Closure Models for Turbulent Reacting Flows

In this paper, a simple procedure based on fast and slow reaction asymptotics has been employed to derive first-order closure models for the nonlinear reaction terms in turbulent mass balances from mechanistic models of turbulent mixing and reaction. The coalescence-redispersion (CRD) model, the interaction by exchange with the mean (IEM) model, the three-environment (3E) model, and the four-environment (4E) model have been used to develop closure equations. The closure models have been tested extensively against experimental data for both single and multiple reactions. The closures based on slow asymptotics for the CRD, 3E and 4E models provide very good predictions of all of the experimental data, while other models available either in the literature or derived here are not adequate. The simple new closure equations developed in this paper may be useful in modeling systems involving turbulent mixing and complex chemical reactions.

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Introduction

Models of mixing and chemical reaction in turbulent flows are often classified as *mechanistic models* or *direct turbulence models* (Hill, 1979). In a mechanistic model, only a few dominant mechanisms in the overall transport process are described, thus permitting the formulation of a relatively simple model often involving the interdiffusion of inhomogeneous slabs or the intermixing of segregated environments at some prescribed rate (Villermaux, 1983; Tarbell and Mehta, 1986). They are attractive because of their simplicity and modest computational demands, but they are viewed with skepticism by many because of their supposed empirical nature and lack of a physical basis. On the other hand, direct turbulence models are based on the Navier-Stokes and component continuity equations and thus have, in a certain sense, a physical basis. In order to arrive at a closed system of equations, however, the fundamental equations of direct turbulence modeling must be supplemented by closure models which relate higher-order statistics to lower-order statistics of the concentration distribution (Patterson, 1981). The crux of the problem of understanding and predicting chemical reactions in turbulent flows lies in the multiplicity of ways in which the closure scheme is realized. The purpose of the present paper is to show how the simple picture of turbulent micromixing underlying a mechanistic model can be used to develop a useful closure equation for direct turbulent modeling.

Let us consider an isothermal, irreversible parallel-consecutive reaction scheme

$$A + B \rightarrow R \tag{1}$$

$$R + B \rightarrow S \tag{2}$$

with bimolecular reaction rates ($r_1 = k_1 C_a C_b$, $r_2 = k_2 C_r C_b$) which is being carried out in a plug flow reactor with separate feedstreams as shown in Figure 1. The parallel-consecutive reaction scheme is of particular interest because recent experiments (Li and Toor, 1986; Mehta and Tarbell, 1987) have shown that the selectivity is very sensitive to the level of turbulent micromixing and that this sensitivity can be used to discriminate among various mechanistic models of turbulent mixing and reaction (Mehta and Tarbell, 1987; Chang et al., 1986).

If Reynolds decomposition is applied to the concentration fields so that the instantaneous concentration, C_i is expressed as

$$C_i = \overline{C}_i + c_i \tag{3}$$

where $\overline{C}_i$ is the time (ensemble)-averaged concentration and c_i is the fluctuating concentration, and the component continuity equations are averaged with axial diffusion assumed negligible, then the following equations for the averaged concentration result:

$$U\frac{d\overline{C}_a}{dz} = -\bar{r}_1 \tag{4}$$

$$U\frac{d\overline{C}_b}{dz} = -\bar{r}_1 - \bar{r}_2 \tag{5}$$

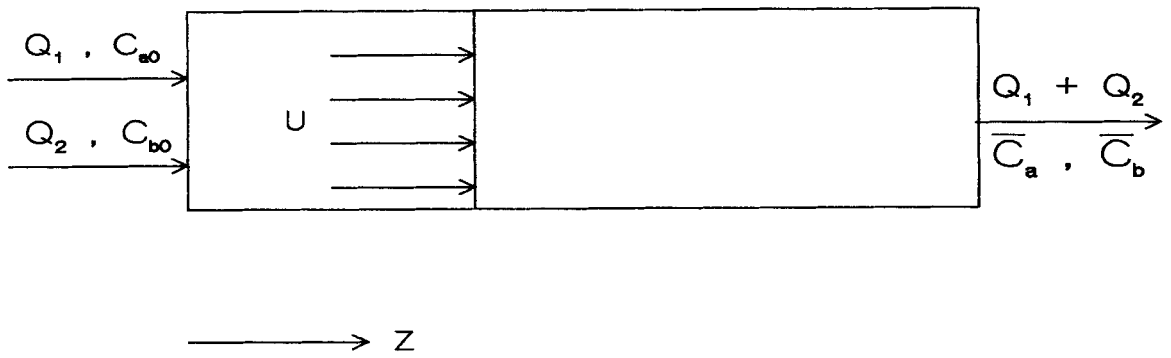


Figure 1. Plug flow reactor.

$$U\frac{d\bar{C}_r}{dz} = \bar{r}_1 - \bar{r}_2 \tag{6}$$

$$U\frac{d\bar{C}_s}{dz} = \bar{r}_2 \tag{7}$$

In the above equations, z is the axial distance from the feed, U is the mean axial velocity, and $\bar{r}_1$ and $\bar{r}_2$ are the averaged reaction rates given by

$$\bar{r}_1 = k_1(\bar{C}_a\bar{C}_b + \overline{c_ac_b}) \tag{8}$$

$$\bar{r}_2 = k_2(\bar{C}_r\bar{C}_b + \overline{c_rc_b}) \tag{9}$$

Equations 4–9 are not closed because of the appearance of the correlations $\overline{c_ac_b}$ and $\overline{c_rc_b}$. It is possible to close the system at the level of the mean equations (Eqs. 4–7) by providing relationships between the correlations and the mean quantities, $\bar{C}_a$, $\bar{C}_b$, and $\bar{C}_r$. Such relationships are referred to as closure models, and in this case they are closure models of the first order since they supplement the mean (first-order) equations.

Pioneering work on first-order closure methods was initiated by Toor (1962, 1969). He proposed a closure model based on analytical solutions for a one-dimensional turbulent tubular reactor in the limits of very fast and very slow single-reaction rates. It was shown that in an ideal nonreactive tubular mixer, the concentration covariance ($\overline{c_ac_b}$) of two initially unmixed streams with equal diffusivities is identical to that found for very rapid irreversible second-order chemical reactions when the reactants are fed in stoichiometric proportions and a Gaussian distribution of concentration fluctuations of the conserved scalar, $C_c = C_a - C_b$, is assumed. The notion that the covariance may depend only on the hydrodynamics and not on the reaction rate is referred to as "Toor's hypothesis" (Toor, 1975). Under these assumptions, the closure approximation for a single reaction takes the form

$$\overline{c_ac_b} = -I_S\bar{C}_{ao}\bar{C}_{bo} \tag{10}$$

where $\bar{C}_{ao}$ and $\bar{C}_{bo}$ are the mixed feed concentrations, and I_S is the intensity of segregation, a unique function of axial position (z) for fixed hydrodynamics, which can be determined from the decay of concentration fluctuations in nonreactive mixing experiments or the mean conversion of infinitely fast reactions (e.g., acid-base reactions). Mao and Toor (1971) successfully tested the hypothesis for near stoichiometric liquid-phase reactions in a multijet tubular reactor for rapid reactions and further found that the dependence of $\overline{c_ac_b}$ on feed stoichiometry can often be neglected; similar conclusions for a gas-phase reaction were obtained by Ajmera (1970). McKelvey et al. (1975) reported successful prediction of stoichiometric and nonstoichiometric intermediate and slow rate chemistry data using stoichiometric fast reaction data for closure. Recent direct numerical simulation results (Leonard and Hill, 1987) are also consistent with the hypothesis.

Closure models for parallel-consecutive reactions (Eqs. 1 and 2) have also been proposed. Bourne and Toor (1977) assumed that $\overline{c_ac_b}$ is unaffected by the second reaction and can be taken from measurements performed in the case of a fast single-step reaction, i.e.,

$$\overline{c_ac_b} = -I_S\bar{C}_{ao}\bar{C}_{bo} \tag{11}$$

while $\overline{c_rc_b}$ is negligible, i.e.,

$$\overline{c_rc_b} \simeq 0 \tag{12}$$

Brodkey and Lewalle (1985) proposed the following closure equations:

$$\overline{c_ac_b} = -I_S\bar{C}_{ao}\bar{C}_{bo} \tag{13}$$

$$\overline{c_rc_b} = \overline{c_ac_b}(\bar{C}_r/\bar{C}_a) \tag{14}$$

However, neither of these models was able to predict the experimental data of Li and Toor (1985) or, as we shall see, the data of Mehta and Tarbell (1987). Hence, there is a clear need for new closure models for multiple reactions which will provide satisfactory prediction of available experimental data. In the present work, a version of Toor's hypothesis has been used to derive new sets of closure equations from various mechanistic models.

Derivation of Closure Models

In this paper we develop closure models from four mechanistic models: the coalescence-redispersion (CRD) model of Curl (1963), the interaction-by-exchange with the mean (IEM) model of Villermaux and Devillon (1972), the three environment model (3E) of Ritchie and Tobgy (1979), and the four environment (4E) model of Mehta and Tarbell (1983). Chang et al. (1986) showed that all of these models possess an analogy to theories of isotropic turbulent micromixing as expressed by Corrsin (1957, 1964) and Rosensweig (1964, 1966). The anal-

ogy is based on the analytical demonstration that the decay law for the concentration variance of a nonreactive tracer as derived from the mechanistic models has the same form as that derived from direct turbulence theory. This type of analogy, first demonstrated by Evangelista et al. (1969) for the CRD model, allows one to relate the micromixing parameter of a mechanistic model directly to turbulence properties and ultimately to macroscopic characteristics of the mixing system such as power input. This turbulence analogy provides a physical basis for the mechanistic models. For a batch (plug flow) mixer the variance decay takes the form (Tarbell and Mehta, 1986)

$$I_S = \frac{\sigma^2}{\sigma_o^2} = \exp\left(-\tau/\tau_m\right) \tag{15}$$

where I_S is the intensity of segregation (Danckwerts, 1953), τ_m is a time scale for turbulent micromixing which is characteristic of the fine structure of the turbulence, and τ is the time (residence time). The following estimates of τ_m have been provided by Corrsin (1964) for large Reynolds number turbulence:

$$\tau_m \simeq 0.5\left[4\left(L_S^2/\epsilon\right)^{1/3} + \left(\nu/\epsilon\right)^{1/2} \ln N_{Sc}\right]; \quad N_{Sc} \gg 1 \text{ (liquids)} \tag{16}$$

$$\tau_m \simeq \frac{2}{\left(3 - N_{Sc}^2\right)} \left(5/\pi\right)^{2/3} \left(L_S/\epsilon\right)^{1/3}; \quad N_{Sc} < 1 \text{ (gases)} \tag{17}$$

where L_S is the integral length scale of the concentration field, ϵ is the turbulent kinetic energy dissipation rate per unit mass, ν is the fluid kinematic viscosity, and N_{Sc} is the Schmidt number. All of these quantities are directly measurable or readily estimated. The relationships between τ_m and the micromixing parameters of various mechanistic models are given elsewhere (Tarbell and Mehta, 1986).

It is implicit in Toor's hypothesis that the micromixing parameter (τ_m) obtained in a nonreactive mixing experiment, such as the variance decay experiment described above, can be used to describe micromixing in a reacting system having the same hydrodynamics. Mehta and Tarbell (1983b) and Tarbell and Mehta (1986) evaluated this concept by comparing predictions of various mechanistic models employing the turbulence analogy with several sets of experimental data for single reactions, and they found very good agreement between models and experiments.

In what follows, we outline the development of the closure models employing the turbulence analogy for each of four mechanistic models. The slab-diffusion (SD) model of Mao and Toor (1971) was not investigated because the turbulence analogy for this model is only approximately valid and only at equal flow rates of the feedstreams. In the spirit of Toor, the behavior of the covariance of the concentration fluctuations will be examined both in the slow chemistry and fast chemistry limits. The closure models thus developed will be tested against available experimental data for both single and multiple reactions.

Limiting Values of Closure Models

The closure models that will be developed ideally should satisfy two important limits: the slow reaction (pure mixing) limit and the fast reaction limit. These limits are useful in assessing the validity of closure models (Toor, 1969, 1975; Kosály, 1987).

For very slow reaction, the Damköhler number, Da (defined as the ratio of characteristic micromixing time, τ_m, to the characteristic reaction time, τ_r) approaches zero. Hence, for the one-dimensional reactor, the covariance of concentration fluctuations is the same as that for pure mixing.

$$\overline{c_a c_b} = -I_S \bar{C}_{ao} \bar{C}_{bo} \tag{18}$$

In the limit of very fast reaction ($Da \to \infty$), mixing of the species is immediately followed by reaction and hence C_a and C_b cannot coexist. Thus $\overline{C_a C_b} = 0$, and it follows from Eq. 8 that

$$\overline{c_a c_b} = -\bar{C}_a \bar{C}_b \tag{19}$$

which is necessary to keep the average rate of reaction, $\bar{r}_1$, finite when $k_1 \to \infty$ (Toor, 1975).

In the next section, closure models will be developed from slow and fast reaction asymptotes for each mechanistic model, and each closure model will be checked to see whether it satisfies the pure mixing limit (Eq. 18) and the fast reaction limit (Eq. 19).

Coalescence-Redispersion Model

The coalescence-redispersion (CRD) model was originally proposed by Curl (1963) to describe dispersed-phase droplet mixing and concurrent chemical reaction. In Curl's view, a chemical reactor population consists of a large number of equal-size droplets, each having uniform concentration and behaving as an ideal batch reactor. Mixing takes place by random and instantaneous pairwise coalescence, concentration homogenization, and subsequent redispersion into an identical pair of droplets. In the turbulence analogy for a homogeneous fluid, we might view Curl's droplets as isotropic turbulent eddies and the coalescence rate as a measure of the rate of turbulent micromixing. The micromixing parameter of the model is the average number of coalescences (I) experienced by an eddy during its passage through the reactor.

We consider the reaction $A + B \to R (r_1 = -kC_aC_b)$ occurring in a tubular reactor with separate feedstreams, each having the same plug flow residence time distribution (RTD). The separate stream concentrations are C_{ao} and C_{bo}; the flow rates are Q_a and Q_b, with the flow rate ratios denoted as $m = Q_a/(Q_a + Q_b)$. For this bimolecular reaction in a plug flow system, the complete integrodifferential equation of the CRD model is given by (Evangelista et al., 1969)

$$\bar{V}_z \frac{\partial}{\partial z} p(C_a, C_b, z) - \frac{\partial}{\partial c}\left[kC_aC_b p(C_a, C_b, z)\right] = \frac{I}{\tau}\left[\int\int\int\int p(C_a', C_b', Z) p(C_a'', C_b'', Z) \delta\left(\frac{C_a' + C_a''}{2} - C_a\right) \cdot \delta\left(\frac{C_b' + C_b''}{2} - C_b\right) dC_a' dC_b' dC_a'' dC_b'' - p(C_a, C_b, z)\right] \tag{20}$$

Here $p(C_a, C_b, z)$ is a properly normalized probability density function satisfying

$$\int_\Omega \int p(C_a, C_b, z)\, dC_a\, dC_b = 1 \tag{21}$$

where Ω is the domain of the concentration vector, (C_a, C_b). In Eq. 20, δ is the Dirac delta function, τ is the mean residence time, and $I/\tau = 2u/N$, where u = the coalescence rate and N = the number of eddies in the system (Curl, 1963). The first term on the lefthand side of Eq. 20 is the convection, the second term is due to chemical reaction, and the righthand side includes the mixing operator. Evangelista et al. (1969) have shown that for the case of a nonreactive batch mixer, I_S is given by Eq. 15 with $\tau_m = (2\tau/I)$. Thus, the turbulence analogy for the CRD model may be summarized in the equation

$$I = 2\tau/\tau_m \tag{22}$$

In order to develop closure equations based on the CRD model, a method of ensemble averaging over the eddies must be defined. This is accomplished by using the definition of the moments of the probability density function. Thus the mean and variance are

$$\overline{C_a} = \int\int C_a p(C_a, C_b, Z)\, dC_a\, dC_b \tag{23}$$

$$\overline{c_a^2} = \int\int (C_a - \overline{C_a})^2 p(C_a, C_b, Z)\, dC_a\, dC_b, \tag{24}$$

and the covariance is given by

$$\sigma^2 = \overline{c_a c_b} = \int\int (C_a - \overline{C_a})(C_b - \overline{C_b}) p(C_a, C_b, z)\, dC_a\, dC_b \tag{25}$$

Pure Mixing Asymptote

To develop a closure model from Eq. 25, it is instructive to look at the behavior of the covariance at the reactor inlet and then invoke the variance decay (Eq. 15) for the pure mixing case. The initial condition satisfied by $p(C_a, C_b, z)$ reflects the fact that the feed streams at concentrations C_{ao} and C_{bo} are unmixed. Thus, we have

$$p(C_a, C_b, Z = 0) = m\delta(C_a - C_{ao})\delta(C_b - 0) + (1 - m)\delta(C_a - 0)\delta(C_b - C_{bo}) \tag{26}$$

Therefore, $\overline{c_a c_b}$ at the entrance (σ_o^2) is given by

$$\sigma_0^2 = \overline{c_a c_b}|_0 = \int\int (C_a - \overline{C_a})(C_b - \overline{C_b}) \cdot p(C_a, C_b, Z = 0)\, dC_a\, dC_b \tag{27}$$

which with the help of Eq. 26 yields

$$\sigma_0^2 = \overline{C_a}\,\overline{C_b} - \overline{C_{ao}}\,\overline{C_b} - \overline{C_a}\,\overline{C_{bo}} \tag{28}$$

where $\overline{C_{ao}}$ and $\overline{C_{bo}}$ are flow-weighted concentrations [$\overline{C_{ao}} = mC_{ao}$; $\overline{C_{bo}} = (1 - m)C_{bo}$]. When the variance decay of a plug flow mixer (no reaction) is invoked (Eq. 15), the closure is completed:

$$\sigma^2 = \overline{c_a c_b} = -I_S[\overline{C_{ao}}\,\overline{C_b} + \overline{C_a}\,\overline{C_{bo}} - \overline{C_a}\,\overline{C_b}] \tag{29}$$

This expression is rigorous for a nonreactive mixing system and its applicability to reacting flow will be investigated in a later section. Equation 29 is easily extended to the second reaction of a parallel-consecutive reaction scheme (Eqs. 1 and 2) by noting that $\overline{C_{ro}} = 0$. The result is:

$$\overline{c_r c_b} = -I_S\overline{C_r}(\overline{C_{bo}} - \overline{C_b}) \tag{30}$$

Equations 29 and 30 constitute a complete set of closure equations for modeling of the parallel-consecutive reaction scheme.

Equation 29 gives the proper limit for pure mixing, since in this limit $\overline{C_a} = \overline{C_{ao}}$ and $\overline{C_b} = \overline{C_{bo}}$, and Eq. 29 reduces to

$$\overline{c_a c_b} = -I_S\overline{C}_{ao}\overline{C}_{bo} \tag{31}$$

In the limit of infinite reaction rate, however, a relationship between mean and feed concentration has not been established for the CRD model, and it remains unclear how to evaluate Eq. 29 in the infinite rate limit. We will return to this point later after discussing the 3E model.

Fast Reaction Asymptote

As discussed earlier, in the limit of very fast reaction, species A and B cannot exist and hence $\overline{C_a}\,\overline{C_b} = 0$. The covariance from the CRD model in this limit becomes

$$\overline{c_a c_b} = \int\int [C_a C_b + \overline{C}_a\overline{C}_b - \overline{C}_a C_b - C_a\overline{C}_b] p(C_a, C_b, Z)\, dC_a\, dC_b \tag{32}$$

Since the first term of the integrand vanishes, the result is

$$\overline{c_a c_b} = -\overline{C}_a\overline{C}_b \tag{33}$$

which is the same as Eq. 19, the limiting expression for very fast reactions. Note, however, that this expression is not useful for modeling finite rate reactions because it produces a mean reaction rate (Eq. 8) which is identically zero.

Interaction by Exchange with the Mean Model

The interaction by exchange with the mean (IEM) model was first described in the context of homogeneous mixing in a perfectly-stirred reactor by Villermaux and Devillon (1972) and Costa and Trevissoi (1972), although it has earlier roots as pointed out by Aubry and Villermaux (1975). For a two-feedstream perfectly-stirred reactor, the IEM model consists of two eddies—one associated with each feedstream, which act as well-mixed chemical reactors having mass exchange with a mean environment whose concentration is assumed to be constant and to coincide with the mean concentration leaving the reactor. Micromixing is described by a first-order exchange process between the mean environment and each eddy (the eddies do not interact directly) with concentration difference as the driving force. The exchange rate is characterized by a mass transfer coefficient, h, which is the micromixing parameter of the model.

For a plug flow reactor fed with pure reactants A and B in separate streams (concentrations C_{a1}^0 and C_{b2}^0) and a single chemical reaction [$A + B \rightarrow R$; rate $= r_i(C_{ai}, C_{bi})$], the governing equations for each eddy are

$$\frac{dC_{ji}}{dt} = h(\overline{C_j} - C_{ji}) - r_i \qquad \begin{matrix} j = A, B \\ i = 1, 2 \end{matrix} \tag{34}$$

with initial conditions given by

$$C_{a1}(0) = C_{a1}^0; \quad C_{b2}(0) = C_{b2}^0; \quad C_{b1}(0) = C_{a2}(0) = 0 \quad (35)$$

The mean concentrations are determined as follows:

$$\overline{C_j} = \int_0^\infty [mC_{j1}(t) + (1 - m)C_{j2}(t)]\, f(t)\, dt \quad (36)$$

where $m = Q_1/(Q_1 + Q_2)$ and $f(t) = \delta(t - \tau)$ is the RTD of a plug flow mixer. Defining the concentration variance of a species as

$$\overline{c_j^2} = \int_0^\infty [m(C_{j1}(t) - \overline{C_j})^2 + (1 - m) \cdot (C_{j2}(t) - \overline{C_j})^2]\, f(t)\, dt \quad (37)$$

it can be shown that I_s is given by Eq. 15 when

$$h = \frac{1}{2\tau_m} \quad (38)$$

This turbulence analogy of the IEM model for a perfectly-stirred mixer was apparently first recognized by Costa and Trevissoi (1972).

A closure equation is easily developed from the definition of the covariance of concentration fluctuations,

$$\overline{c_a c_b} = \int_0^\infty [m(C_{a1}(t) - \overline{C_a})(C_{b1}(t) - \overline{C_b}) + (1 - m)(C_{a2}(t) - \overline{C_a})(C_{b2}(t) - \overline{C_b})]\, f(t)\, dt \quad (39)$$

For a plug flow reactor, integration of Eq. 39 yields

$$\overline{c_a c_b} = m(C_{a1} - \overline{C_a})(C_{b1} - \overline{C_b}) + (1 - m)(C_{a2} - \overline{C_a})(C_{b2} - \overline{C_b}) \quad (40)$$

where the concentrations are now functions of the residence time in the reactor.

Pure Mixing Asymptote

In the pure mixing asymptote, the model equations become

$$\frac{dC_{a1}}{dt} = h(\overline{C_a} - C_{a1}) \quad (41a)$$

$$\frac{dC_{a2}}{dt} = h(\overline{C_a} - C_{a2}) \quad (41b)$$

$$\frac{dC_{b1}}{dt} = h(\overline{C_b} - C_{b1}) \quad (41c)$$

$$\frac{dC_{b2}}{dt} = h(\overline{C_b} - C_{b2}) \quad (41d)$$

with the initial conditions expressed in Eq. 35. These ordinary differential equations can be solved to give

$$C_{a1} = mC_{a1}^0 + (1 - m)C_{a1}^0 \exp(-ht) \quad (42)$$

$$C_{a2} = mC_{a1}^0[1 - \exp(-ht)] \quad (43)$$

$$C_{b1} = (1 - m)C_{b2}^0[1 - \exp(-ht)] \quad (44)$$

$$C_{b2} = C_{b2}^0(1 - m) + mC_{b2}^0 \exp(-ht) \quad (45)$$

In these expressions, t is interpreted as the residence time inside the plug flow reactor. After substitution of Eqs. 42–45 into Eq. 36, the mean concentrations are found to be the flow weighted inlet concentrations, i.e.,

$$\overline{C_a} = mC_{a1}^0 = \overline{C_{a0}}; \quad \overline{C_b} = (1 - m)C_{b2}^0 = \overline{C_{b0}} \quad (46)$$

When these expressions are substituted into Eq. 40 along with Eqs. 42–45, we find

$$\overline{c_a c_b} = -I_S \overline{C_{a0}}\,\overline{C_{b0}} \quad (47)$$

where

$$I_S = \exp(-2ht) = \exp(-t/\tau_m) \quad (48)$$

from the turbulence analogy. Thus, the closure model for the slow reaction asymptote (Eq. 47) is the same as Eq. 18, and hence it satisfies the pure mixing limit.

Fast Reaction Asymptote

For the case of infinitely fast reaction with stoichiometric feed, A and B cannot coexist. Under this condition, eddy 1 will be devoid of B and eddy 2 will be devoid of A since they are associated with feedstreams of pure A and pure B, respectively. This is equivalent to saying that C_{a2} and C_{b1} will be identically zero at all points inside the reactor and hence the mean concentrations $\overline{C_a}$ and $\overline{C_b}$ are given by

$$\overline{C_a} = mC_{a1}; \quad \overline{C_b} = (1 - m)C_{b2} \quad (49)$$

When these expressions are substituted into Eq. 40, the closure equation for the fast chemistry asymptote becomes:

$$\overline{c_a c_b} = -\overline{C_a}\,\overline{C_b} \quad (50)$$

which is the same as Eq. 19 derived for the infinite reaction limit. Thus, the IEM model, like the CRD model, does not produce a useful closure model in the fast reaction asymptote.

Three-Environment Model

The three-environment (3E) model was developed by Ritchie and Tobgy (1979) to describe chemical reactors with two feedstreams. It is an extension of Ng and Rippin's (1965) "two-environment model" for premixed feed reactors to separate feedstream reactors. In the 3E model, two entering environments (EE's), one for each reactant feedstream in a two-reactant system, are assumed to supply a single leaving environment (LE). While each EE acts as a totally-segregated reactor, the LE behaves as a maximum mixedness reactor. As pointed out by Mehta and Tarbell (1983a), the EE's should be viewed as lumped representations of turbulent eddies of pure reactant which have only interacted with other pure reactant eddies and, as such, they model the extremes of the turbulent concentration

spectrum. The LE is a lumped representation of eddies in the intermediate region of the turbulent concentration spectrum. Micromixing is modeled by the first-order transfer of material from the EE's to the LE with a transfer coefficient R_s which is the model's micromixing parameter. In a plug flow reactor, the three environments move in unison down the reactor at the mean velocity and chemical reaction takes place in the LE. In the nonreactive mixing case, the LE is always at the mean concentration.

The relationships among the reactor variables and the environment variables are described below. Let ϕ_i be the volume fraction of the ith environment ($i = 1, 2$, for the EE's; $i = 3$ for the LE). The ϕ_i's are related directly to the flow rate fraction $m = Q_1/(Q_1 + Q_2)$ as follows:

$$\phi_1 = mI_S \tag{51a}$$

$$\phi_2 = (1 - m)I_S \tag{51b}$$

$$\phi_3 = 1 - I_S \tag{51c}$$

where

$$I_S = \exp(-R_s\tau) \tag{52}$$

In Eq. 52, τ is the residence time, R_s is the micromixing parameter of the model, and, as we shall see, I_S can be identified as the intensity of segregation.

Mehta and Tarbell (1983a) showed that the decay of the concentration variance of a nonreactive tracer in a plug flow (batch) mixer as predicted by the 3E model has the same form as prescribed by Corrsin's isotropic turbulent mixing theory (Corrsin, 1957, 1964). The ensemble average of a quantity was computed by volume fraction weighting over the environment values. The variance (σ^2) of the concentration of component A in the unmixed feedstream tubular reactor of Figure 1 is given by the following expression for the 3E model:

$$\sigma^2 = \overline{c_a^2} = \phi_1(C_{a0} - \bar{C}_a)^2 + \phi_2(0 - \bar{C}_a)^2 + \phi_3(C_a^L - \bar{C}_a)^2 \tag{53}$$

where C_a^L is the concentration of A in the LE, C_{a0} is the concentration of A in EE1, and the concentration of A in EE2 is zero. For the case where component A is nonreactive, it is easily shown (Mehta and Tarbell, 1983a) that the LE is at the mean concentration,

$$C_a^L = \bar{C}_a = \bar{C}_{a0} = mC_{a0} \tag{54}$$

Clearly, in the nonreactive case, the LE makes no contribution to the variance. Substituting Eq. 54 into Eq. 53, it is seen that the variance σ^2 is given by Eq. 15 when the micromixing parameter of the model, R_s, is related to the mixing time scale, τ_m in the following manner

$$R_s = \frac{1}{\tau_m} \tag{55}$$

This is the turbulence analogy of the 3E model.

Pure Mixing Asymptote

A closure model for turbulent reacting flows is easily derived by inspecting the behavior of the covariance of the concentration fluctuation in the asymptote of pure mixing. Following Eq. 53, the covariance is given by:

$$\overline{c_a c_b} = \phi_1(C_{a0} - \bar{C}_a)(0 - \bar{C}_b) + \phi_2(0 - \bar{C}_a)(C_{b0} - \bar{C}_b) + \phi_3(C_a^L - \bar{C}_a)(C_b^L - \bar{C}_b) \tag{56}$$

In the case of pure mixing, the LE is always at the mean concentration and hence does not contribute to the covariance. With this assumption and substitutions from Eq. 51, the final result is obtained

$$\overline{c_a c_b} = -I_S(\bar{C}_a\bar{C}_{b0} + \bar{C}_{a0}\bar{C}_b - \bar{C}_a\bar{C}_b) \tag{57}$$

This closure model can easily be shown to satisfy the pure mixing limit (Eq. 18). Simply note that, for a pure mixer, we have $\bar{C}_a = \bar{C}_{a0}$, $\bar{C}_b = \bar{C}_{b0}$, and Eq. 57 reduces to

$$\overline{c_a c_b} = -I_S\bar{C}_{a0}\bar{C}_{b0} \tag{58}$$

which is the proper limit.

The fast reaction limit can be checked by noting (as shown in the next section) that $\bar{C}_a = I_S\bar{C}_{a0}$, $\bar{C}_b = I_S\bar{C}_{b0}$ for infinite reaction rate and stoichiometric feed conditions. When these relations are introduced into Eq. 57, the result is Eq. 19, the proper limiting form for fast reactions. Thus, Eq. 57 satisfies both limits and looks promising. For the parallel-consecutive reaction system (Eqs. 1 and 2), the appropriate closure equation for the second reaction is readily deduced by setting $\bar{C}_{r0} = 0$, with the result

$$\overline{c_r c_b} = -I_S\bar{C}_r(\bar{C}_{b0} - \bar{C}_b) \tag{59}$$

Fast Reaction Asymptote

Here we inspect the covariance of the 3E model in the fast reaction asymptote assuming stoichiometric feed ($\beta = \bar{C}_{b0}/\bar{C}_{a0} = 1$). For fast reaction, species A and B cannot coexist in the mixed (leaving) environment, and therefore, C_a^L and C_b^L must be identically zero. Utilizing this concept, the covariance (Eq. 56) becomes

$$\overline{c_a c_b} = \bar{C}_a\bar{C}_b - I_S\bar{C}_{a0}\bar{C}_b - I_S\bar{C}_a\bar{C}_{b0} \tag{60}$$

That this closure model satisfies the asymptotic limit for infinitely fast reaction (Eq. 19) can be shown in the following manner. The mean concentrations $\bar{C}_a$ and $\bar{C}_b$ are given by volume fraction weighting of the environment concentrations as follows:

$$\bar{C}_a = \phi_1 C_{a0} + \phi_3 C_a^L \tag{61}$$

$$\bar{C}_b = \phi_2 C_{b0} + \phi_3 C_b^L \tag{62}$$

C_a^L and C_b^L are identically zero in this limit. Therefore, using the definition of volume fraction (Eq. 51), it can be seen that the mean concentrations are related to the feed concentrations by

$$\bar{C}_a = I_S\bar{C}_{a0} \tag{63}$$

$$\bar{C}_b = I_S\bar{C}_{b0} \tag{64}$$

Utilizing Eqs. 63 and 64 in Eq. 60, we recover the proper limit of

the covariance for infinitely fast reaction (Eq. 19). However, the closure model of Eq. 60 does not satisfy the pure mixing limit (Eq. 18). Thus, the use of Eq. 60 as a closure model for slow reactions will have to be verified by analysis of experimental data.

The closure model of Eq. 60 is easily extended to the parallel-consecutive reaction scheme (Eqs. 1 and 2) by setting $\overline{C_{r0}} = 0$. The result is:

$$\overline{c_r c_b} = \bar{C}_r \bar{C}_b - I_S \bar{C}_r \bar{C}_{b0} \tag{65}$$

Equations 60 and 65 thus constitute a set of closure equations for the parallel-consecutive reaction scheme.

It is interesting to note that the closure models developed in the slow reaction asymptote (Eq. 57) and the fast reaction asymptote (Eq. 60) are almost identical, the only difference being the appearance of the term I_S factoring $\bar{C}_a \bar{C}_b$ in Eq. 57).

Four-Environment Model

To overcome the limitation of only a single reacting environment in the three-environment (3E) model, Mehta and Tarbell (1983a) developed the 4E model by introducing a separate LE for each feedstream and allowing mutual interaction between the LE's. The reactant stoichiometry of each LE may now be rich in the reactant fed through its respective EE.

The 4E model retains the basic features of the 3E model. The EE's are segregated flow reactors; the LE's are maximum mixedness reactors; and the transfer of material from EE to LE is first order in the mass of the EE with a transfer coefficient R_S. It is further assumed that the reversible transfer between LE's is first order in the mass of each LE and also with a transfer coefficient R_S.

The starting point for development of closure equations is an expression for the covariance of concentration fluctuations, which for the 4E model is given by:

$$\overline{c_a c_b} = \phi_1 (C_{a1}^0 - \bar{C}_a)(0 - \bar{C}_b) + \phi_2 (0 - \bar{C}_a)(C_{b2}^0 - \bar{C}_b) + \phi_3 (C_{a1}^L - \bar{C}_a)(C_{b1}^L - \bar{C}_b) + \phi_4 (C_{a2}^L - \bar{C}_a)(C_{b2}^L - \bar{C}_b) \tag{67}$$

In Eq. 67, the ϕ_i's ($i = 1, 2$ for EE's; $i = 3, 4$ for LE's) are the volume fractions of the entering and leaving environments, C_{a1}^0 and C_{b2}^0 are the feed concentrations of pure A and pure B fed to entering environment 1 and 2, respectively, and $C_a^L j$ and $C_b^L j$ are the leaving environment concentrations of A and B, respectively ($j = 1$ for LE 1; $j = 2$ for LE 2). The development of closure models from Eq. 67 is quite complex and mathematically unwieldy for the general case. However, some degree of simplification is achievable if we assume equal flow rates for the feed streams. Hence, we will restrict our analysis to this case.

Pure Mixing Asymptote

For the case of pure mixing and equal flow rates, the volume fractions are given by:

$$\phi_1 = \phi_2 = \tfrac{1}{2} I_S \tag{68a}$$

$$\phi_3 = \phi_4 = \tfrac{1}{2} (1 - I_S) \tag{68b}$$

the leaving environment concentrations are given by

$$C_{a1}^L = \frac{C_{a1}^0}{2} (1 + I_S) \tag{69a}$$

$$C_{a2}^L = \frac{C_{a1}^0}{2} (1 - I_S) \tag{69b}$$

$$C_{b1}^L = \frac{C_{b2}^0}{2} (1 - I_S) \tag{69c}$$

$$C_{b2}^L = \frac{C_{b2}^0}{2} (1 + I_S) \tag{69d}$$

and by analogy to turbulence theory

$$I_S = \exp(-R_S \tau) = \exp(-\tau/\tau_m) \tag{70}$$

The reader is referred to Mehta and Tarbell (1983a) for the derivation of Eqs. 68–70. When these expressions are substituted into Eq. 67, the result is:

$$\overline{c_a c_b} = \bar{C}_a \bar{C}_b - I_S \bar{C}_{a0} \bar{C}_b - I_S \bar{C}_a \bar{C}_{b0} + \bar{C}_a \bar{C}_b (I_S^3 - I_S^2 + I_S - 1) \tag{71}$$

This expression for the covariance can be simplified further for the limiting cases of the magnitude of I_S. For the limit of very small Damkohler number ($Da \to 0$), we can take $\tau_m \to 0$ for a fixed value of reaction time, τ_r. Hence, in this limit, $I_S \to 0$, and the second- and higher-order terms in I_S can be neglected in Eq. 71, yielding

$$\overline{c_a c_b} = I_S \bar{C}_a \bar{C}_b - I_S \bar{C}_{a0} \bar{C}_b - I_S \bar{C}_a \bar{C}_{b0} \tag{72}$$

which is the same expression derived for the pure mixing case from the CRD model (Eq. 29) and from the 3E model (Eq. 57). As illustrated for the CRD and 3E model, Eq. 72 satisfies the pure mixing limit (Eq. 18).

Equation 71 can also be simplified for values of I_S close to unity. This is equivalent to the fast reaction case ($Da \to \infty$) if we take $\tau_m \to \infty$ for a fixed value of reaction time, τ_r. In this case, the last term of Eq. 71 can be neglected compared to the other terms, and the closure model becomes

$$\overline{c_a c_b} = \bar{C}_a \bar{C}_b - I_S \bar{C}_{a0} \bar{C}_b - I_S \bar{C}_a \bar{C}_{b0} \tag{73}$$

This is the same as Eq. 60 which was derived from the 3E model under the fast chemistry assumption. Equation 73 can be shown to satisfy the fast chemistry limit (Eq. 19) in the following manner. For $Da \to \infty$, the species A and B will be segregated in the leaving environments and

$$C_{a2}^L = C_{b1}^L = 0 \tag{74}$$

Therefore, the mean concentrations $\bar{C}_a$ and $\bar{C}_b$ are given by volume fraction weighting of the environment concentrations as follows:

$$\bar{C}_a = \phi_1 C_{a0} + \phi_3 C_{a1}^L \tag{75}$$

$$\overline{C}_b = \phi_2 C_{b0} + \phi_4 C_{b2}^L \tag{76}$$

However, for values of I_S close to unity, the volume fractions ϕ_3 and ϕ_4 are very small and can be neglected, since

$$\phi_3 = \phi_4 = \tfrac{1}{2}(1 - I_S) \tag{77}$$

Therefore, the mean concentrations are given by:

$$\overline{C}_a = I_S \overline{C}_{a0} \tag{78}$$

$$\overline{C}_b = I_S \overline{C}_{b0} \tag{79}$$

Using Eqs. 78 and 79 in Eq. 73, we recover the proper limit of the covariance for very fast reaction

$$\overline{c_a c_b} = -\overline{C}_a \overline{C}_b \tag{80}$$

Therefore, the closure model derived from the 4E model at the pure mixing asymptote (Eq. 71) satisfies both the limits of pure mixing (Eq. 18) and fast reaction (Eq. 19). Equation 71 is easily extended to the second reaction of a parallel-consecutive reaction scheme (Eqs. 1 and 2) as follows:

$$\overline{c_r c_b} = \overline{C}_r \overline{C}_b - I_S \overline{C}_r \overline{C}_{b0} + \overline{C}_r \overline{C}_b (I_S^3 - I_S^2 + I_S - 1) \tag{81}$$

Fast Reaction Asymptote

If Equations 74–76 are substituted into Eq. 67, the result is:

$$\overline{c_a c_b} = -\overline{C}_a \overline{C}_b \tag{82}$$

which is the proper fast reaction-limiting expression. But, as discussed earlier, this is not a useful closure equation for finite reaction rates.

It is intriguing to note that in the limit of very fast reaction with stoichiometric feed, both the 3E and 4E model predict the same relationship between mean and feed concentrations of species A and B (Eqs. 63 and 78, and Eqs. 64 and 79). It should be recognized that this relationship is different from that obtained by Toor (1969) who arrived at

$$\overline{C}_a = \sqrt{I_S \overline{C}_{a0}} \tag{83}$$

This disagreement, however, is not a weakness of the 3E and 4E models because Toor's approach has been criticized for being based on a Gaussian distribution of concentration fluctuations in the limit $Da \to \infty$ which is unrealistic (Kosály, 1987). The 3E, 4E and CRD models are actually based on a bimodal distribution (cf., Eq. 26) which is more realistic for $Da \to \infty$.

Summary of Closure Models

Four different mechanistic models have been examined to derive closure models based on pure mixing and very fast reaction assumptions. The resulting equations are compiled in Table 1, which summarizes the source mechanistic model, the asymptotic assumption and resulting closure equation, and an indication of whether the equation satisfies the pure mixing and infinite reaction limits. As indicated in the table, the closure models derived from the pure mixing asymptote satisfy the pure mixing limit and those derived from the fast reaction asymptote satisfy the infinite reaction limit. Only two closure models, those derived from the 3E and 4E models at the pure mixing asymptote satisfy both limits. Note that the CRD and 3E models under the pure mixing assumption produce the same closure equation.

It has not been possible, however, to prove that this equation satisfies the infinite reaction limit from a basis of the CRD model whereas this can easily be demonstrated for the 3E model. It is also important to realize that the 4E model under the pure mixing assumption produces a closure equation which is nearly identical to the one associated with the CRD and 3E models under the same assumption. It differs by the term $I_S^2(1 - I_S)\overline{C}_a\overline{C}_b$ which has a coefficient approaching zero in the extreme limits ($I_S \to 0, 1$) and having a maximum value of only 0.15 at $I_S = 0.67$. Thus closure equation (Eq. 3) of Table 1 (and the nearly identical Eq. 5) can be derived from three different mechanistic models (3E, 4E, and CRD) and thus possesses a certain generality. In addition, it has the virtue of satisfying both the pure mixing and infinite reaction rate limits, and it can be applied to multiple reaction cases. This last point is amplified below.

For the parallel-consecutive scheme (Eqs. 1 and 2) with A and B in separate feedstreams, the closure equation for the second reaction ($\overline{c_r c_b}$) is obtained from Eq. 3 (Table 1) by replacing the subscript a by r and noting that $\overline{C_{r0}} = 0$. This same procedure applied to Eq. 1 (Table 1) produces $\overline{c_r c_b} = 0$, a result suggested approximately by Bourne and Toor (1977) which has been shown to be of limited validity (Kosály, 1988). Note also that Eq. 3 (Table 1) produces a nontrivial expression for a reaction between components, neither of which is present in a feedstream. Thus, this closure approximation may be useful for describing reacting mixtures of considerable complexity.

Comparison with Experiments of Vassilatos and Toor

First, we will model the experiments of Vassilatos and Toor (1965) using the various closure equations summarized in the preceding section. In these often quoted experiments, single, irreversible, second-order reactions ($A + B \to P$; $r_a = -kC_aC_b$) were studied in an isothermal, turbulent flow, tubular reactor. The hydrodynamics were maintained constant while the reaction rate was varied over nine orders of magnitude. For brevity, we restrict ourselves to simulation of only three experiments, although they span the entire range of reaction rates (see Table 2). In these experiments, the two aqueous reactant solutions were separately introduced through 100 alternate jets, and the reaction proceeded in the resulting microscale inhomogeneous mixture. Since no RTD measurements were reported, it has generally been assumed in models of this reactor that an ideal plug flow RTD is appropriate. Since the flow rate of each stream was maintained constant, the feed stoichiometry was varied by changing the concentration in one of the feed streams. This work of Vassilatos and Toor has been used widely for the validation of models of mixing and chemical reaction (e.g., Kattan and Adler, 1967; Harris and Srivastava, 1968; Mao and Toor, 1970; Rao and Dunn, 1970).

In a previous work, Mehta and Tarbell (1983b) simulated Vassilatos and Toor's data with both the 3E and 4E models assuming a plug flow RTD. For each model, they determined the value of the parameter R_S which provided the best fit (mean square error minimization) to the entire data set. That resulted in a value of $\tau_m = 0.0082$ s through the use of the turbulence

Table 1. Summary of Closure Models

Source Model	Pure Mixing Asymptote	Satisfy Limit: Pure Mixing	Satisfy Limit: Infinite Reaction	Fast Reaction Asymptote	Satisfy Limit: Pure Mixing	Satisfy Limit: Infinite Reaction
3E	3**	Yes	Yes	4**	No	Yes
4E*	5	Yes	Yes	2	No	Yes
CRD	3	Yes	?	2	No	Yes
IEM	1	Yes	No	2	No	Yes

$$\overline{c_a c_b} = -I_S \bar{C}_{a0}\bar{C}_{b0} \quad (1)$$

$$\overline{c_a c_b} = -\bar{C}_a\bar{C}_b \quad (2)$$

$$\overline{c_a c_b} = -I_S(\bar{C}_a\bar{C}_{b0} + \bar{C}_{a0}\bar{C}_b - \bar{C}_a\bar{C}_b) \quad (3)$$

$$\overline{c_a c_b} = \bar{C}_a\bar{C}_b - I_S\bar{C}_{a0}\bar{C}_b - I_S\bar{C}_a\bar{C}_{b0} \quad (4)$$

$$\overline{c_a c_b} = -I_S(\bar{C}_a\bar{C}_{b0} + \bar{C}_{a0}\bar{C}_b - \bar{C}_a\bar{C}_b) + I_S^2(1 - I_S)\bar{C}_a\bar{C}_b \quad (5)$$

*Valid for equal flow rates.
**Numbers denote the equations at the bottom of the table.

analogy. In the present work, we used this value of τ_m to simulate the three cases listed in Table 2.

The mathematical model of Vassilatos and Toor's reactor consists of the averaged material balances (Eqs. 4–9 with $k_2 = 0$), the closure model equations summarized in Table 1 [Eq. 1, Toor (T); Eq. 3, 3E slow reaction asymptote; Eq. 4, 3E fast reaction asymptote; Eq. 5, 4E slow reaction asymptote], the intensity of segregation profile (Eqn. 15), the micromixing parameter τ_m, and the kinetic parameters of Table 2. The same value of the micromixing parameter ($\tau_m = 0.0082$ s) was used for all models and all operating conditions. The simulations were carried out with an ordinary differential equation solver based on Gear's method (IMSL subroutine DGEAR). Relative error parameters were maintained at 10^{-6} for the simulations. Reduction of error parameters to 10^{-7} had a negligible effect on the results.

Figures 2–4 display the model predictions for the four closure schemes as compared to the experimental data of Vassilatos and Toor (1965). Data points for the experimental runs were taken from Vassilatos (1965). Note that the 3E slow and 4E slow closure predictions are virtually identical for this set of data. For the slow reaction (Figure 2) and moderately fast reaction (Figure 3), the Toor closure (T) and 3E/4E slow closures are essentially equivalent and they all fit the experimental conversion profile very well. Predictions of the 3E fast closure for the slow reaction case (Figure 2) are in poor accord with the data, unlike the other three models. This is not surprising since the 3E fast closure model does not satisfy the slow reaction (pure mixing) limit. For moderately fast and very fast reactions (Figures 3 and 4), the predictions of the 3E fast closure are closer to the experimental data. For very fast reactions (Figure 4), the 3E/4E slow closures seem to provide the best fit to the data.

Comparison with Experiments of Mao and Toor

Mao and Toor (1971) conducted experiments in the same reactor used by Vassilatos and Toor (1965), but with improved design of the mixing device. More stainless steel tubes were installed in the mixer to reduce any back flow in the regions between the jets of the mixing head as well as to improve the flow in the reactor. The data obtained in this work were more accurate than those of Vassilatos and Toor's work, especially for the moderately fast reaction rate.

Since the mixing device was changed, it was necessary to estimate the micromixing time, τ_m, in the reactor. This was done by fitting Toor's closure and the 3E closure independently to the data for very fast acid-base reaction. These two closure models fit the fast reaction data very well (Figure 5) with somewhat different micromixing times ($\tau_m = 0.0067$ s for Toor; $\tau_m = 0.0095$ s for 3E). Although the decay of variance in their reactor was originally modeled by a power law (Figure 3 of Mao and Toor, 1971), it can be well approximated by an exponential decay function such as Eq. 15, within the length of the reaction zone. In fact, the use in Eq. 15 of $\tau_m = 0.0067$ s, as obtained from fitting fast reaction data, leads to a very good prediction of the variance decay. Since the predictions of the 4E slow closure are virtually identical to those of the 3E slow closure, only 3E slow closure predictions are shown in the subsequent figures. The 3E fast closure will not be considered further because of its inability

Table 2. Parameters for Simulated Experiments of Vassilatos and Toor (1965)*

Case	Reaction Type	Reaction	Rate Constant k $m^3/mol/s$	Stoichiom. Ratio β**	Conc. of Limiting Reactant mol/m^3
I	Slow	$CH_3COOH + NaOH$	4.7×10^{-2}	1.56	13.69
II	Moderately Fast	$CO_2 + 2NaOH$	1.24×10^{1}	1.26	6.99
III	Very Fast	$HCl + NaOH$	1.0×10^{8}	1.75	13.94

*Average axial flow velocity was 0.405 m/s.
**$\beta = (C_{B0}/nC_{A0})$.

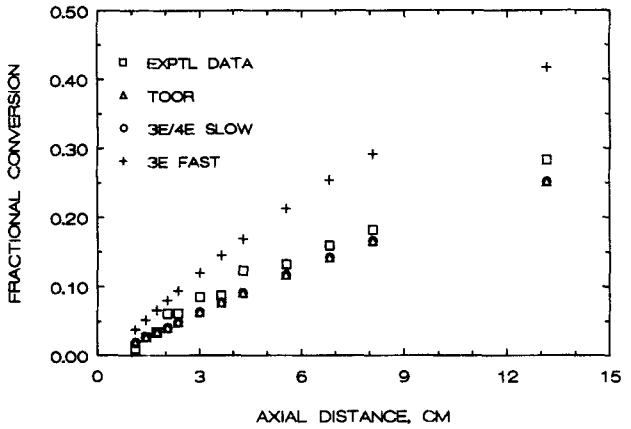


Figure 2. Predicted and measured profiles for the slow reactions of Vassilatos and Toor (1965).
$Da = 0.88$; $\beta = 1.56$

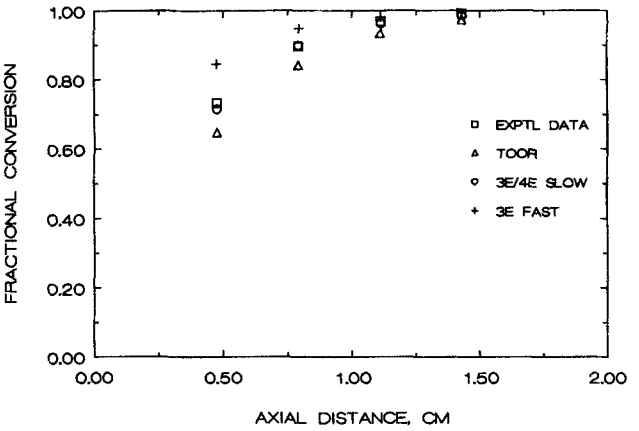


Figure 4. Predicted and measured profiles for the very fast reactions of Vassilatos and Toor (1965).
$Da \sim 10^9$; $\beta = 1.75$

to predict slow reaction data. The predictions for the moderately fast reaction of CO_2—2NaOH ($k = 8.32$ m^3/mol · s) are shown in Figure 6. The fits of models to data are fairly good. The effect of stoichiometry for the moderately fast reaction is shown in Figure 7 ($\beta = 1.5$) and Figure 8 ($\beta = 3.0$). Again, for this case, 3E slow closure and Toor's closure do a good job of fitting the data.

Therefore, we have demonstrated that the 3E slow closure model is able to fit single-reaction experimental data from reactors having slow to very fast reaction rates and varying feed stoichiometry.

Comparison with Experiments of Mehta and Tarbell

It has been recognized in recent years that rapid competing reactions, such as the parallel-consecutive reaction scheme described previously (Eqs. 1 and 2), are particularly sensitive to mixing. Mehta and Tarbell (1987) carried out experiments involving the azo coupling of 1-naphthol (A) with diazotised sulfanilic acid (B) to produce monoazo dye (R) and diazo dye (S) in an unmixed feedstream multijet tubular reactor under conditions where both reactions were mixing-limited. They found that several mechanistic micromixing models could be discriminated readily with their data. Therefore, the data of Mehta and Tarbell will next be used to evaluate the new closure models.

The reactor operating conditions, kinetic rate constants, mean axial velocity, and micromixing time constant required for simulation of Mehta and Tarbell's data are given in Table 3. The value of τ_m was determined by Mehta and Tarbell to provide the best fit of the four environment model to the data. It should be noted that the four environment model was the only mechanistic model tested which fit the data well and that the best fit value of τ_m was close to estimates based on turbulence measurements (Mehta and Tarbell, 1987). It should also be recognized that there is some uncertainty in the rate constants employed as three sets of values have been reported by Bourne and his coworkers (Bourne et al., 1981; Baldyga and Bourne, 1984; Bourne et al., 1985). The exact value of k_1 is not critical since it is three orders of magnitude larger than k_2. There is about a factor of two variation in the value of k_2 among the three studies reported. This variation, however, is not critical, as Mehta and Tarbell (1987) have shown that the sensitivity of model predictions to a twofold variation in the value of k_2 is not great and that slight changes in

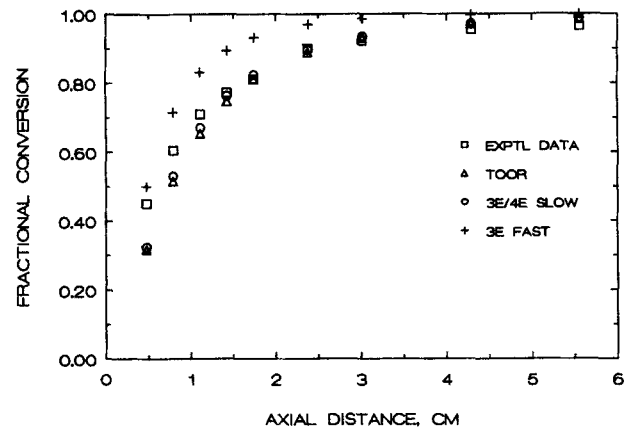


Figure 3. Predicted and measured profiles for the moderately fast reactions of Vassilatos and Toor (1965).
$Da = 119$; $\beta = 1.26$

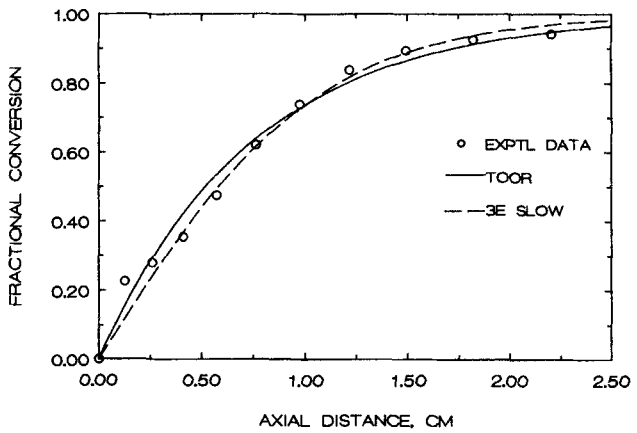


Figure 5. Predicted and measured profiles for the very fast reaction of Mao and Toor (1971).
$k = 1.4 \times 10^8$ m^3/mol · s; $\beta = 1$

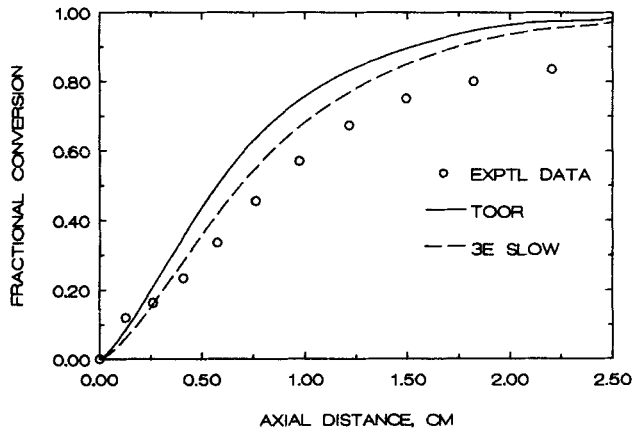


Figure 6. Predicted and measured profiles for the moderately fast reaction of Mao and Toor (1971).
$k = 8.32$ m^3/mol · s; $\beta = 1$

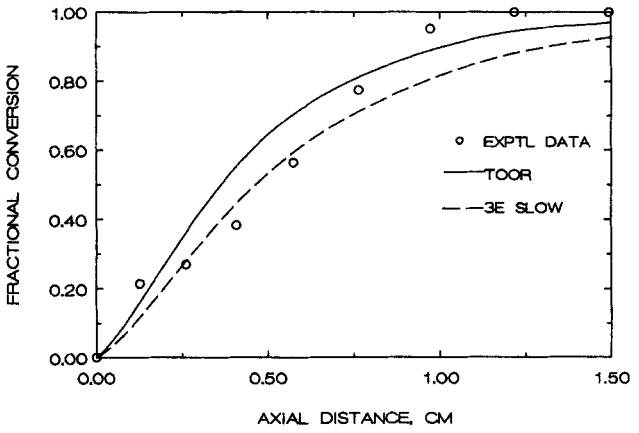


Figure 8. Predicted and measured profiles for the moderately fast reaction of Mao and Toor (1971).
$k = 8.32$ m^3/mol · s; $\beta = 3.0$

τ_m can compensate for changes in k_2. We have used the recent kinetic data of Bourne et al. (1985), which at the average reaction temperature of 27°C gives a k_2 value of 2.3 m^3/mol · s.

The closure model equations [Eqs. 11 and 12, Bourne and Toor (B-T); Eqs. 13 and 14, Brodkey and Lewalle (B-L); Eqs. 29 and 30, 3E slow asymptote ($3E\ S$); Eqs. 71 and 81, 4E slow asymptote ($4E\ S$)] were solved along with the material balances for each species (Eqs. 4–9) and the intensity of segregation profile (Eq. 15). The same value of the micromixing parameter ($\tau_m = 2$ s) was used for all models and all operating conditions. Although we refer to Eqs. 11 and 12 as the B-T model, we should realize that Bourne and Toor (1977) originally suggested $\overline{c_r c_b} \sim 0$ for purposes of qualitative discussion.

Figures 9–11 display the model predictions for the three closure schemes as compared to the experimental data of Mehta and Tarbell (1987). The 4E slow predictions are similar to the 3E slow predictions and are not displayed. Figure 9 ($\beta = 0.39$) does not contain data for the S profiles as S levels were below the level at which they could be measured with confidence. The 3E slow closure model provides a very good fit to the experimental R and S profiles over the entire range of operating conditions. The other models are less satisfactory.

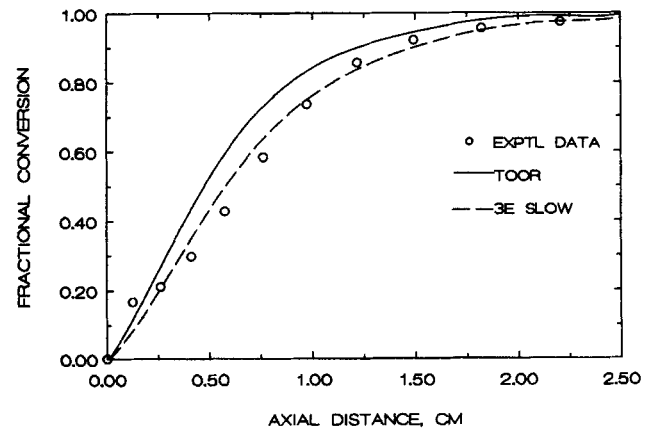


Figure 7. Predicted and measured profiles for the moderately fast reaction of Mao and Toor (1971).
$k = 8.32$ m^3/mol · s; $\beta = 1.5$

One might argue that the other models would look better if a different value of the micromixing parameter (τ_m) were employed. However, if we keep in mind the fact that τ_m should be the same for all operating conditions because the reactor was run under conditions of fixed hydrodynamics, then we see that a single value of τ_m cannot provide good predictions for all operating conditions. For example, the B-L model with $\tau_m = 2$ s fits the data reasonably well at $\beta = 0.39$ (Figure 9), but very poorly at $\beta = 1.0$ and 1.54 (Figures 10 and 11). The B-T model with $\tau_m = 2$ s fits the S profile very well at $\beta = 1.54$, but the fit of the R profile is inadequate, and the fits at $\beta = 0.39$ and 1.0 are less than satisfactory. It appears that only the 3E slow closure is capable of providing a satisfactory fit to all of the data with a single value of the micromixing parameter.

Comparison with Experiments of Li and Toor

Li and Toor (1986) measured the yield of the diazo-coupling reactions at complete conversion in a turbulent, tubular reactor with single and multijet feeds. Their data show that the yield of the intermediate product (R) decreased as mixing was retarded relative to the chemical kinetics by decreasing the Reynolds number, using a less efficient mixing device, or increasing the feed concentrations. The experiments were carried out at 22°C at which condition $k_2 = 1.8$ m^3/mol · s (Bourne et al., 1985). Again, the precise value of k_1 is not required since it is three orders of magnitude larger than k_2.

For simulation of their experimental data, the micromixing time (τ_m) in their reactor must be determined. To accomplish this, we used Li and Toor's data on the yield of the intermediate (R) as a function of the Reynolds number. The 4E slow closure

Table 3. Parameters for the Reactor of Mehta and Tarbell (1987)

Q_1	Q_2	C_{a0}	C_{b0}	$\beta = Q_b C_{b0}/Q_a C_{a0}$
cm^3/s		mol/m^3		
131.0	1.31	0.3	30.0	1.00
136.0	2.12	0.3	29.5	1.54
135.0	2.13	0.3	7.45	0.39

$k_1 = 7.3 \times 10^3$ m^3/mol/s; $k_2 = 2.3$ m^3/mol/s; $\tau_m = 2.0$ s; $U = 7.6$ cm/s

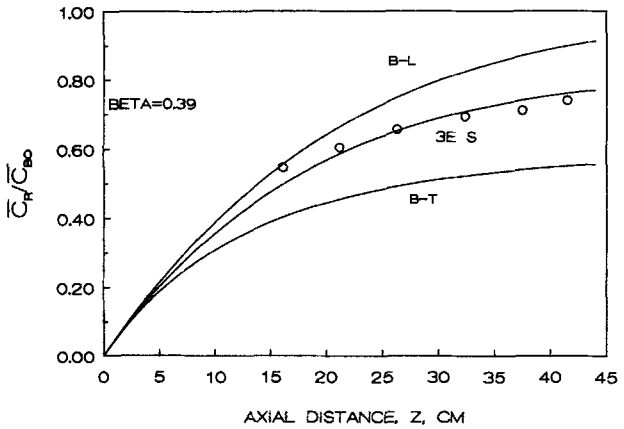
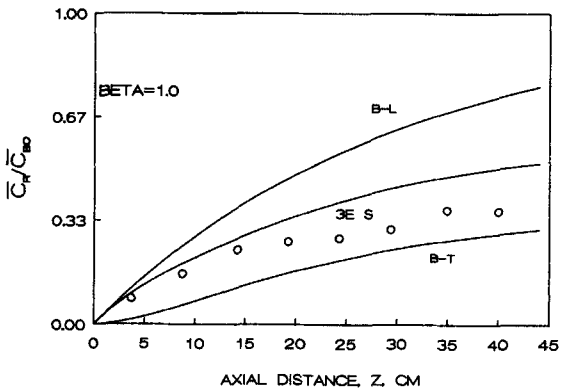


Figure 9. Predicted and measured profiles for the parallel-consecutive reaction scheme of Mehta and Tarbell (1987).
$\beta = 0.39$

model (Eqs. 71 and 81) was used to fit the experimentally determined yield by adjustment of the mixing time (τ_m). One might reasonably ask: how can this data fitting exercise be used to evaluate the closure models? First, the best fit values of τ_m should decrease with increasing Reynolds number (more intense



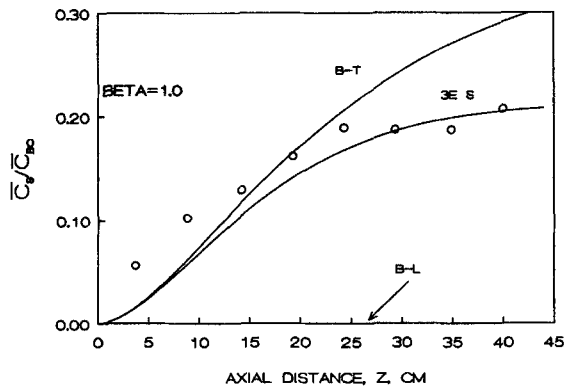
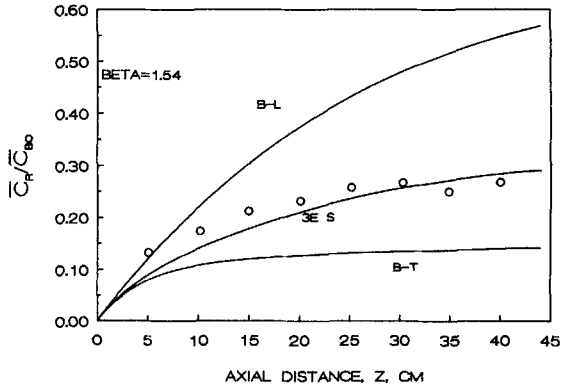


Figure 10. Predicted and measured profiles for the parallel-consecutive reaction scheme of Mehta and Tarbell (1987).
$\beta = 1.01$



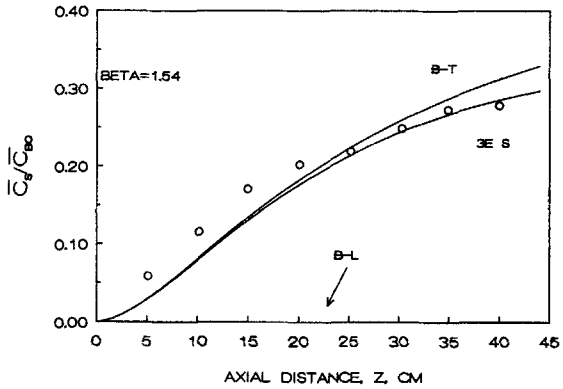


Figure 11. Predicted and measured profiles for the parallel-consecutive reaction scheme of Mehta and Tarbell (1987).
$\beta = 1.54$

turbulence). Second, and a much more severe constraint, the value of τ_m, determined for one Reynolds number should be the same for other experimental runs conducted at the same Reynolds number, even when the Damköhler number is altered by varying the feed concentration. Once the values of τ_m were obtained in such a fashion, the same value was used to simulate the experimental data with the 3E slow closure model (Eqs. 29 and 30).

The adequacy of the 4E slow closure model to predict the yield of R at a fixed Reynolds number when the feed concentration is varied is shown in Figure 12. At each Reynolds number, one value of the experimental yield was used to calculate the micromixing time, τ_m, and the same value of τ_m was used for other feed concentrations. The data for $Re = 1{,}000$ are for the multiple-jet reactor and the data at higher Reynolds numbers are for the single-jet reactor. Clearly, the closure model predicts the experimental yield satisfactorily with a single value of τ_m at a fixed Reynolds number.

Li and Toor report two different data sets: one each for a single-jet reactor and a multiple-jet reactor. For the single-jet reactor, they employed three different Reynolds numbers and three different feed concentrations at each Reynolds number. For the multiple-jet reactor, only one Reynolds number was used while the feed concentration was varied. Li and Toor found the closure models of Bourne and Toor (1977) and Brodkey and Lewalle (1985) to be inadequate for their data prediction. Figures 13

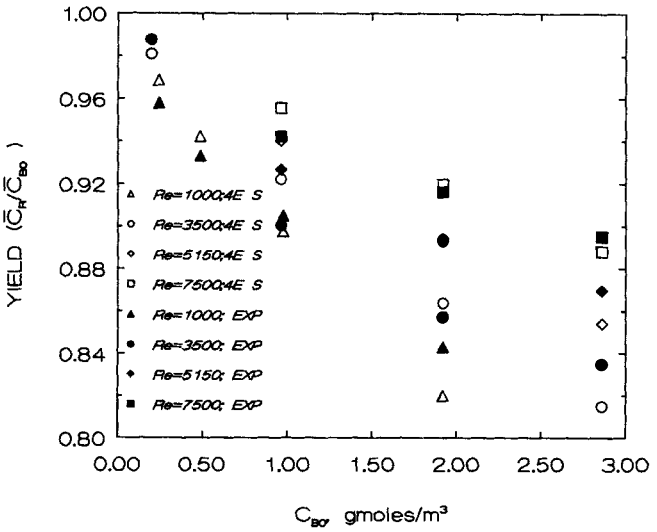


Figure 12. Yield of intermediate product vs. feed concentrations at different Reynolds numbers for the data of Li and Toor (1986).

and 14 display the model predictions of the 3E slow closure, 4E slow closure, and the closure model employed by Li and Toor (L-T), for the single-jet and the multiple-jet reactor, respectively. The closure models of the present work result in a good fit to the experimental yield.

In order to quantify how well a model fit the experimental data, Li (1985) computed the standard deviation between experimental data and theoretical prediction (σ_e) for each reactor. For the single-jet reactor, we find: $\sigma_e = 0.019$ for the 3E slow closure; $\sigma_e = 0.013$ for the 4E slow closure; and $\sigma_e = 0.011$ for Li and Toor (L-T) closure. For the multiple-jet reactor, we find: $\sigma_e = 0.015$ for the 3E slow closure; $\sigma_e = 0.01$ for the 4E slow closure; and $\sigma_e = 0.05$ for Li and Toor (L-T) closure.

Discussion

Simple models for closing direct turbulence equations have been derived from various mechanistic models of turbulent

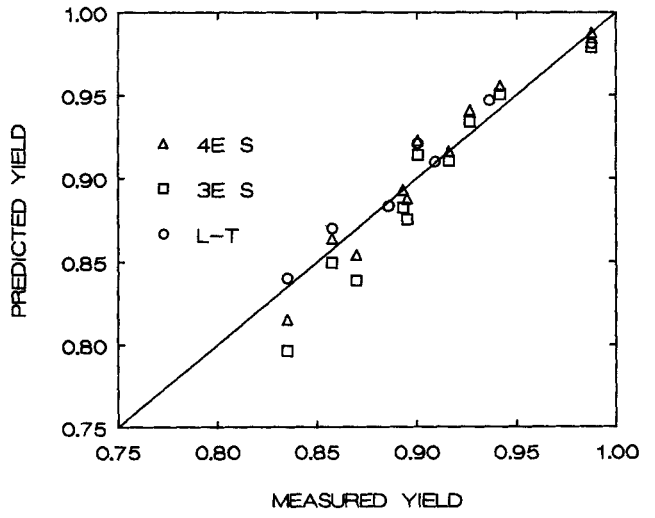


Figure 13. Comparison of predicted with measured yield in single-jet reactor of Li and Toor (1986).

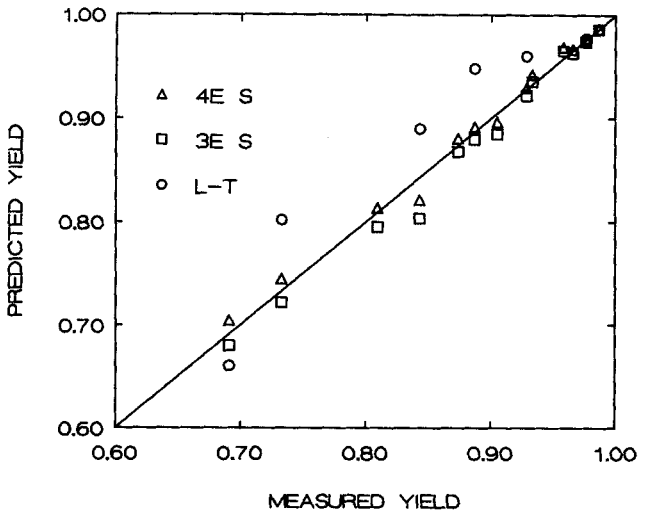


Figure 14. Comparison of predicted with measured yield in multijet reactor of Li and Toor (1986).

micromixing using the asymptotes of slow and fast reactions. Although the mechanistic models start from different points of view, they yield similar closure models. The two new closure models which were evaluated in this paper (3E slow closure and 4E slow closure at equal flow rates) have much in common, and indeed they result in similar predictions for the experimental data evaluated.

The essential philosophy we have used in developing closure models is the one postulated by Toor (1969). However, Toor's approach has recently come under scrutiny, and Kosály (1987) has questioned the use of a Gaussian distribution function for the conserved scalar ($C = A - B$) at short times. Using a more realistic bimodal shape for the distribution function for short times, he has shown that the covariance of concentration fluctuations for a fast, stoichiometric reaction is actually $2/\pi$ times that for pure mixing of two species without reaction. However, as pointed out by Kosály (1987), in actual finite rate cases, the error involved in closing the covariance term ($\overline{c_a c_b}$) by the data taken from pure-mixing experiments may not be too large. In a recent article, Givi and McMurtry (1988) have shown via direct numerical simulation that indeed the factor $2/\pi$ is reached asymptotically for fast reaction. Based on this result, the authors concluded that the application of Toor's hypothesis is not appropriate and should be replaced by the factor $2/\pi$. Their results, however, are not in agreement with those previously obtained by Leonard and Hill (1987), who found little change in the covariance of the concentration fluctuation with different reaction rates. Their direct numerical simulation results agree reasonably well with Toor's closure (Eq. 10) in predicting the conversion profile in a plug flow reactor with separate feedstreams. We suspect that, although Toor's closure is not exact for infinite reaction rate, the error involved in its use for finite but large rate reaction cases is not too great.

It is of interest to note that, although the 3E slow closure model (Eqs. 57 and 59) was successful in predicting experimental data for single and parallel-consecutive reaction schemes, the 3E mechanistic model itself was unable to do so (Mehta and Tarbell, 1983b, 1987). The inability of the 3E mechanistic model to predict conversion and selectivity for the multiple-reaction scheme was attributed to the fact that it has only one

reacting region, *viz.*, the leaving environment (Mehta and Tarbell, 1983a). Indeed, the 4E model was developed to improve this situation by introducing two reacting regions, one A-rich and one B-rich in a reactor fed with A and B in separate streams. Inspection of the closure equation for the 3E model (Eq. 57) reveals that it has three terms and each could be construed as a contribution from a different reacting region, i.e., A-rich ($\overline{C}_{a0}\overline{C}_b$), B-rich ($\overline{C}_a\overline{C}_{b0}$), and mean reacting region ($\overline{C}_a\overline{C}_b$). This feature of the 3E slow closure model (contributions to reaction from the extremes of the concentration distribution) seems to be responsible for its success and distinguishes it from the 3E mechanistic model itself.

In a recent article, Kosály (1988) determined conditions for the validity of the Bourne and Toor (B-T) closure and the Brodkey and Lewalle (B-L) closure models for series-parallel reactions. If the characteristic times of the first and the second reaction are defined as $\tau_1 = 1/k_1C_{b0}$ and $\tau_2 = 1/k_2C_{b0}$, then the Damkohler numbers of the two reactions can be defined as $Da_1 = \tau_m/\tau_1$, $Da_2 = \tau_m/\tau_2$, where τ_m is the characteristic time of turbulent micromixing. Kosály concluded that both the B-T and the B-L closure schemes are valid if $Da_2 \ll 1$. In the experiment of Mehta and Tarbell (1987), $Da_1 \gg 1$ and $Da_2 \sim 0(1)$. Therefore, the application of the B-T and B-L closure is not appropriate, as was indeed found from the simulations. Li and Toor's (1986) data indicate that in their reaction $Da_1 \gg 1$ and Da_2 (based on slab thickness and turbulence analogy) varied from about 0.015 to 0.7, which again makes the B-T and B-L closure schemes of marginal validity for this case. However, since the series-parallel reactions appear to offer a stringent test of closure models for reactive mixing, the success of the 3E slow closure and the 4E slow closure models developed in this paper for these two experimental data sets seems to indicate that they can be applied with confidence to reactions of moderate rate. Direct numerical simulation results for the series-parallel reaction scheme over a broad range of Da_2 are required to further evaluate the closure models.

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Notation

A, B, R, S = chemical species
C_j = concentration of species j
c_j = fluctuating concentration of species j
C_{j0} = initial (feed) concentration of species j
CRD = coalescence-redispersion model
D = molecular diffusion coefficient
Da = Damkohler number
EE = entering environment
f = residence-time distribution function
h = micromixing parameter of IEM model
I = micromixing parameter of CRD model
I_S = intensity of segregation
IEM = interaction by exchange with mean model
k, k_1, k_2 = rate constants
L_S = integral length scale of concentration field
m = flow rate ratio, $Q_1/(Q_1 + Q_2)$
N = number of eddies
n = sample size
N_{Sc} = Schmidt number
p = probability density function of reactor population
PFR = plug flow reactor
Q_i = volumetric flow rate of stream i
r_1, r_2 = reaction rate
Re = Reynolds number
R_S = micromixing parameter of three- and four-environment model
RTD = residence-time distribution
SD = slab diffusion model
U = mean velocity
u = coalescence rate
v_z = axial velocity
y = yield of parallel-consecutive reaction
z = axial distance down the reactor

Greek letters

α = flow rate ratio
β = feed stoichiometric ratio, Q_bC_{b0}/Q_aC_{a0}
δ = Dirac delta function
ϵ = turbulent energy dissipation rate per unit mass
ϕ = volume fraction
ν = kinematic viscosity
σ^2 = variance of concentration distribution
σ_2^0 = initial or feed value of σ^2
σ_e = standard deviation
τ = mean residence time
τ_1, τ_2 = characteristic reaction time
τ_m = micromixing time
Ω = domain of concentration

Subscript

A, B, R, S = chemical species
i, j = index variables
0 = feed condition

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