_B$) is also captured conveniently by the TMM, in which case, the conversion (for the case of stoichiometric feed, that is, $C_{A,\text{in}} = C_{B,\text{in}}$) is given by

$$X = 1 - \left\{\frac{\sqrt{(1+4Da)\kappa^2 + 2\eta_A Da\kappa(\kappa+1) + \left[\eta_A Da\kappa(\kappa-1)\right]^2} + \eta_A Da(2\eta_A + \kappa + 1) - \kappa}{2Da(1+\eta_A)(\kappa+\eta_A)}\right\}$$

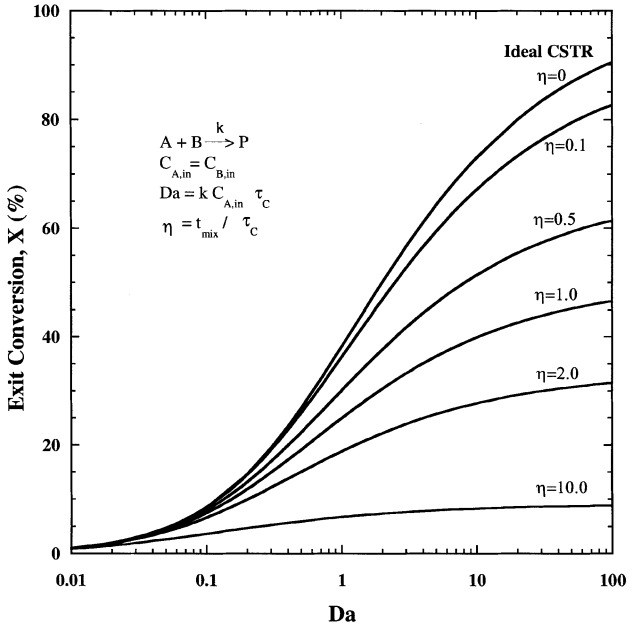

Figure 6. Variation of exit conversion with Damköhler number, *Da*, for a second-order reaction in a CSTR, for different values of dimensionless local mixing time, η.

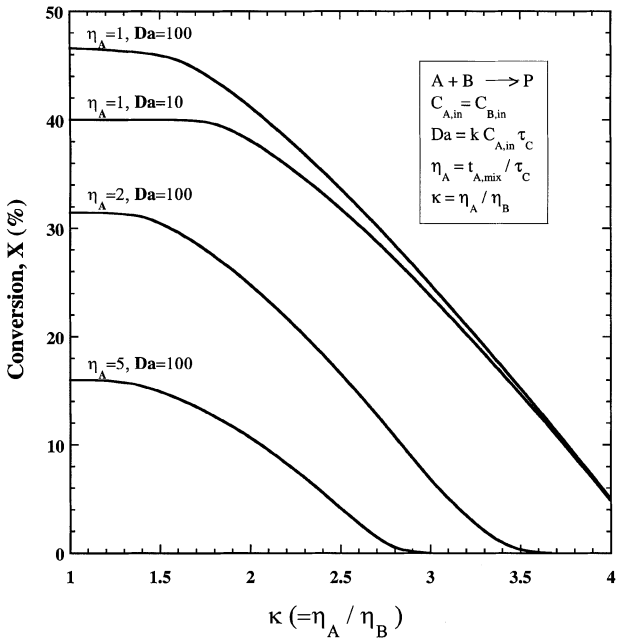

Figure 7. Effect of difference in local mixing times of species *A* and *B* on conversion for a second-order biomolecular reaction occurring in a CSTR.

where the ratio of the two mixng times is $\kappa(=\eta_A/\eta_B)$. Figure 7 shows that a difference in the two mixing times by a factor of 4 leads to a large decrease in the reactant conversion X.

Multiple reactions

The advantage of TMMs is best seen in the case of multiple reactions with nonlinear kinetics. While the solution of the CDR equation requires elaborate and expensive numerical schemes (especially for large Schmidt numbers and when a large number of species are involved), the TMMs require only a numerical effort comparable to that of the classic ideal reactor models. Calculations confirm that the solution of the TMMs is in excellent agreement with the solution of the CDR equation (Chakraborty and Balakotaiah, 2002). In this section, we use two examples to show how the TMMs bring forth the local mixing effects on product yields in multiple reactions, even in the case of infinitely fast kinetics.

Reactions of the Type $A \xrightarrow{k_1} B \xrightarrow{k_2} C,\ A + C \xrightarrow{k_3} D$. An example of practical interest is the class of organic reactions leading to Durene formation, which is given by

$$\text{Methanol} \rightarrow \text{Olefins} \rightarrow \text{Aromatics} + \text{Paraffins},$$
$$\text{Aromatics} + \text{Methanol} \rightarrow \text{Durene}$$

A symbolic representation of this (and many other similar) reaction(s) is

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C,$$
$$A + C \xrightarrow{k_3} D$$

If D is desirable, it has been shown that a CSTR is recommended instead of a PFR (Shinnar, 1986). We use the TMM to study the effects of micromixing limitations in a CSTR on the formation of D. The balance equations are obtained using the TMMs for multiple reactions (Eqs. 48 and 49), which on simplification, give

$$C_{A,m} - C_{A,\text{in}} = -DaR_A \tag{74}$$

$$C_{A,m} - \langle C_A \rangle = \eta DaR_A \tag{75}$$

$$C_{B,m} - C_{B,\text{in}} = -DaR_B \tag{76}$$

$$C_{B,m} - \langle C_B \rangle = \eta DaR_B \tag{77}$$

$$C_{C,m} - C_{C,\text{in}} = -DaR_C \tag{78}$$

$$C_{C,m} - \langle C_C \rangle = \eta DaR_C \tag{79}$$

where

$$R_A = \langle C_A \rangle + \frac{k_3}{k_1}\langle C_A \rangle \langle C_C \rangle \tag{80}$$

$$R_B = -\langle C_A \rangle + \frac{k_2}{k_1}\langle C_B \rangle \tag{81}$$

$$R_C = -\frac{k_2}{k_1}\langle C_B \rangle + \frac{k_3}{k_1}\langle C_A \rangle \langle C_C \rangle \tag{82}$$

$$R_D = -\frac{k_3}{k_1}\langle C_A\rangle\langle C_C\rangle \tag{83}$$

and $Da = k_1\tau_C$ and $\eta = t_{\text{mix}}/\tau_C$. The exit mixing-cup concentration of D is obtained as

$$C_{D,m} - C_{D,\text{in}} = -DaR_D \tag{84}$$

An analytical solution of the preceding set of equations is possible. For the case of $C_{B,\text{in}} = C_{C,\text{in}} = C_{D,\text{in}} = 0$, it is given by

$$\frac{\langle C_A\rangle}{C_{A,\text{in}}} = \frac{1}{2b}\left\{\sqrt{\left[(1+\eta)Da\left(1-\frac{k_3}{k_1}\right)+1\right]^2+4b} - \left[(1+\eta)Da\left(1-\frac{k_3}{k_1}\right)+1\right],\right\}$$

$$b = (1+\eta)Da\frac{k_3}{k_1}\left[\frac{(1+\eta)^2Da^2(k_2/k_1)}{1+(1+\eta)Da(k_2/k_1)}+1\right],$$

$$\langle C_C\rangle = \frac{(1+\eta)^2Da^2(k_2/k_1)\langle C_A\rangle}{\left[1+(1+\eta)Da(k_3/k_1)\langle C_A\rangle\right]\left[1+(1+\eta)Da(k_2/k_1)\right]},$$

$$C_{D,m} = Da\frac{k_3}{k_1}\langle C_A\rangle\langle C_C\rangle \tag{85}$$

For the case of mixing-limited fast reactions ($\eta > 1$, $Da \gg 1$), the exit concentration of D is given by the asymptotic limit of the preceding equation (Eq. 85)

$$\frac{C_{D,m}}{C_{A,\text{in}}} = \left(\frac{k_3C_{A,\text{in}}}{k_1 + k_3C_{A,\text{in}}}\right)\frac{1}{1+\eta} \tag{86}$$

Figure 8 illustrates these results (Eq. 85) and the attainment of the mixing-limited asymptote (Eq. 86), which depends only on the characteristic local mixing time of the system (η), for the case of $k_1 = k_2 = 10k_3C_{A,\text{in}}$. It shows that increased mixing limitations in the tank result in decreased yield of D, and minimal mixing limitations in the CSTR, are, therefore, preferable for the maximum yield of D.

Reactions of the Type $A + B \xrightarrow{k_1} C$, $B + C \xrightarrow{k_2} D$. Competitive–consecutive reactions of the type

$$A + B \xrightarrow{k_1} C,$$
$$B + C \xrightarrow{k_2} D$$

are the prototype of many multistep reactions, such as, nitration of benzene and toluene, diazo coupling, and bromination reactions. Experimental observations (Li and Toor, 1986) show that if the first reaction is infinitely fast as compared to the second one (that is, $k_1/k_2 \to \infty$), under perfectly mixed conditions B is completely consumed by the first reaction and the yield of D is zero (if A and B are fed in stoichiometric amounts). However, it was observed that if the mixing of A and B is not attained down to the molecular scale, the first

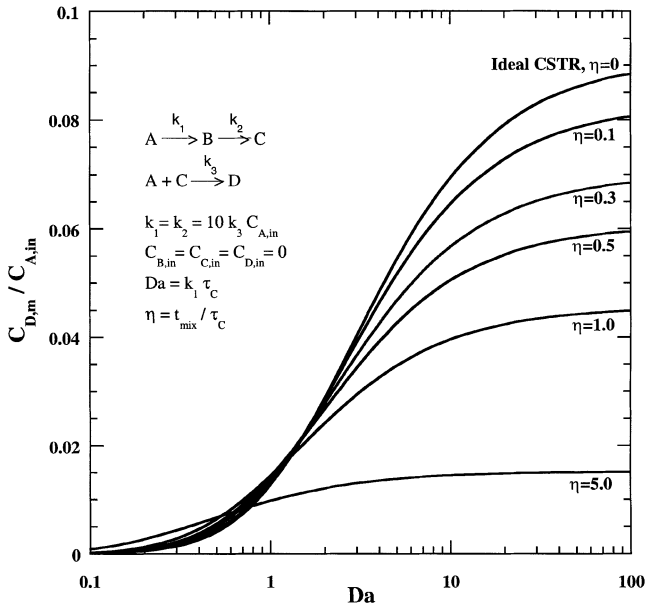

Figure 8. Variation of concentration of *D* with *Da* (Damköhler number) for multiple reactions of the type $A \to B \to C$, $A + C \to D$, occurring in a CSTR, for different values of dimensionless local mixing time, η.

reaction is not complete and there remains a local excess of B, which can then react with C to produce D. The yield of D increases monotonically as the reaction rate of the second reaction increases, finally attaining a mixing-limited asymptote.

We use the TMM for a CSTR to verify this observation. If A and B are fed in stoichiometric amounts ($C_{B,\text{in}} = C_{A,\text{in}} = C_{\text{in}}$), the local excess of B that remains after the first reaction attains its mixing-limited asymptote (in the limit of $Da_1 = k_1C_{\text{in}}\tau_C \to \infty$) is obtained from Eq. 73 as

$$\frac{C^1_{Bm}}{C_{\text{in}}} = \frac{\eta}{1+\eta}$$

while the amount of C formed from the first reaction is given by

$$\frac{C^1_{Cm}}{C_{\text{in}}} = \frac{1}{1+\eta}$$

where η is the dimensionless mixing time of the system. The second reaction is then simply a bimolecular second-order reaction between B and C. The resultant yield of D is given by Y_D, where

$$Y_D = \frac{2C_{Dm}}{C_{Cm}+2C_{Dm}} \tag{87}$$

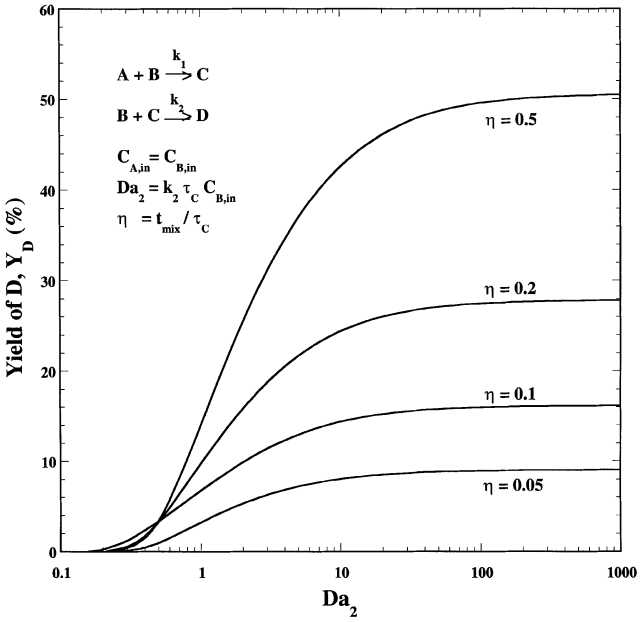

Figure 9. Variation of the yield of *D* with Damköhler number for a competitive–consecutive reaction scheme $A + B \rightarrow C$, $B + C \rightarrow D$, when the first reaction is infinitely fast, for different values of the dimensionless local mixing time, η.

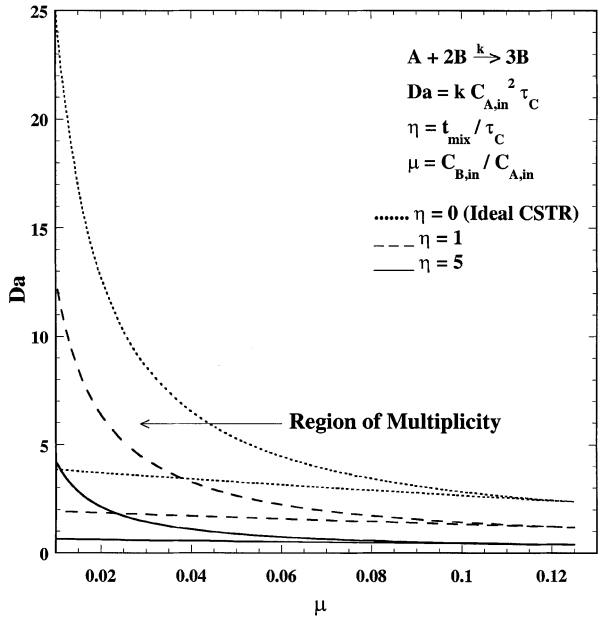

Figure 10. Bifurcation set showing the region of multiple solutions in the parameter space of *Da* and μ, for different values of local mixing times, η, for an autocatalytic reaction occurring in a CSTR (with mixing times of all species being identical).

and C_{Cm} and C_{Dm} are the exit concentrations in a CSTR in which only the second reaction occurs with feed concentrations of C^1_{Bm} and C^1_{Cm}. Figure 9 shows the increase in the yield of D with Da_2, the Damköhler number of the second reaction, given by $Da_2 = k_2 C_{\text{in}} \tau_C$, for the case when the first reaction is infinitely fast and A and B are fed in stoichiometric amounts (that is, $C_{B,\text{in}} = C_{A,\text{in}} = C_{\text{in}}$ and $C_{C,\text{in}} = C_{D,\text{in}} = 0$). While no D is formed for the case of $\eta = 0$ (ideal CSTR), a significant increase in yield of D is obtained if finite micromixing limitations are present in the system. The maximum yield of D, obtained when the mixing-limited asymptote is attained also for the second reaction, is

$$Y_{D,\max} = \begin{cases} \dfrac{2\eta}{1+2\eta}, & \text{for} \quad \eta \le 1 \\ \dfrac{2}{1+2\eta}, & \text{for} \quad \eta > 1 \end{cases} \tag{88}$$

Thus, in this case, an optimal yield of D exists, and is obtained for $\eta = 1$, the reason for which is intuitively obvious.

Autocatalytic reactions

Mixing effects on bifurcation features of isothermal autocatalytic reactions have attracted attention before (Kumpinsky and Epstein, 1985). We examine the same effects by using the TMM for the case of an activator–deactivator-type kinetics given by

$$A + 2B \xrightarrow{k} 3B$$

with the reaction rate of the disappearance of A and B being given by

$$R_A = -R_B = k\langle C_A\rangle\langle C_B\rangle^2$$

where A is the deactivator, B is the activator, and k is the rate constant. The TMM for a CSTR written for the preceding reaction kinetics is given by

$$C_{A,m} - C_{A,\text{in}} = -\frac{Da}{C^2_{A,\text{in}}} R_A \tag{89}$$

$$C_{A,m} - \langle C_A\rangle = \eta_A \frac{Da}{C^2_{A,\text{in}}} R_A \tag{90}$$

$$C_{B,m} - C_{B,\text{in}} = -\frac{Da}{C^2_{A,\text{in}}} R_B \tag{91}$$

$$C_{B,m} - \langle C_B\rangle = \eta_B \frac{Da}{C^2_{A,\text{in}}} R_B \tag{92}$$

where $Da = kC^2_{A,\text{in}}\tau_C$; η_A and η_B are the dimensionless mixing times of A and B, given by $\eta_A = t_{A\text{mix}}/\tau_C$ and $\eta_B = t_{B\text{mix}}/\tau_C$, respectively; and $\mu = C_{B,\text{in}}/C_{A,\text{in}}$.

Figure 10 shows the bifurcation set (region of three solutions) in the (Da,μ) space for different values of η (for the case where the mixing times of A and B are equal, that is, $\eta_A = \eta_B = \eta$), obtained by solving the preceding set of equations (Eqs. 89–92). For any Da and μ that lie within the curve, there exist three distinct solutions of the exit conversion of A (or B), while for points lying outside the curve

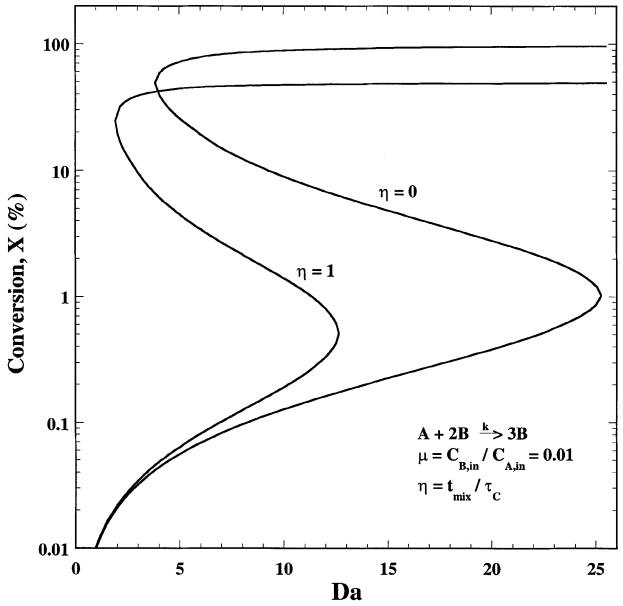

Figure 11. Bifurcation diagram of exit conversion *X* vs. Damköhler number, *Da*, for an autocatalytic reaction occurring in a CSTR (with mixing times of all species being identical).

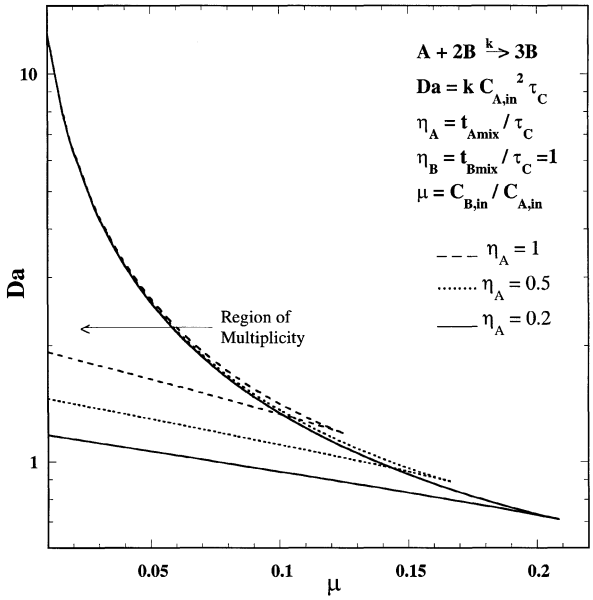

Figure 12. Bifurcation set showing the region of multiple solutions in the parameter space of *Da* and μ, for different values of local mixing time of species *A*, η_A, for an autocatalytic reaction occurring in a CSTR (with mixing times of the species being nonidentical).

there exists only one solution for the exit conversion. It can be seen that the region of multiplicity shrinks, as mixing limitations in the system (that is, the dimensionless mixing time η) increases. However, the multiplicity region exists for any finitely large value of η, and vanishes only for the case of segregated flow ($\eta \to \infty$).

Figure 11 presents a typical bifurcation diagram of the exit conversion (X), with the Damköhler number, Da, as a bifurcation parameter, for the case of $\mu = 0.01$ and two different values of η. It can be noted that the exit conversion X on the ignited branch decreases by a factor of 2 as η increases from 0 to 1.

Interestingly, the TMMs capture the effects of mixing limitations for the case of nonidentical mixing times (that is, $\eta_A \neq \eta_B$) almost as easily as in the case of equal mixing times. Figure 12 presents the bifurcation set in the (Da, μ) space for different values of η_A and for a fixed value of η_B ($= 1$). The region of multiplicity expands as η_A decreases (for $\eta_A < \eta_B$). Figure 13 shows the bifurcation diagram of the exit conversion X with the Damköhler number, Da, as the bifurcation parameter for the case of $\mu = 0.01$ and two different values of η_A. The exit conversion X on the ignited branch increases by a factor of 1.7 as η_A decreases from 1 to 0.2.

Conclusions

In the hierarchy of homogeneous reactor models, the classical ideal reactor models stand at one end as the simplest, while the generalized convective–diffusion–reaction (CDR) model stands at the other end as the most detailed one. While the former cannot capture micromixing effects on reactions, the latter requires expensive numerical schemes, especially for large Schmidt and/Damköhler numbers, and for multiple reactions with a large number of species. The two-mode models (TMMs) proposed here bridge the gap between the two extreme cases of reactor models and provide a practical approach for describing mixing effects on reactor perfor-

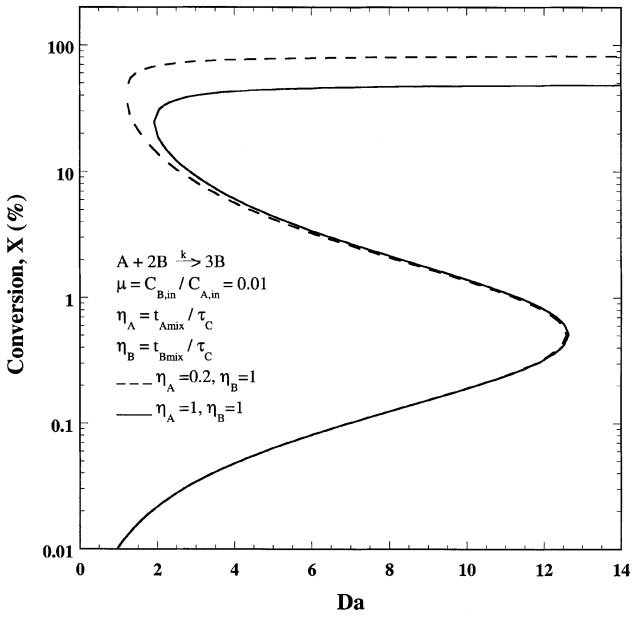

Figure 13. Bifurcation diagram of exit conversion *X* vs. Damköhler number, *Da*, for an autocatalytic reaction occurring in a CSTR (with mixing times of the species being nonidentical).

mance. They retain all the parameters present in the full CDR model, and, therefore, all the qualitative features of the latter, and yet, their solution requires a numerical effort comparable to that of the ideal reactor models.

The two-mode models describe micromixing in homogeneous reactions as an effective exchange between the global (convection) and the local (reaction–diffusion) scales, represented here by the mixing-cup concentration and the spatially averaged concentrations, respectively. This exchange is characterized by a local mixing time, which depends on the local diffusional time and the local shear rates. It has been shown that the two-mode models can predict micromixing effects on bifurcation features in the case of autocatalytic kinetics, capture effects of differences in species diffusivities and nonuniform reactant feeding on conversion, and predict mixing-limited asymptotes in nonlinear reactions. The TMMs can also be easily extended to the case of nonisothermal reactions.

As discussed earlier, there exists a striking analogy between the two-mode mode models of homogeneous reactors and two-phase models of catalytic reactors. This analogy can be carried further by noting that for all cases of well-defined flow-fields, where two-phase mass-transfer coefficients can be estimated theoretically, we can also estimate the exchange coefficient (β_1) or the local mixing time (t_{mix}) of the TMMs. For more complex flow fields (such as, packed bed), the local mixing time, like the mass-transfer coefficient, could be correlated to *Re*, *Sc*, and the geometrical characteristics of the system. Thus, the *two-mode models of homogeneous reactors are as general as the two-phase models of catalytic reactors, and have a similar range of applicability.*

To summarize, the two-mode models are the *minimal models* that provide a low-dimensional description of micromixing, by coupling the interaction between chemical reaction, diffusion, and velocity gradients at the local scales to the macroscale reactor variables (such as, mixing-cup concentration, flow rate, and reactor size or residence time). Due to their simplicity and generality, it is hoped that they will find applications in the preliminary design and optimization of homogeneous chemical reactors.

Acknowledgments

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Notation

a = radius of the tube
$C(c)$ = reactant (dimensionless) concentration
$\mathbb{D}$ = relative (normalized) molecular diffusivity matrix
Da = Damköhler number
Da_{loc} = local Damköhler number
D_e = effective diffusity in turbulent flow
D_m = molecular diffusivity
D_T = turbulent diffusivity
f = friction factor
k = reaction rate constant
$\boldsymbol{K}$ = reaction rate constant matrix (in multiple reactions)
$\boldsymbol{K}_{\mathrm{mix}}$ = mixing-disguised rate-constant matrix (in multiple reactions)
L = length of the reactor
p = transverse Peclet number
Pe = axial Peclet number
Q = volumetric flow rate of recycle
q_{in} = volumetric flow rate of reactants
R = rate of reaction (dimensional)
t = time
u_x = velocity
X = conversion
x = coordinate along the length of the reactor (dimensional)
Y = yield
z = dimensionless coordinate along the length of the reactor

Greek letters

β = exchange coefficient
η = dimensionless local mixing time (t_{mix}/τ_C)
θ = azimuthal coordinate
κ = ratio of molecular diffusivities of B and A (in bimolecular reactions)
Λ = recycle ratio
μ = feeding ratio of B to A (in autocatalytic reactions)
ξ = dimensionless radial coordinate
τ = residence time in the reactor
τ_C = total residence time in the reactor/characteristic convection time
ϕ^2 = Thiele modulus or local Damköhler number

Subscripts and superscripts

D = transverse diffusion
m = mixing cup
mix = local mixing
R = reaction
Z = axial diffusion
$\langle \cdot \rangle$ = transverse averaged

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