

# A Novel Approach for Describing Micromixing Effects in Homogeneous Reactors

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## I. Introduction

Reacting flow systems are hierarchical in nature, i.e. they are characterized by multiple length (or time) scales. However, scale separation exists in most reactors, and these disparate scales are typically characterized by three representative ones, namely, micro (molecular), meso (catalyst particle or tube diameter) and macro (reactor or process) scales. In most cases of practical interest, a strong non-linear coupling exists between reaction and transport at micro and meso scales, and the reactor performance at the macro scale. As a result, transport limitations at the smaller scales influence the reactor and hence the process performance significantly. Such effects could be quantified by numerically solving the convection-diffusion-reaction (CDR) equation from the macro down to the micro scale. However, the solution of the CDR equation from the reactor (macro) scale down to the local diffusional (micro) scale using computational fluid dynamics (CFD) is prohibitive in terms of numerical effort, and impractical for the purpose of reactor control and optimization. Moreover, even with the present day computational power, it is impractical to explore the different types of bifurcation features and spatio-temporal behaviors that exist in the multi-dimensional parameter space, using CFD codes. In such cases, low dimensional models are a natural alternative.

Historically, chemical engineers have derived low dimensional models for reactors using a top-down approach, which is based on *a priori* assumptions on the length and time scales of convection, diffusion and reaction. The classical ideal reactor (CSTR and PFR) models are examples of such low-dimensional models obtained on the basis of simplified (or rather over-simplified) assumptions. These assumptions are usually not justified since justification requires comparison of the solution obtained from the simplified models with that obtained from the CDR model. In order to account for experimental observations which could not be explained by these ideal reactor models, the latter have been modified by introducing the concepts of dispersion coefficients (Langmuir, 1908; Damköhler, 1937; Danckwerts, 1953; Taylor, 1956; Aris, 1959) and residence time distribution (Förster & Geib, 1934; Danckwerts, 1953; Zwietering, 1959) to account for macro- and micro-mixing effects. Several other reactive mixing models have followed in the next forty years – Two- & Three-environment Model (Ng & Rippin, 1965; Miyawaki et al, 1975), Coalescence-redispersion model (Harada, 1962), Interaction by exchange with mean model (Villermoux & Devillon, 1972), Engulfment-deformation-diffusion model (Baldyga & Bourne, 1984), and CFD models using probability density functions (PDF) and direct numerical simulation (DNS).

This article presents an alternative (bottom-up) approach and an elementary treatment of mixing effects on reactor performance. We present a brief historical review of homogeneous reactor models before discussing this new approach.

## II. Brief History of Homogeneous Reactor Models

The most widely used homogeneous reactor models are the three classical ideal reactor models, namely the plug-flow reactor (PFR) model, the continuous stirred tank reactor (CSTR) model, and the batch reactor (BR) model. While the BR model and the PFR model (which are identical for constant density systems with time replaced by space time or dimensionless distance along the tube) have existed since the late eighteenth century, a conceptual leap came in the form of the CSTR model through the work of Bodenstein and Wohlgast in 1908. Unlike the PFR model, which assumes no gradients in the radial direction and no mixing in the axial direction, the CSTR model assumes complete mixing at all scales. For constant density systems, the three classical reactor models are described by the equations:

$$\text{PFR: } \langle u \rangle \frac{d\langle C \rangle}{dx} = -R(\langle C \rangle) \text{ with } \langle C \rangle = C_{in} @ x = 0, \quad (1)$$

$$\text{BR: } \frac{d\langle C \rangle}{dt} = -R(\langle C \rangle) \text{ with } \langle C \rangle = C_{in} @ t = 0, \quad (2)$$

$$\text{CSTR: } \frac{\langle C \rangle - C_{in}}{\tau_C} = -R(\langle C \rangle), \quad (3)$$

where  $\langle C \rangle$  is the spatially (or cross-sectional) averaged reactant concentration,  $C_{in}$  is the mean inlet concentration of the reactant,  $R(\langle C \rangle)$  is the sink term due to the presence of homogeneous reaction,  $x$  is the coordinate along the length of the PFR,  $\langle u \rangle$  is the mean fluid velocity in the reactor,  $t$  is the time, and  $\tau_C$  is the total residence time of the reactor.

Irving Langmuir (1908) first replaced the assumption of no axial mixing of the PFR model with finite axial mixing and the accompanying Dirichlet boundary condition ( $\langle C \rangle = C_{in} @ x = 0$ ) by a flux type boundary condition:

$$D_m \frac{d\langle C \rangle}{dx} = \langle u \rangle [\langle C \rangle - C_{in}] @ x = 0, \quad (4)$$

where  $D_m$  is the molecular diffusivity of the species. The above boundary condition was rediscovered several times later: first by Förster and Geib (1934), which was quoted and

applied by Damköhler (1937); and then finally by Danckwerts (1953); and it has since then been known as ‘Danckwerts’ boundary condition’. In this paper, Langmuir dealt with both the limiting cases of “mixing nearly complete” and “only slight mixing”.

Thirty years later, Gerhard Damköhler (1937) in his historic paper, summarized various reactor models and formulated the two-dimensional CDR model for tubular reactors in complete generality, allowing for finite mixing both in the radial and axial directions. In this paper, Damköhler used the flux type boundary condition at the inlet and also replaced the assumption of plug flow with parabolic velocity profile, which is typical of laminar flow in tubes.

Förster and Geib (1934) first introduced the concept of residence time distribution (RTD) to study the case of longitudinal dispersion in tubes. Twenty years later, Danckwerts (1953) in his much celebrated paper devised a generalised treatment of RTD and introduced the concepts of “hold-back” and “segregation”. Following this, it was Zweitering (1959) who quantified the degrees of mixing with the ideas of “complete segregation” and “maximum mixedness” and brought forth the concept of *micromixing* or mixing at the molecular scale in homogeneous reactions.

In the last forty years, a wide range of micromixing models for homogeneous reactors have been formulated. While most of these low-dimensional mixing models are phenomenological in nature, the rigorously derived CFD models are high-dimensional and therefore numerically very expensive, especially for the case of multiple reactions with fast/ non-isothermal kinetics. As a result, in spite of the simplifying assumptions present, the century-old ideal classical reactor models (Eqns. 1–3) are still the most popular choices amongst chemical engineering practitioners (and teachers). The classical ideal reactor models, which are easy-to-solve ordinary differential or algebraic equations with no adjustable parameter, are particularly preferred to the full CDR models (which are partial differential equations in more than one dimension) in case of multiple reactions with complex kinetics.

### III. Spatial Averaging of Convection-Diffusion-Reaction equation

The main goal of this article is to illustrate a new approach for deriving low-dimensional homogeneous reactor models, capable of predicting mixing effects. These models are derived through rigorous spatial averaging of the three-dimensional CDR equations over local length scales by using the *Liapunov-Schmidt (L-S) technique* of classical bifurcation theory. We

illustrate this spatial averaging technique using the simple case of laminar flow in a tube with homogeneous reaction. The scalar concentration  $C(r, \theta, x, t')$  in a tubular reactor is assumed to obey the CDR equation

$$\frac{\partial C}{\partial t'} + u(r) \frac{\partial C}{\partial x} = \frac{1}{r} \frac{\partial}{\partial r} \left( D_{\perp} r \frac{\partial C}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \theta} \left( D_{\perp} \frac{\partial C}{\partial \theta} \right) + \frac{\partial}{\partial x} \left( D_x \frac{\partial C}{\partial x} \right) - R(C), \quad (5)$$

with accompanying initial and boundary conditions, given by

$$\begin{aligned} C(r, \theta, x, t' = 0) &= C_0; \quad \frac{\partial C}{\partial r} = 0 @ r = a; \quad C(r, \theta, x, t') = C(r, \theta + 2\pi, x, t'); \\ D_x \frac{\partial C}{\partial x} &= u(r)[C(r, \theta, x, t') - C_{in}] @ x = 0; \quad \frac{\partial C}{\partial x} = 0 @ x = L, \end{aligned} \quad (6)$$

where  $D_{\perp}$  and  $D_x$  are the transverse and axial diffusivities, respectively,  $r, \theta, x$  are the radial, azimuthal and axial coordinates, respectively, and  $u(r)$  is the fluid velocity profile. We take  $a$  (radius of the pipe) and  $L$  (length of the pipe) to be the characteristic lengths in the radial and axial directions respectively,  $\langle u \rangle$  is the cross-sectional average velocity and  $C_R$  is a reference concentration. Then, we obtain four time-scales in the system associated with convection ( $\tau_C$ ), radial diffusion ( $t_D$ ), axial diffusion ( $t_X$ ) and reaction ( $t_R$ ):

$$t_D = \frac{a^2}{D_{\perp}}, \quad t_X = \frac{L^2}{D_x}, \quad \tau_C = \frac{L}{\langle u \rangle}, \quad t_R = \frac{C_R}{R(C_R)}, \quad (7)$$

and the ratios of these time scales give rise to the dimensionless parameters:  $p$  (transverse Peclet number),  $Pe$  (axial Peclet number),  $Da$  (Damköhler number) and  $\phi^2$  (local Damköhler number), given by

$$p = \frac{a^2 \langle u \rangle}{L D_{\perp}} = \frac{t_D}{\tau_C}, \quad Pe = \frac{\langle u \rangle L}{D_x} = \frac{t_X}{\tau_C}, \quad Da = \frac{L R(C_R)}{\langle u \rangle C_R} = \frac{\tau_C}{t_R}, \quad \phi^2 = \frac{a^2 R(C_R)}{D_x C_R} = \frac{t_D}{t_R} = p Da.$$

In dimensionless form, eqn (5) for the case of constant species diffusivities, may be rearranged as

$$\nabla_{\perp}^2 c = \frac{1}{\xi} \frac{\partial}{\partial \xi} \left( \xi \frac{\partial c}{\partial \xi} \right) + \frac{1}{\xi^2} \left( \frac{\partial^2 c}{\partial \theta^2} \right) = p \left[ \frac{\partial c}{\partial t} - \frac{1}{Pe} \frac{\partial^2 c}{\partial z^2} + u(\xi) \frac{\partial c}{\partial z} + Da \hat{r}(c) \right] \triangleq p g(c), \quad (8)$$

with initial and boundary conditions being given by

$$\begin{aligned} c(\xi, \theta, z, t = 0) &= c_0; \quad \frac{\partial c}{\partial \xi} = 0 @ \xi = 1; \quad c(\xi, \theta, z, t) = c(\xi, \theta + 2\pi, z, t), \\ \frac{1}{Pe} \frac{\partial c}{\partial z} &= u(\xi) [c - c_{in}] @ z = 0; \quad \frac{\partial c}{\partial z} = 0 @ z = 1, \end{aligned} \quad (9)$$

where

$$t = \frac{t'}{\tau_C}, \quad \xi = \frac{r}{a}, \quad z = \frac{x}{L}, \quad u = \frac{u}{\langle u \rangle}, \quad c = \frac{C}{C_R}, \quad \widehat{r}(c) = \frac{R(C)}{R(C_R)}. \quad (10)$$

The form of the CDR equation (eqn. 8) clearly illustrates that a scale separation exists in the system, with  $p$  being the ratio of the local to the global scale (when  $Pe$  and  $Da$  are of order unity), and spatial averaging over the local scales is possible. It could be seen from eqn. (8–9) that in the limit of  $p \rightarrow 0$ ,  $\nabla_{\perp}^2 c \rightarrow 0$  and transverse (or small scale) concentration gradients vanish, in which case the equations simplify to the classical one mode axial dispersion model. If local diffusion time is small but finite compared to convection, reaction and axial diffusion time, local (transverse) gradients remain small and we can write

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

where  $\langle c \rangle$  is the transverse averaged concentration and  $c'$  is the fluctuation about this average, and  $c' \rightarrow 0$  as  $p \rightarrow 0$ . [Also, by definition,  $\langle c' \rangle = 0$ .] Multiplying eqn. (11) by the local velocity profile,  $u(\xi) = \langle u \rangle + u'$ , and averaging over the cross-section gives

$$c_m = \langle c \rangle + \langle u'c' \rangle, \quad (12)$$

where  $c_m$  is the mixing-cup (velocity weighted) concentration. Similarly, transverse averaging of eqn.(8) over the cross-section gives

$$\frac{\partial \langle c \rangle}{\partial t} - \frac{1}{Pe} \frac{\partial^2 \langle c \rangle}{\partial z^2} + \frac{\partial c_m}{\partial z} + Da \int_{\xi=0}^{\xi=1} \int_{\theta=0}^{\theta=2\pi} \xi \widehat{r}(c) d\theta d\xi = 0. \quad (13)$$

For the case of a tubular reactor, the spatial (transverse) average and mixing-cup concentrations are defined by

$$\langle c \rangle = \frac{\int_{\xi=0}^{\xi=1} \int_{\theta=0}^{\theta=2\pi} \xi c(\xi, \theta, x, t) d\theta d\xi}{\int_{\xi=0}^{\xi=1} \int_{\theta=0}^{\theta=2\pi} \xi d\theta d\xi}, \quad (14)$$

$$c_m = \frac{\int_{\xi=0}^{\xi=1} \int_{\theta=0}^{\theta=2\pi} \xi u(\xi) c(\xi, \theta, x, t) d\theta d\xi}{\int_{\xi=0}^{\xi=1} \int_{\theta=0}^{\theta=2\pi} \xi u(\xi) d\theta d\xi}. \quad (15)$$

[It may be noted that in all flow reactors  $c_m$  is the experimentally measured variable.] We refer to  $\langle c \rangle$  and  $c_m$  as the *two modes* of the system and our spatially averaged reactor models as *Two-Mode Models (TMMs)*. Equation (13) is called the *global equation*, while eqn. (12) is called the *local equation*. The local equation shows 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 captured by the local equation as an exchange between the two modes (scales),  $c_m$  and  $\langle c \rangle$ .

In order to determine  $c'$  (and hence the term  $\langle u'c' \rangle$  or the difference between  $c_m$  and  $\langle c \rangle$ ), we substitute eqn. (11) in eqn. (8) to obtain

$$\nabla_{\perp}^2 c' = p g (\langle c \rangle + c'). \quad (16)$$

The L-S technique solves eqn. (16) for  $c'$  by expanding it in the parameter  $p$  as

$$c' = \sum_{i=1}^n p^i c_i, \quad (17)$$

and by using the Fredholm Alternative (i.e. the fact  $c'$  lies in the function space orthogonal to which  $\langle c \rangle$  resides). Such an expansion (eqn. 17) is possible, since for  $p = 0$ , the transverse diffusion operator in eqn. (8) has a zero eigenvalue with a constant eigenfunction. Thus,  $\langle u'c' \rangle$  could be determined to any order in  $p$ , i.e. closure of the local equation could be accomplished to any desired of accuracy. In practice, the leading term (that is of order  $p$ ) is sufficient to retain all the qualitative features of the full CDR equation. For example, for the case of azimuthally symmetric feeding, we have

$$c' = -p \frac{\partial \langle c \rangle}{\partial z} \left[ \frac{1}{12} - \frac{\xi^2}{4} + \frac{\xi^4}{8} \right] + O(p^2). \quad (18)$$

Substituting eqn. (18) in eqns. (12–13) gives the two-mode model to  $O(p)$  as

$$\frac{\partial \langle c \rangle}{\partial t} + \frac{\partial c_m}{\partial z} - \frac{1}{Pe} \frac{\partial^2 \langle c \rangle}{\partial z^2} + Da r(\langle c \rangle) + O(p^2) = 0, \quad (19)$$

$$\begin{aligned} \langle c \rangle - c_m &= \beta_1 p \frac{\partial \langle c \rangle}{\partial z} + O(p^2), \\ &= \beta_1 p \frac{\partial c_m}{\partial z} + O(p^2), \end{aligned} \quad (20)$$

with boundary and initial conditions given by

$$\frac{1}{Pe} \frac{\partial \langle c \rangle}{\partial z} = c_m - c_{m,in}, \quad @ z = 0, \quad (21)$$

$$\frac{\partial c_m}{\partial z} = 0, \quad @ z = 1, \quad (22)$$

$$\langle c \rangle = \langle c_0 \rangle, \quad @ t = 0, \quad (23)$$

where  $1/\beta_1$  is called the *exchange coefficient*, which depends on the local shear rates. For the case of fully developed laminar flows,  $D_{\perp} = D_x = D_m$  (molecular diffusivity of the species),

and  $\beta_1 = 1/48$ . We refer to this model as the *two-mode axial dispersion model*. (Further details of the spatial averaging procedure using L-S technique can be found in Chakraborty & Balakotaiah, 2002a, 2002b).

It may be noted that the spatially averaged CDR equation (eqns. 19–20) retains all the parameters ( $p$ ,  $Pe$ ,  $Da$ ) of the three-dimensional CDR equation (eqn. 8) and hence all the qualitative features of the latter. It should also be mentioned that *this model is capable of capturing macromixing effects through the axial Peclet number  $Pe$  in the global equation (eqn. 19), as well micromixing effects through the exchange coefficient  $\beta_1^{-1}$  and transverse Peclet number  $p$  in the local equation (eqn. 20)*. In fact, the L-S technique guarantees that the solution of the averaged model (eqns. 19–23) agrees with the exact solution of the three-dimensional CDR equation to  $O(p)$ . [Three decimal accuracy is obtained for a second order reaction for the case of  $Pe \rightarrow \infty$ , if  $\phi^2 < 1$ , see Chakraborty & Balakotaiah, 2002a.]

Using the spatial averaging technique illustrated above, accurate low-dimensional models could be obtained for different types of reactors and flow profiles. For example, the two-mode model for a tubular reactor with fully developed turbulent flow is same as eqns. (19–23), where  $D_{\perp}$  is the effective turbulent diffusivity and  $\beta_1$  is a function of Reynolds number ( $Re$ ) and friction factor  $f$ . This model is obtained by starting with the time-smoothed (Reynolds averaged) CDR equation, where the reaction rate  $R(C)$  in eqn.(5) is replaced by the Reynolds averaged reaction rate (after closure)  $R_{av}(C)$ . Spatial averaging by L-S technique is then performed on the time averaged CDR equation (i.e. spatial averaging follows time averaging) to obtain the two-mode model. (Please refer to Chakraborty & Balakotaiah, 2002b for details.) In the next section, we present the two-mode models for other types of homogenous reactors.

## IV. Two-Mode Models for Homogeneous Reactors

### A. Tubular Reactors

The steady state two mode model for a tubular reactor for the case of  $Pe \rightarrow \infty$  (i.e. no macromixing present) may be obtained from eqns. (19–21). In dimensional form, it is given by

$$\langle u \rangle \frac{dC_m}{dx} = -R(\langle C \rangle) \text{ with } C_m(x=0) = C_{m,in}, \quad (24)$$

$$C_m - \langle C \rangle = -t_{mix} \langle u \rangle \frac{dC_m}{dx} = t_{mix} R(\langle C \rangle), \quad (25)$$



where the local mixing time  $t_{mix}$  (in the local equation 25 describing micromixing effects) is given by

$$t_{mix} = \beta_1 \frac{a^2}{D_\perp}, \quad (26)$$

$a$  is the local diffusional length scale over which spatial averaging is performed,  $D_\perp$  is the local diffusion coefficient and  $\beta_1^{-1}$  is the exchange coefficient. In the limit of complete micromixing (i.e.  $t_{mix} \rightarrow 0$ ), the two-mode convection model reduces to the ideal one-mode zero-parameter PFR model.

## B. Loop and Recycle Reactors

In a 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). 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  $\Lambda$  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 such a loop reactor may be obtained as

$$\langle u_{in} \rangle \frac{dC_m}{dx} = \begin{cases} -\frac{1}{1+\Lambda} R(\langle C \rangle), & 0 \leq x < l, \\ -\frac{1}{\Lambda} R(\langle C \rangle), & l \leq x \leq L, \end{cases} \quad (27)$$

$$C_m - \langle C \rangle = t_{mix} R(\langle C \rangle), \quad 0 \leq x < L, \quad (28)$$

with the boundary conditions

$$C_m(x=0) = \frac{C_{m,in} + \Lambda C_m(x=L)}{1 + \Lambda}; \quad \langle C \rangle(x=l^-) = \langle C \rangle(x=l^+); \quad (29)$$

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

$$\langle u_{in} \rangle \frac{dC_m}{dx} = -\frac{1}{1+\Lambda} R(\langle C \rangle), \quad \text{with } C_m(x=0) = \frac{C_{m,in} + \Lambda C_m(x=l)}{1 + \Lambda} \quad (30)$$

$$C_m - \langle C \rangle = t_{mix} R(\langle C \rangle), \quad 0 \leq x < l, \quad (31)$$

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  $\Lambda$ , and the local mixing time  $t_{mix}$ , which describe macro- and micro-mixing effects in the system, respectively.

### C. Tank Reactors (CSTRs)

It is well known that as the recycle ratio  $\Lambda$  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 eqn. (30) along the length of the reactor  $x$  and simplifying the resulting equation for  $\Lambda \gg 1$ . This gives the two-mode model for a perfectly macromixed CSTR as

$$\frac{C_m - \langle C \rangle}{t_{mix}} = \frac{C_{m,in} - C_m}{\tau_C}, \quad (32)$$

$$C_m - \langle C \rangle = t_{mix} R(\langle C \rangle), \quad (33)$$

where  $\tau_C (= V/q_{in})$  is the total residence time in the reactor and  $t_{mix}$  is the characteristic local mixing time, which captures micromixing effects. In the limit of complete micromixing (i.e.  $t_{mix} \rightarrow 0$ ), the TMM for a CSTR reduces to the ideal one-mode zero-parameter CSTR model.

It should be pointed out that *the local equation (eqns. 25, 28, 31, 33) is the same for all reactor types*. This is an important observation, which shows that scale separation exists in all types of homogeneous reactors.

### V. 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 non-reacting convection zone ( $A$ ), represented by  $C_m$ , and a reaction zone ( $B$ ), represented by  $\langle C \rangle$ . Thus,  $C_m$  is representative of the convection scale of the system and  $\langle C \rangle$  is representative of the reaction scale of the system. The interaction between the two scales (or the two zones  $A$  and  $B$ ) is quantified by an exchange of materials at a rate of  $q_E$ . This exchange occurs only through local diffusion, and  $t_{mix} (= V/q_E)$ , which is the characteristic time scale for this exchange, therefore depends on the local shear rate and diffusion coefficient. Equations (32) and (33) represent the steady state 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 (eqns. 32–33) for the volume  $dV$ . If macromixing in the tank is complete, the two-mode model for any

control volume  $dV$  could be integrated over the entire volume of the tank to generate a single two-mode model (eqns. 32–33) for the whole tank.

However, macromixing effects are often 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. Several macromixing models are available in the literature, e.g. the two-compartment model, recycle model, tanks-in-series model, exchange-with-stagnant-zone model, any of which could be suitably coupled with the TMM to describe both macro- and micro-mixing in tanks. However, if micromixing effects are dominant as compared to macromixing ones (as in well stirred tanks), it could be shown by using *L-S reduction in finite dimensions*, that these models (i.e. the two-mode  $n$ -compartment model, etc.) could be reduced to eqns. 32–33, where the local mixing time  $t_{mix}$  is replaced by an effective mixing time  $t_M$ , which captures both macro- and micro-mixing 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.

## VI. Similarity between Two-Mode Models of Homogeneous Reactors and Two-Phase Models of Catalytic Reactors

A striking structural similarity between the two-mode models for homogeneous reactors and two-phase models for heterogeneous catalytic reactors exists. This could be seen more clearly when eqns. (24) and (25) are rewritten as

$$\langle u_x \rangle \frac{dC_m}{dx} = -\frac{C_m - \langle C \rangle}{t_{mix}} = -R(\langle C \rangle), \text{ with } C_m = C_{m,in} \text{ @ } x = 0. \quad (34)$$

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

$$\langle u_x \rangle \frac{dC_m}{dx} = -\frac{C_m - C_S}{t_{TP}} = -R(C_S), \text{ with } C_m = C_{m,in} \text{ @ } x = 0. \quad (35)$$

It may be noticed that the spatially averaged concentration  $\langle C \rangle$  of the TMM (in eqn. 34) is replaced by the surface (wall) concentration  $C_S$  in the two-phase model (eqn. 35), 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

$$t_{TP} = \beta_{TP} t_D = \frac{1}{Sh_{\infty,T}} \frac{a^2}{D_m}, \quad (36)$$

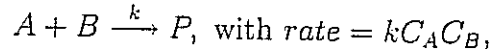
where  $t_D$  is the transverse diffusion time scale, and  $Sh_{\infty,T}$  ( $= 1/\beta_{TP}$ ) is the two-phase (dimensionless mass) transfer coefficient (asymptotic Sherwood number) that depends on the velocity profile and tube geometry. For the case of fully developed laminar flow in a circular tube,  $Sh_{\infty,T} = \frac{48}{11} = 4.36$ , while its analogue in the TMM (comparing eqn. (26) and (36)) is  $Sh_{\infty,E} = \frac{1}{\beta_1} = 48$  (the dimensionless mass exchange coefficient in the TMMs).

As illustrated in the next section, just as the two-phase models can capture the mass-transfer limited asymptote in heterogeneous reactions (which is missed by the pseudo-homogeneous 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 ( $t_{TP}$ )  $\rightarrow$  local mixing time ( $t_{mix}$ ), two-phase transfer coefficient ( $Sh_{\infty,T}$ )  $\rightarrow$  two-mode exchange coefficient ( $Sh_{\infty,E}$ ), surface (wall) concentration  $C_S$   $\rightarrow$  spatially averaged concentration  $\langle C \rangle$ , mass-transfer limited reaction  $\rightarrow$  mixing-limited reaction.

## VII. Applications of Two-Mode Models

### A. Bimolecular Second Order Reactions

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



occurring in a CSTR, where  $k$  is the reaction rate constant. For the case of stoichiometric feeding (i.e.  $C_{A,in} = C_{B,in} = C_{in}$ ), the conversion ( $X$ ) obtained by using the TMM is given by

$$X = \frac{1}{1 + \eta} - \frac{\sqrt{4Da(1 + \eta) + 1} - 1}{2Da(1 + \eta)^2}, \quad (37)$$

where  $\eta$  ( $= t_{mix}/\tau_C$ ) is the dimensionless local mixing time, and  $Da$  ( $= kC_{in}\tau_C$ ) is the Damköhler number. Figure 1 shows the variation of conversion  $X$  with  $Da$  for different values of the dimensionless local mixing time  $\eta$ . The case of  $\eta = 0$  corresponds to the ideal CSTR. For  $\eta > 0$  and  $Da \rightarrow \infty$ , the local concentrations  $\langle C_i \rangle$  ( $i = A, B$ ) approach zero, while the

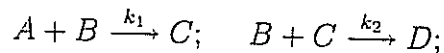
*mixing-cup concentrations approach a mixing limited asymptote*, given by

$$\langle C_A \rangle = \langle C_B \rangle = 0; \quad C_{A,m} = C_{B,m} = \frac{\eta}{1 + \eta}; \quad X = \frac{1}{1 + \eta}. \quad (38)$$

As mentioned in the previous section, 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 exchange between the phases occurs at the solid-fluid boundary, the exchange between modes (scales) in homogeneous reactors occurs in the entire domain.

## B. Competitive-Consecutive Reactions

Competitive-consecutive reactions of the type



are prototype of many multistep reactions like nitration of benzene and toluene, diazo coupling, bromination reactions, etc. Experimental observations (Li & Toor, 1986) show that if the first reaction is infinitely fast as compared to the second one (i.e.  $k_1/k_2 \rightarrow \infty$ ), 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 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 rate of the second reaction increases, finally attaining a mixing limited asymptote. We use the TMM for a CSTR to verify this observation. Figure 2 shows the increase in the yield of  $D$ ,  $Y_D$ , with Damköhler number of the second reaction,  $Da_2$ , where  $Y_D = 2C_{Dm} / (C_{Cm} + 2C_{Dm})$ , and  $Da_2 = k_2 C_{in} \tau_C$ . The figure corresponds to the case when the first reaction is infinitely fast (i.e.  $k_1/k_2 \rightarrow \infty$ ), and  $A$  and  $B$  are fed in stoichiometric amounts [i.e.  $C_{B,in} = C_{A,in} = C_{in}$  and  $C_{C,in} = C_{D,in} = 0$ ]. 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

$$Y_{D,\max} = \begin{cases} \frac{2\eta}{1+2\eta}, & \text{for } \eta \leq 1, \\ \frac{2}{1+2\eta}, & \text{for } \eta > 1. \end{cases} \quad (39)$$

Thus, in this case, an optimal yield of  $D$  is obtained for  $\eta = 1$ .

## VIII. 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 the mixing effects due to local velocity gradients, molecular diffusion and reaction, the latter requires extensive computations, especially for large Schmidt and/ Damköhler numbers, and for multiple reactions with 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 performance. 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 classical ideal reactor models.

The analogy between the two-mode models of homogeneous reactors and two-phase models of catalytic reactors could be carried further by noting that for all cases of well-defined flow-fields, where two-phase mass-transfer coefficients ( $Sh_T$ ) can be estimated theoretically, the exchange coefficient ( $Sh_E$ ) or the local mixing time ( $t_{mix}$ ) of the TMMs could also be estimated. For more complex flow-fields (e.g. 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.* [In fact, the classical two-phase models are also two-mode models, the modes being the cup-mixing and the surface (or solid-phase) concentrations. Thus, the two-mode / two-scale approach may be used to present a unified theory of homogeneous and heterogeneous reactors!]

To summarize, the two-mode models are the *minimal models* that provide a low-dimensional description of mixing, by coupling the interaction between chemical reaction, diffusion and velocity gradients at the local scales to the macro-scale reactor variables. Due to their simplicity and generality, it is hoped that they will find applications in the preliminary design

and optimization of homogeneous chemical reactors, as well as provide an alternative method for teaching micromixing effects in homogeneous reactors.

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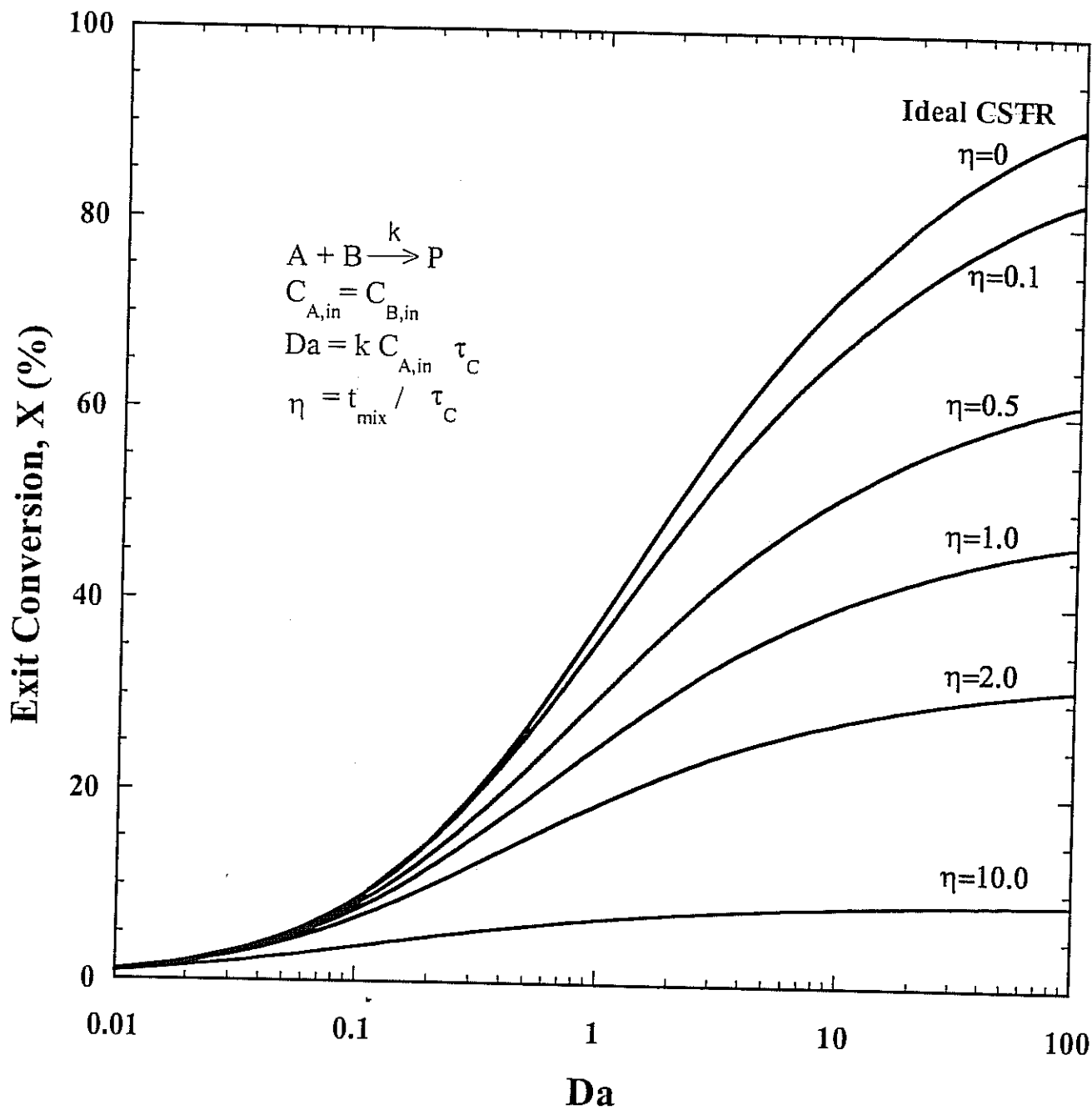


Figure 1. Variation of exit conversion with Damköhler number,  $Da$ , for a second order reaction in a CSTR, for different values of dimensionless local mixing time,  $\eta$ .



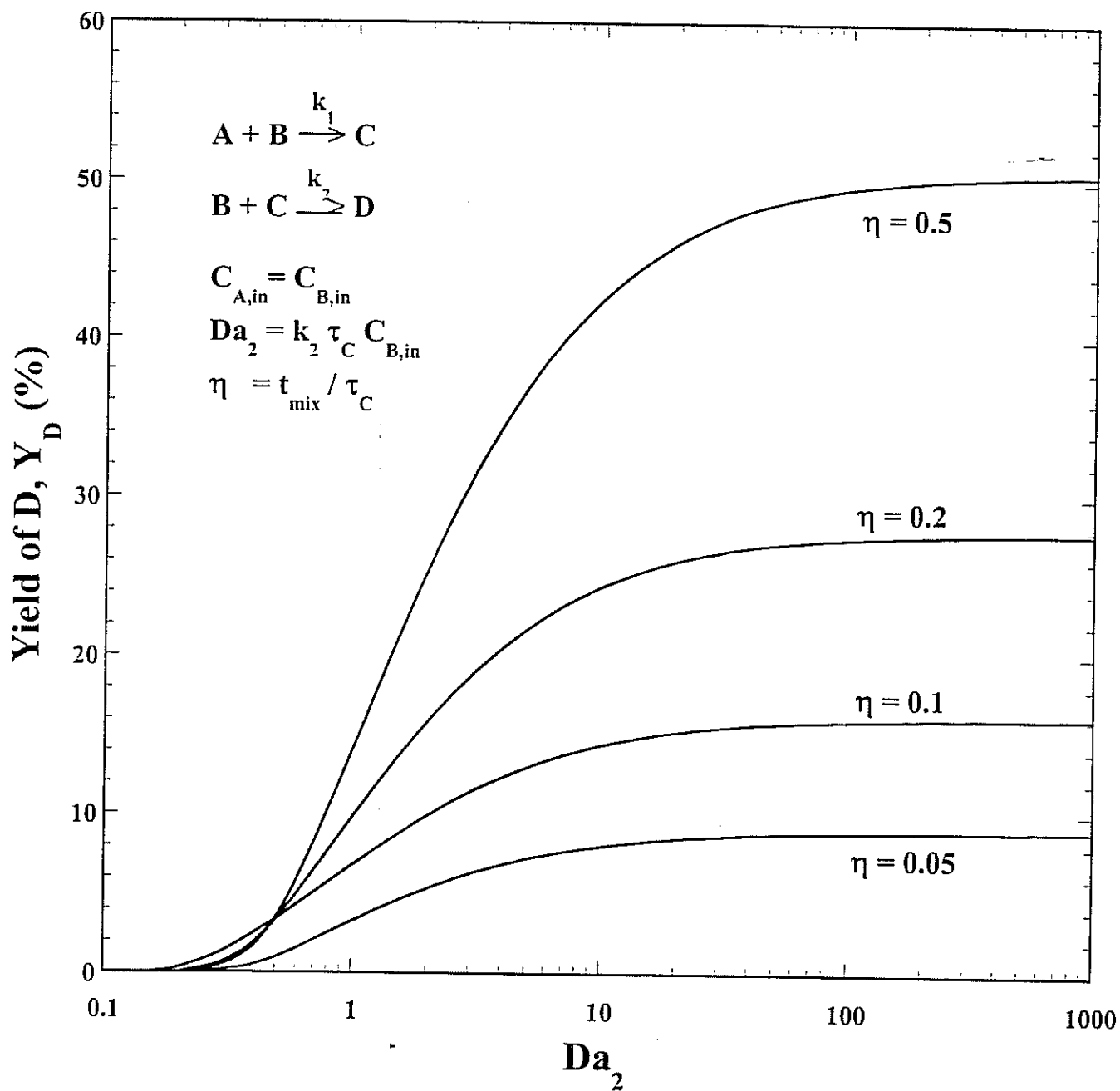


Figure 2. Variation of the yield of D with Damköhler number for a competitive-consecutive reaction scheme  $A+B \rightarrow C$ ,  $B+C \rightarrow D$ , when the first reaction is infinitely fast, for different values of the dimensionless local mixing time,  $\eta$ .