

Four Environment Model of Mixing and Chemical Reaction

Part I. Model Development

A new mathematical model (the four environment model) to describe turbulent flow chemical reactors with complex reactions and separate reactant feed streams is developed. The feed stream residence time distributions, the batch chemical kinetics, and a single turbulent micromixing parameter, which may be estimated from direct turbulence theory, are required as input information to the model. The model is computationally efficient as it involves only ordinary differential equations.

R. V. MEHTA and
J. M. TARBELL

Department of Chemical Engineering
and Center for Air Environment Studies
The Pennsylvania State University
University Park, PA 16802

SCOPE

Mixing and chemical reaction are concurrent phenomena in many chemical reactors, particularly those of industrial scale. The design and development of reactors with unmixed feedstreams, complicated large-scale mixing patterns, and competing chemical reactions is a challenge which often requires significant pilot-plant experience. A mathematical model capable of describing these complex chemical reactor phenomena is clearly desirable. However, most existing models are either too complex—involving many empirical parameters, or too inefficient computationally—requiring the solution of coupled partial differential equations or Monte Carlo simulations. A notable exception is the three environment model of Ritchie and Tobgy

(1979), which is computationally efficient and provides a reasonable description of the mixing processes. Unfortunately, the three environment model does not properly account for the effect of micromixing on the selectivity of competing reactions—a significant problem in industrial reactor design.

Our objective in this work was to develop a computationally efficient mathematical model of mixing and chemical reaction which would retain the overall structure and desirable features of the three environment model while allowing a more realistic description of the effect of micromixing on selectivity of competing reactions.

CONCLUSIONS AND SIGNIFICANCE

We have developed a computationally efficient chemical reactor model (the four environment model), having an ordinary differential equation structure, which can account for competing chemical reactions, arbitrary macromixing patterns, and turbulent micromixing of unmixed reactants. The input information required by the model includes: the (perfectly mixed) batch chemical kinetics; the residence time distribution function for each reactor feedstream; and a single micromixing parameter which may be determined by a reactive tracer experiment. An analogy between the four environment model and isotropic turbulence mixing as expressed in the theories of Corrsin (1964) and Rosensweig (1964) provides a means of estimating (corre-

lating) the micromixing parameter from knowledge of the reactor geometry and the power input.

The four environment model is a refinement and extension of the three environment model of Ritchie and Tobgy (1979). By adding an additional "leaving environment" (the three environment model has only one leaving environment) to the three environment model we allow for reacting regions which are rich in each of the reactants in a two feedstream reactor. We feel that this feature is the key to proper modeling of selectivity which is required in many industrial chemical reactor designs. Extensive comparisons of the four environment model with experimental data are provided in Part II.

1. INTRODUCTION

In this paper we present a new model to describe turbulent flow chemical reactors having complex kinetics and reactant feedstreams with an arbitrary degree of premixing. The phenomena involved in turbulent flow chemical reactors are very complex and

despite numerous research efforts in the past, the mutual interactions of flow, mixing, and chemical reaction remain poorly understood. Several of the more popular approaches to turbulent reactor modeling are discussed below.

Hill (1979) terms the conventional approach of solving the Navier-Stokes and component continuity equations as "dynamical turbulence modeling." The closure scheme associated with any such model is somewhat arbitrary and regardless of the order of

the scheme adopted, no *a priori* success can be guaranteed. Addition of complex kinetics to this problem leads to staggering computational requirements and makes this approach rather unattractive.

In "mechanistic turbulence models" (Hill's terminology), a few dominant mechanisms in the overall transport process are singled out permitting the formulation of a relatively simple model which can be solved exactly. The characteristic parameters of such models are generally determined by empirical data fitting, and this must be considered an undesirable feature. However, the simplicity of these models offers the possibility of computational efficiency in problems involving complex kinetics.

Of the many mechanistic models (e.g., mixing length models, surface renewal models), we consider the "population balance" models to hold the most promise for complex chemical reactor analysis. Population balance models have been broadly classified by Ritchie et al. (1978) as (1) Coalescence-Redispersion Models and (2) Environment Models.

In Coalescence-Redispersion Models as originated by Curl (1963), the reactor volume is treated as an ensemble of fluid droplets ("eddies") which coalesce randomly—two at a time, at some characteristic frequency which is the mixing parameter of the model. This coalescence is followed by instantaneous concentration homogenization and redispersion. Between collisions, each droplet behaves as a batch reactor. The coalescence-redispersion frequency may be determined experimentally from fast reaction (mixing limited) data. One of the positive features of the Coalescence-Redispersion Model developed by Curl (1963) is its analogy to the theory of isotropic turbulence. Evangelista et al. (1969) pointed out that the frequency parameter of Curl's model can be estimated readily with Corrsin's turbulent mixing theory (Corrsin, 1957). However, the integro-partial differential equation of the model is difficult to solve. Approximate analytical (e.g., Evangelista et al., 1969) and numerical (e.g., Curl, 1963; Shain, 1966) methods have been suggested, but have found only limited applicability. Instead, such random coalescence models are often simulated by Monte Carlo techniques, which are computationally laborious (e.g., Spielman et al., 1965; Kattan et al., 1967; Harris et al., 1968; Rao et al., 1970; Treleaven et al., 1972). This is especially true for reactors with complex kinetics.

Environment models assume that the reactor volume consists of two or more separate environments having extreme states of mixedness—either total segregation or maximum mixedness (Danckwerts, 1958; Zwietering, 1959). Turbulent diffusion is modeled either by splitting the feed into segregated and maximum mixedness environments and combining them at the reactor exit, with no interaction among the "parallel" environments (e.g., Villermaux et al., 1969) or by sending the entire feed stream into a segregated "entering" environment and subsequently transferring it to a maximum mixedness "leaving" environment at a prescribed rate—the effluents of these "series" environments being combined at the reactor exit (e.g., Ng and Rippin, 1965). Several variations of these environment models have been proposed—differing either in structure of environment interaction or in terms of transfer rates (Weinstein and Adler, 1967; Nishimura and Matsubara, 1970). Most recently, Ritchie (1980) incorporated coalescence-redispersion features into an environment model structure. Environment models offer substantial computational economy and are relatively simple, easy-to-use, and versatile. However, none of them has been compared extensively against experimental data.

Of all the environment models developed to date, the one which comes closest to satisfying the demands of a general chemical reactor model is the "three environment model" of Ritchie and Tobgy (1979). This model is an outgrowth of Ng and Rippin's original "two environment model" for a premixed feed reactor (Ng and Rippin, 1965). In the three environment model, two entering environments (E.E.'s), one for each reactant feedstream in a two reactant system, are assumed to supply a single leaving environment (L.E.) at rates proportional to their respective masses. While each E.E. acts as a totally segregated reactor, the L.E. behaves as a maximum mixedness reactor. The model can accommodate

unmixed feed flow reactors having arbitrary feed flow rates and arbitrary stream residence time distributions (RTD's). It has been compared favorably with chemical reactor data in the case of a single reaction in a plug-flow-type reactor (Ritchie and Tobgy, 1979). However, it has not been compared with data for complex (more than one reaction) chemical reactors where selectivity is of paramount importance.

The model we develop in this paper is a refinement and extension of the three environment model and our presentation is organized as follows: First we establish an analogy between the three environment model and the theory of isotropic turbulent mixing as expressed by Corrsin (1964) and Rosensweig (1966). As a result we are able to show how the micromixing parameter of the three environment model is related to turbulence properties and how it may be estimated *a priori*. Subsequently, we suggest that the three environment model has intrinsic limitations associated with the structure of its leaving environment which make it inappropriate for modeling reactors with complex kinetics. This is demonstrated in Part II. To overcome this limitation, the leaving environment is modified to what we call a "two eddy" form. This new model, applicable to complex reactors, contains elements of both the coalescence-redispersion models and the environment models. Its mixing parameter can be related to turbulence properties; it can accommodate arbitrary flow rates and residence-time distributions; and it is computationally efficient.

Since the three environment model is the starting point for our model, it is described in some detail in the next section.

2. THREE ENVIRONMENT MODEL

A schematic representation of the three environment model in the case of two feedstreams is shown in Figure 1. Reactants A and B are admitted through their respective entering environments where they reside unreacted for their age (α) and subsequently transfer to the single leaving environment where they spend their residual lifetime (λ) reacting. The entering environments are totally segregated and the leaving environment is maximally mixed. Each feedstream is characterized by a flow rate (Q_i), a residence time-distribution (f_i) and composition variables (e.g., C_{A2}^0).

At any time t , a fraction $F_i(t)$ of the population of fluid elements at the reactor exit entered via stream i and remained in the reactor

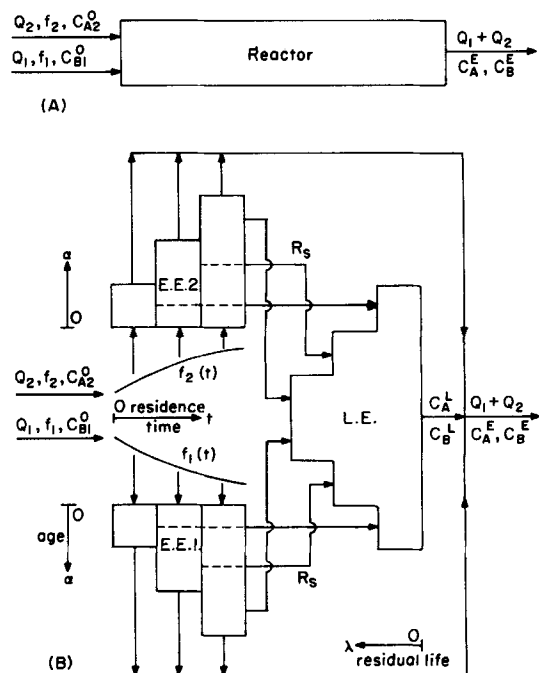


Figure 1. Schematic representation of three environment model: (A) actual reactor; (B) the model.

for a time between 0 and t . This fraction is related to the residence time-distribution of stream i in a simple way,

$$f_i(t) = \frac{d}{dt} F_i(t) \quad i = 1, 2, \quad (1)$$

and to the hold up volumes of the streams which are given by

$$V_i = Q_i \int_0^\infty (1 - F_i(t)) dt \quad i = 1, 2. \quad (2)$$

The transfer of material between environments is assumed to be first order in the mass of the entering environment and is described by a transfer function which depends only on the age,

$$T(\alpha) = \exp(-R_S \alpha), \quad (3)$$

where R_S is the micromixing parameter of the model.

Material balance considerations lead to the following mathematical description of the leaving environment (see Ritchie and Tobgy, 1979, for details):

$$\frac{dC_A^L}{d\lambda} = r_A + \frac{R_S[(III_1 V_1 + III_2 V_2) C_A^L - III_2 V_2 C_{A2}^0]}{II_1 V_1 + II_2 V_2}, \quad (4)$$

where $C_A^L(\lambda)$ is the concentration of species A in the leaving environment, r_A is the intrinsic chemical reaction rate and,

$$II_i = \frac{1}{\tau_i} \int_0^\infty [1 - \exp(-R_S \alpha)] f_i(\alpha + \lambda) d\alpha; \quad i = 1, 2 \quad (5)$$

$$III_i = \frac{1}{\tau_i} \int_0^\infty \exp(-R_S \alpha) f_i(\alpha + \lambda) d\alpha; \quad i = 1, 2 \quad (6)$$

with τ_i representing the mean residence time of stream i . The boundary condition is given by

$$\left. \frac{dC_A^L}{d\lambda} \right|_{\lambda=\infty} = 0. \quad (7)$$

The reactor exit concentration is obtained by mixing effluents from the entering and leaving environments,

$$C_A^E = \frac{1}{Q_1 + Q_2} [(II_1|_{\lambda=0} V_1 + II_2|_{\lambda=0} V_2) C_A^L(0) + III_2|_{\lambda=0} V_2 C_{A2}^0]. \quad (8)$$

The three environment model, briefly outlined above, is attractive because it accounts for macromixing (through the residence-time distributions), micromixing (through the parameter R_S), and chemical kinetics (multiple reactions are readily included) all within the computationally efficient format of ordinary differential equations. It has been compared favorably with experimental data (a single liquid-phase reaction in a confined jet reactor) with values of micromixing parameter, $R_S \tau$ being nearly constant (Ritchie and Tobgy, 1979). However, the physical significance of R_S has not been elucidated (Section 3) and the ability of the model to accurately describe the effect of mixing on selectivity in complex reactions has not been demonstrated (Part II).

3. TURBULENCE ANALOGY FOR THREE ENVIRONMENT MODEL

Corrsin (1957, 1964) derived a simple expression for the time dependence of the variance (σ^2) in concentration inhomogeneity of an inert tracer in a batch mixer. He assumed that the turbulence was isotropic, homogeneous and stationary, and by making ingenious dimensional arguments, arrived at

$$\frac{\sigma^2}{\sigma_0^2} = \exp(-\tau/\tau_m), \quad (9)$$

where τ is time and τ_m is a time scale of mixing characteristic of the fine structure of the turbulence. The following estimates of τ_m have been provided:

$$\tau_m \approx 0.5(4(L_S^2/\epsilon)^{1/3} + (\nu/\epsilon)^{1/2} \ln N_{Sc}); N_{Sc} \gg 1 \text{ (liquids)} \quad (10a)$$

$$\tau_m \approx \frac{2}{(3 - N_{Sc}^2)} (5/\pi)^{2/3} (L_S^2/\epsilon)^{1/3}; N_{Sc} \leq 1 \text{ (gases)} \quad (10b)$$

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 batch mixer expression (Eq. 9) applies to steady-state plug-flow mixers when τ is interpreted as the residence time.

Rosensweig (1964, 1966) analyzed turbulent micromixing in a continuous flow (steady state), perfectly stirred vessel. By considering the conservation of "unmixedness," he derived the following expression for the concentration variance of an inert tracer:

$$\frac{\sigma^2}{\sigma_0^2} = (1 + \tau/\tau_m)^{-1} \quad (11)$$

In Eq. 11, τ is the mean residence time of the vessel and τ_m is a characteristic turbulent mixing time scale having the following estimate based on isotropic turbulence theory:

$$\tau_m = (L_S^2/\epsilon)^{1/3} \quad (12)$$

It is interesting to note that the various estimates of τ_m show the same dependence on L_S and ϵ (except in the case of high viscosity fluids) independent of the macromixing present—be it plug flow or perfectly stirred. This reflects the identical nature of the fine scale turbulent processes at the extreme conditions of macromixing.

Evangelista, Katz and Shinnar (1969) showed that the variance decay of a batch mixer as prescribed by Curl's coalescence-redispersion model (Curl, 1963) follows Eq. 9, and therefore they suggested that coalescence-redispersion is analogous to turbulent micromixing and Corrsin's theory can be used to estimate the coalescence frequency. Although it was not pointed out explicitly by Evangelista et al., it may easily be inferred from their Eq. 11 that the variance decay of a steady-state perfectly-stirred vessel as predicted by Curl's model follows our Eq. 11 which comes from Rosensweig's analysis of turbulent mixing in perfectly-stirred vessels. Thus, in the case of Curl's model, the turbulence analogy holds up in the two extreme cases of macromixing. We now determine the variance decay laws as predicted by the three environment model for both plug-flow and perfectly-stirred vessels.

Consider a vessel into which two feed streams are introduced at constant rates. One of the streams is tagged with an inert tracer (A). The flow weighted variance at the vessel exit is calculated by adding contributions from each of the three effluent streams (cf., Eq. 8).

$$\sigma^2 = \frac{1}{Q_1 + Q_2} [(II_1|_{\lambda=0} V_1 + II_2|_{\lambda=0} V_2) (C_A^L(0) - \bar{C}_A)^2 + III_2|_{\lambda=0} V_2 (C_{A2}^0 - \bar{C}_A)^2 + III_1|_{\lambda=0} V_1 (0 - \bar{C}_A)^2]. \quad (13)$$

In Eq. 13, \bar{C}_A is the average concentration,

$$\bar{C}_A = \left(\frac{Q_2}{Q_1 + Q_2} \right) C_{A2}^0. \quad (14)$$

For a plug-flow vessel, the residence time distributions are given by

$$f_i(t) = \delta(t - \tau) \quad i = 1, 2, \quad (15)$$

where τ is the mean residence time. The exit concentration of the leaving environment is computed by setting $r_A = 0$ in Eq. 4 and making use of Eqs. 5 and 6 to find

$$\frac{dC_A^L}{d\lambda} = \frac{R_S \exp[-R_S(\tau - \lambda)]}{1 - \exp[-R_S(\tau - \lambda)]} \left[C_A - \left(\frac{Q_1}{Q_1 + Q_2} \right) C_{A2}^0 \right]. \quad (16)$$

The only solution of Eq. 16 which satisfies the required boundary condition (Eq. 7) is

$$C_A^L(\lambda) = \bar{C}_A. \quad (17)$$

The variance is obtained by substituting Eq. 17 into Eq. 13 with the result

$$\sigma^2 = \exp(-R_S \tau) (C_{A2}^0/2)^2. \quad (18)$$

$(C_{A2}^0/2)^2$ represents the variance of the streams entering the vessel, σ_0^2 . Therefore

$$\frac{\sigma^2}{\sigma_0^2} = \exp(-R_S \tau) \quad (19)$$

which is the form resulting from Corrsin's turbulence theory (cf., Eq. 9).

For perfectly-stirred vessels, the residence-time distributions are given by

$$f_i(t) = \frac{1}{\tau} \exp(-t/\tau) \quad (20)$$

where τ is the mean residence time. The leaving environment is described by

$$\frac{dC_A^L}{d\lambda} = \frac{1}{\tau} \left[C_A^L - \left(\frac{Q_1}{Q_1 + Q_2} \right) C_{A2}^0 \right], \quad (21)$$

and the only bounded solution is again

$$C_A^L(\lambda) = \overline{C_A} \quad (22)$$

as in the case of the plug-flow vessel. The resulting variance is

$$\sigma^2 = \frac{1}{1 + R_S \tau} (C_{A2}^0/2)^2. \quad (23)$$

And finally we see that

$$\frac{\sigma^2}{\sigma_0^2} = (1 + R_S \tau)^{-1} \quad (24)$$

which is the form resulting from Rosensweig's turbulence theory (cf., Eq. 11).

The conclusion is that the three environment model is analogous to turbulence in the same sense as Curl's coalescence-redispersion model. The analogy is completed by the relationship

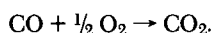
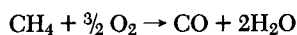
$$R_S = \frac{1}{\tau_m} \quad (25)$$

where τ_m is the turbulent mixing time which may be estimated with Eqs. 10–12. Whether or not the values of R_S required to fit experimental data conform to the turbulence theory is a question which is taken up in Part II. We should also note that the leaving environment, which is perfectly mixed, makes no contribution to the variance; only the segregated material in the entering environments contributes.

4. CRITIQUE OF THREE ENVIRONMENT MODEL

In spite of the significant merits outlined in Sections 2 and 3, the three environment model has a serious deficiency which becomes apparent when the effect of imperfect mixing on the selectivity of competing reactions is considered. To illustrate this deficiency, we will focus on a familiar chemical reaction process—methane combustion.

Methane combustion is often described by two overall reactions of kinetic significance (Tarbell and Petty, 1977), viz.,



When fuel and oxidizer are fed to the reactor in separate streams, as is usually the case in combustion processes, the emission of the undesirable intermediate, CO, is governed by two major factors: (1) the reactant stoichiometry—be it fuel rich or fuel lean; and (2) the intensity of mixing between the reactant streams. In an idealized combustor where the mixing is perfect, CO emissions are not observed until the fuel-air equivalence ratio, ϕ ($\phi \equiv$ actual fuel to air ratio/stoichiometric fuel to air ratio for complete combustion), exceeds 1. However, in real combustors with imperfect mixing, significant CO emissions are observed at $\phi < 1$, and fuel lean (ϕ

< 1) operating conditions are generally required to suppress CO emissions.

The presence of CO in an imperfectly-mixed fuel-lean combustor is qualitatively explained by the existence of fuel-rich ($\phi > 1$) regions (eddies) in the combustor which produce CO. Unfortunately, the three environment model does not possess this qualitative feature of reacting regions with reactant stoichiometry differing from the feed stoichiometry. The three environment model has only a single reacting environment—the leaving environment, and its stoichiometry is that of the feedstreams. Thus, regardless of the value of the mixing parameter, R_S , the three environment model will predict negligible CO production when the feed stoichiometry is fuel-lean. This qualitative argument is substantiated by numerical simulations in Part II.

5. FOUR ENVIRONMENT MODEL

To overcome the limitation described in Section 4, which makes the three environment model inappropriate for modeling competing reaction systems, we propose a new model (we call it the "Four Environment" model), Figure 2. It contains an entering environment for each feed stream, as in the three environment model, but now there is a separate leaving environment for each feedstream, and the leaving environments interact. The reactant stoichiometry of each leaving environment may now be quite different from that of the feed streams. In modeling methane combustion with the four environment model, one of the leaving environments could be fuel-rich, even in an overall fuel-lean system, and this allows for the observed production of CO in a poorly-mixed system.

The four environment model retains the basic features of the three environment model. The entering environments are segregated flow reactors; the leaving environments are maximum mixedness reactors; and the transfer of material from entering to leaving environments is first order in the mass of the entering environment with a transfer coefficient, R_S' . We will assume that the reversible transfer between the leaving environments is also first order in the mass of each leaving environment, but with a different transfer coefficient R_S . The four environment model can be formulated in such a way that it reduces to the three environment

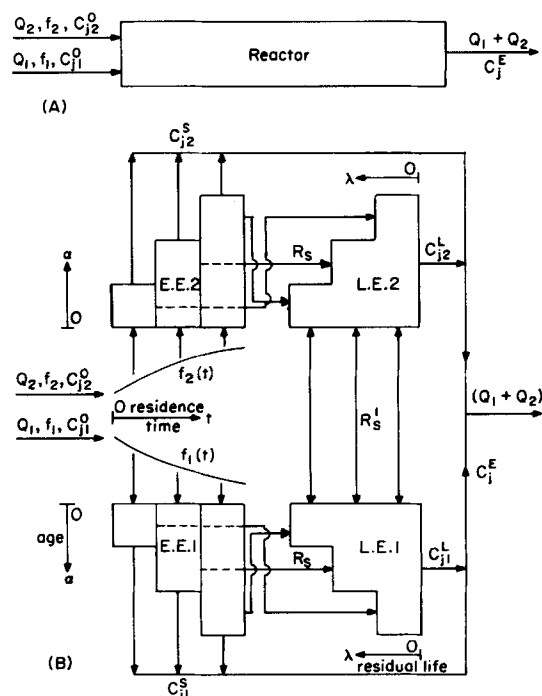


Figure 2. Schematic representation of four environment model: (A) actual reactor; (B) the model.

model when $R_S' \rightarrow \infty$. However, we will present arguments later to support the relationship:

$$R_S' = R_S. \quad (26)$$

If Eq. 26 is invoked, then the four environment model has only a single micromixing parameter.

One may wonder if there is anything special about the use of two leaving environments as opposed to three or more. Based on the arguments of Section 4, we feel that one leaving environment for each entering environment is a minimal requirement and leads to the simplest model capable of describing competing reactions in an imperfectly-mixed system. Additional leaving environments could be included at the expense of complexity and associated computation time. At this point, it should also be noted that for a reactor with N feedstreams, a $2N$ environment model would be considered minimal. In this paper we will only consider $N = 2$.

General Equations

For a general formulation of the four environment model, we will allow an arbitrary degree of premixing of the feedstreams; thus, chemical reactions may occur in the entering environments. A general set of M chemical reactions among N species will be accounted for,

$$\sum_{j=1}^N \alpha_{jk} A_j = 0; \quad k = 1, \dots, M. \quad (26)$$

The molar rate of the k th reaction, r_k , is assumed to depend only on the N species concentrations, i.e.,

$$r_k = r_k(C) \quad (27)$$

where $C = (C_1, C_2, \dots, C_N)$ is the concentration vector.

The total volume of material in the leaving environments coming from the i th feedstream and having a residual life between λ and $\lambda + d\lambda$ is

$$\Pi_i V_i d\lambda = \frac{V_i d\lambda}{\tau} \int_0^\infty [1 - \exp(-R_S \alpha)] f_i(\alpha + \lambda) d\alpha; \quad i = 1, 2 \quad (28)$$

while the total material in the i th entering environment lying in the same residual life interval is

$$\text{III}_i V_i d\lambda = \frac{V_i d\lambda}{\tau} \int_0^\infty \exp(-R_S \alpha) f_i(\alpha + \lambda) d\alpha; \quad i = 1, 2. \quad (29)$$

The total amount of species j in the i th entering environment having a residual life between λ and $\lambda + d\lambda$ is

$$\text{IV}_{ji} V_i d\lambda = \frac{V_i d\lambda}{\tau_i} \int_0^\infty C_{ji}^S \exp(-R_S \alpha) f_i(\alpha + \lambda) d\alpha; \quad j = 1, \dots, N \quad (30)$$

$i = 1, 2$

$C_{ji}^S = C_{ji}^S(\alpha)$ is the solution of the batch kinetics

$$\frac{dC_{ji}^S}{d\alpha} = \sum_{k=1}^M \alpha_{jk} r_k(C_i^S); \quad j = 1, \dots, N \quad (31)$$

$i = 1, 2$

subject to the initial condition

$$C_{ji}^S(\alpha = 0) = C_{ji}^0. \quad (32)$$

The volume of the i th leaving environment in the λ to $\lambda + d\lambda$ interval will be denoted $\hat{V}_i^L d\lambda$.

With the above definitions in hand, we now present the total material balance for the i th leaving environment,

$$-\frac{d\hat{V}_i^L}{d\lambda} = R_S(\text{III}_i V_i + \hat{V}_i^L - \hat{V}_i^L); \quad i = 1, 2 \quad (33)$$

$k = 3 - i$

subject to the boundary condition

$$\hat{V}_i^L(\lambda = \infty) = 0. \quad (34a)$$

In the special case of an ideal plug-flow residence-time distribution ($f_i(t) = \delta(t - \tau)$), boundary condition 34a may be replaced by

$$\hat{V}_i^L(\lambda = \tau) = 0. \quad (34b)$$

In addition we have

$$\sum_{i=1}^2 \Pi_i V_i = \sum_{i=1}^2 \hat{V}_i^L. \quad (35)$$

The component material balances for the i th leaving environment have the following form:

$$-\frac{d}{d\lambda} (\hat{V}_i^L C_{ji}^L) = R_S(\text{IV}_{ji} V_i + \hat{V}_i^L C_{jk}^L - \hat{V}_i^L C_{ji}^L) + \hat{V}_i^L \sum_{\ell=1}^M \alpha_{j\ell} r_\ell(C_i^L); \quad i = 1, 2 \quad (36)$$

$k = 3 - i$
 $j = 1, \dots, N$

Making use of Eqs. 33, Eqs. 36 reduce to

$$-\frac{dC_{ji}^L}{d\lambda} = R_S \left[\frac{V_i}{\hat{V}_i^L} (\text{IV}_{ji} - \text{III}_i C_{ji}^L) + \frac{\hat{V}_i^L}{\hat{V}_i^L} (C_{jk}^L - C_{ji}^L) \right] + \sum_{\ell=1}^M \alpha_{j\ell} r_\ell(C_i^L); \quad i = 1, 2. \quad (37)$$

$k = 3 - i$
 $j = 1, \dots, N$

The appropriate boundary conditions for Eqs. 37 are

$$\left. \frac{dC_{ji}^L}{d\lambda} \right|_{\lambda=\infty} = 0; \quad (38)$$

which for the purpose of numerical integration may be taken as

$$C_{ji}^L(\lambda = \infty) = C_{ji}^0. \quad (39a)$$

In the special case of an ideal plug-flow residence-time distribution ($f_i(t) = \delta(t - \tau)$), boundary conditions 39a may be replaced by

$$C_{ji}^L(\lambda = \tau) = C_{ji}^0. \quad (39b)$$

Finally, the exit concentration of species j is given by

$$\bar{C}_j^E = \frac{1}{Q_1 + Q_2} \left[\sum_{i=1}^2 ([\hat{V}_i^L C_{ji}^L]_{\lambda=0} + [\text{IV}_{ji}]_{\lambda=0} V_i) \right]; \quad j = 1, \dots, N \quad (40)$$

Equations 1, 2 and 28–40 provide a complete mathematical description of the four environment model.

The four environment model reduces to a segregated-flow reactor as $R_S \rightarrow 0$, and to a maximum-mixedness reactor as $R_S \rightarrow \infty$. The conversion of a first order reaction as predicted by the four environment model is easily shown to be independent of the mixing parameter, R_S (Appendix A). These features are required of a generally acceptable model of mixing and chemical reaction. However, a turbulence analogy, of the type established for the three environment model in section 3, does not hold exactly in the case of the four environment model. The following variance decay laws are predicted by the four environment model (Appendix B):

Plug-Flow Mixer

$$\frac{\sigma^2}{\sigma_0^2} = \exp(-R_S \tau) [1 + \exp(-R_S \tau) (1 - \exp(-R_S \tau))]; \quad (41)$$

Stirred-Tank Mixer

$$\frac{\sigma^2}{\sigma_0^2} = \frac{1}{R_S \tau + 1} \left[1 + \frac{R_S \tau}{(1 + 2R_S \tau)^2} \right] \quad (42)$$

The maximum value of the second term inside the square brackets in Eq. 41 is 0.25 and in Eq. 42 is 0.125—it occurs at $R_S \tau = 0.7$ for the plug-flow mixer and at $R_S \tau = 0.5$ for the stirred-tank

mixer. The same terms approach zero asymptotically in the limits $R_S \tau \rightarrow 0, \infty$. Thus, we can say that a turbulence analogy based on variance decay is approximately obeyed by the four environment model when we invoke the relationship

$$R_S = \frac{1}{\tau_m} \quad (43)$$

with τ_m provided by the turbulence theory of Corrsin and Rosenzweig (i.e., Eqs. 10 and 12).

6. TURBULENCE FOUNDATIONS OF FOUR ENVIRONMENT MODEL

Turbulent flow is characterized by the eddy like motion of the fluid which occurs at various length scales in the flow field. Hence, it may be possible to describe mixing processes from a turbulence structure point of view. Beek and Miller (1959) suggested that the overall mixing process occurs in three concurrent stages. The first is the coarse-scale intermixing of incoming streams which homogenizes the content of the vessel on a scale much smaller than the dimensions of the vessel, yet much larger than the microstructure of the turbulence. The local concentration gradients remain unaffected during this stage. This is the so-called macromixing and is performed by convective transport in the large eddies. The second stage is the superimposed local turbulent mixing during which large regions of fixed composition are divided into smaller ones. This may be caused by the stretching of vortex structures which effectively increases the area available for local mass transfer. However, vortex stretching alone cannot reduce eddy dimensions to zero because as eddies get smaller, viscous dissipation begins to play an increasingly important role. In fact, the smallest dimension to which an eddy is reduced by vortex stretching is determined mainly by the viscous forces, and the flow field adjusts itself accordingly. Finally, the resultant fine structures of the turbulent concentration field are smeared away by molecular diffusion.

This diffusion is a prerequisite for the occurrence of a chemical reaction when reactants are fed in separate streams.

The classical theories of turbulent mixing (Corrsin, 1964; Rosenzweig, 1964) are applicable only to the last two stages of the turbulent mixing (Reith, 1965). This suggests that mixing models which are analogous to these turbulent mixing theories (in the sense of Section 3) such as Curl's model and the three and four environment models, implicitly assume that the characteristic time scale of macromixing is negligibly small compared to time scales of the final two stages of mixing.

In light of the foregoing description of turbulent mixing, we present qualitative analogies between the idealized second and third stages of the turbulent mixing process and those processes visualized in Curl's model and the three and four environment models. These qualitative analogies provide some physical basis for the analytical analogies (Sections 3 and 6).

Consider a plug-flow mixer fed with two separate streams carrying A and B respectively. Assuming instantaneous macromixing of the two streams, we may represent an initial microscale inhomogeneity in the turbulent concentration field by the configuration of fine structures (eddies), (Figure 3A-1). The microscale inhomogeneities at successive residence times in the plug-flow mixer are depicted by successive movement to the right in Figure 3. Figure 3B is a representation of the concentration spectrum characterizing Curl's model with a finite number of "droplets" (eddies), while Figures 3C and 3D display the entering and leaving environments of the three and four environment models, respectively.

The entering environments are lumped representations of the macromixed eddies of pure components which have only interacted with other pure-component eddies. When a pure-component eddy interacts with an unlike eddy, it is no longer pure, and thus it becomes a member of a leaving environment. The transfer of material from an entering to a leaving environment, depicted by the one-way arrows in Figures 3C and 3D, represents this turbulent interaction in the environment models. For analogy to turbulence,

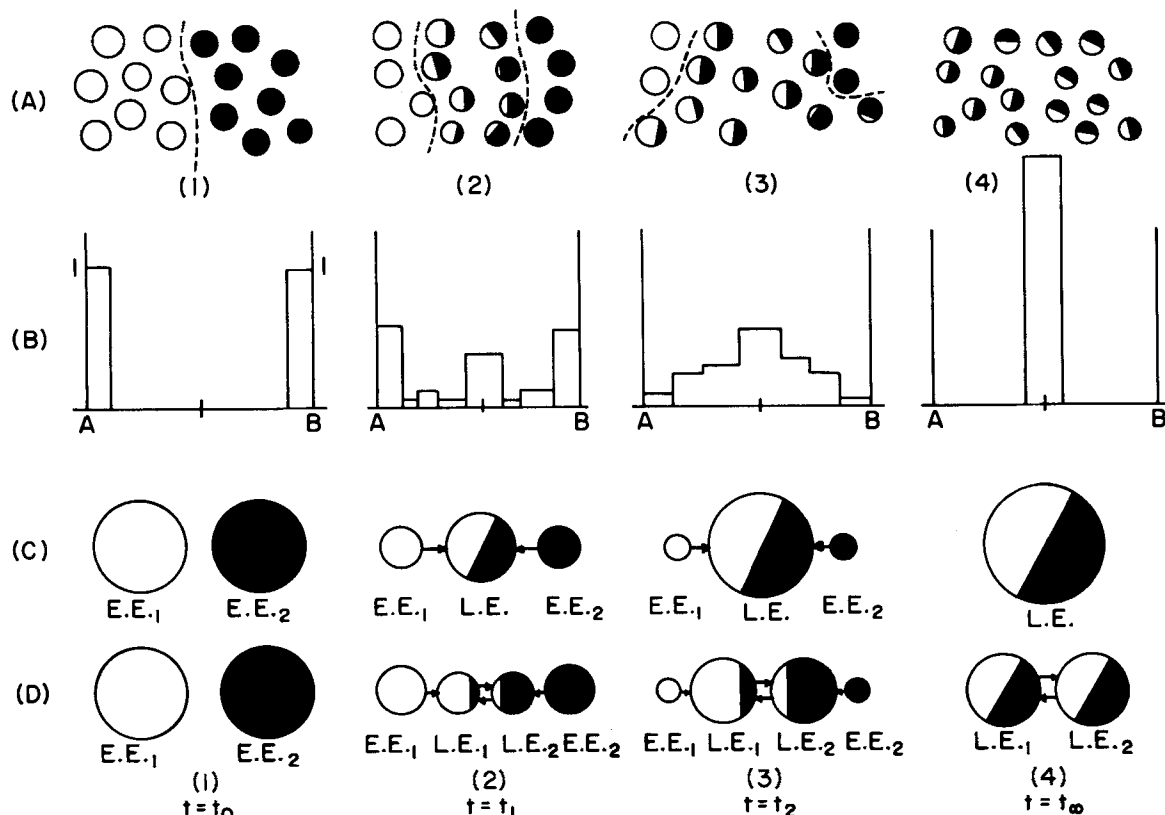


Figure 3. Schematic representation of micromixing process: (A) eddy process; (B) Curl's model; (C) three environment model; (D) four environment model.

the rate of this transfer process in the environment models should be characteristic of turbulent-eddy transport. Clearly this transfer must only be in one direction (there is no transfer from leaving to entering environments) as unmixing by turbulent action is not physically possible.

The leaving environments of the three and four environment models may be viewed as lumped representations of the intermediate portion of the turbulent concentration spectrum. A single mean eddy (leaving environment) is employed in the three environment model, while two interacting eddies are used in the four environment model. Obviously, two leaving environments provide a finer representation of the intermediate region of the turbulent concentration spectrum than does one leaving environment. But of perhaps greater significance, when one considers chemical reactions, is the qualitative feature of rich and lean (relative to the mean) reactive regions present in the four environment model which is not present in the three environment model. This qualitative feature requires at least two leaving environments.

Following through on the physical analogy between the four environment model and turbulent-eddy transport, we see that the transfer of material between leaving environments is analogous to the interaction of turbulent eddies which are not pure, and thus the transfer is in two directions. Since the underlying turbulent transfer mechanism should be the same for an interaction between pure and mixed structures (i.e., entering and leaving environments) as it is for an interaction between mixed structures of different composition (i.e., two leaving environments), we expect the rates of material transfer, characterized by the parameters R_S and R_λ , to be the same. That is, physically we expect

$$R'_S = R_S \quad (44)$$

and this is how we have presented the model (Section 5).

Now we will briefly consider the conditions under which we expect the turbulence theory, and by analogy the four environment model, to be valid.

Since the underlying theory is based on the properties of isotropic turbulence, it will be useful to examine the conditions required for the practical attainment of this idealized turbulent state. Both Corrsin (1964) and Rosensweig (1966) justified the assumption of isotropy by focusing on the inertial convective subrange in the turbulent kinetic energy spectrum. Hinze (1975) provides the following criteria for the existence of an extensive inertial subrange:

$$(Re_\ell)^{3/8} \gg \gg 1 \quad (45)$$

or

$$(Re_\lambda)^{3/4} \gg \gg 1 \quad (46)$$

where

$$Re_\ell = u' \ell_e / \nu \quad (47)$$

$$Re_\lambda = \frac{u' \lambda_d}{\nu} \quad (48)$$

ℓ_e is the integral length scale of the flow field; λ_d represents the dissipation length scale or microscale of turbulence; and u' denotes the r.m.s. turbulent fluctuating velocity, and ν is kinematic viscosity of the fluid.

One useful procedure by which Re_ℓ and Re_λ may be estimated is through the following expressions for the kinetic energy dissipation rate per unit mass (ϵ) suggested by Hinze (1975):

$$\epsilon = 15 \nu \frac{u'^2}{\lambda_d^2} \quad (49)$$

$$\epsilon = A^* \frac{u'^3}{\ell_e} \quad (50)$$

where A^* is a parameter of order unity. It follows from Eqs. 44, 46, 47 and 49 that

$$Re_\ell = \frac{A^*}{15} Re_\lambda^2 \quad (51)$$

ϵ is related to the power input per unit mass of fluid (P), a macroscopic measurable quantity, through an efficiency factor

$$\epsilon = \eta P, \quad (52)$$

where η is of order unity (e.g., Corrsin, 1957, suggested $\eta = 0.5$ for pipe flow). ℓ_e may be estimated as a characteristic dimension of the turbulence generator. For example, in pipe flow where mean flow is the dominant turbulence generator, ℓ_e may be taken as the pipe diameter. Estimates of ℓ_e for several chemical reactor configurations are discussed in Part II. Knowledge of P and ℓ_e allows an estimate of u' through Eqs. 52 and 50, and this determines Re_ℓ directly and Re_λ through Eq. 51.

It is interesting to note that using similar kinds of criteria, Brtko and Kabel (1978) found that a mixing model based on isotropic turbulence was in satisfactory agreement with experimental data when

$$Re_\ell > 70 \quad (53)$$

or

$$Re_\lambda > 30. \quad (54)$$

We note this only to stress that Eqs. 45 and 46 may be satisfied only "loosely."

There is also some uncertainty in the estimation of the micro-mixing time scale (τ_m) by Eqs. 10 and 12. In an *a priori* estimation, based on knowledge of the power input per unit mass, one may have to guess the efficiency factor in Eq. 52. In general, the length scales L_S and ℓ_e are not equal. However, as suggested by Rosensweig (1964), when a substantial inertial subrange of the turbulent kinetic energy spectrum exists, as would be guaranteed by conditions 45 and 46, they are nearly equal.

7. CONCLUDING REMARKS

The four environment model can describe many of the complexities encountered in realistic chemical reactors, viz., complex kinetics, micromixing of unmixed streams and arbitrary macromixing—all within the computationally efficient format of ordinary differential equations. The model's parameters can be determined by well-defined experiments: The kinetic parameters in well agitated batch reactor experiments; the residence time distribution through inert-tracer response experiments; and the micromixing parameter (R_S) in reactive tracer experiments involving a single reaction with known kinetics.

In many modeling applications, the kinetics are known, the macromixing can be well approximated by a simple residence time distribution, and it is micromixing which presents an obstacle. Because of the turbulence analogy established in Section 6, we recommend use of the Corrsin-Rosensweig turbulent mixing theory for: (1) *a priori* estimation of R_S ; (2) correlation of experimental data on micromixing; and (3) scaleup of the micromixing process.

Extensive comparisons of the four environment model with experimental data are clearly required if it is to be accepted as a general chemical reactor model. Our initial efforts in that direction are described in Part II.

ACKNOWLEDGMENT

Partial support of this work by the Mick A. Naulin Foundation, Ltd., is gratefully acknowledged.

NOTATION

A, B, S	= chemical species
A^*	= dimensionless constant in Eq. 50
C_j^i	= concentration of j in i^{th} environment
D	= molecular diffusivity

$E.E.$	= entering environment
f	= residence time frequency function
F	= cumulative residence time distribution
k_r	= reactive rate constant
ℓ_e	= integral length scale of the turbulence field
$L.E.$	= leaving environment
L_S	= scalar macroscale
N_{Sc}	= Schmidt number = ν/D
P	= power input per unit mass
Q	= flow rate
r	= chemical reaction rate
Re	= Reynolds number defined by Eqs. 45 and 46
R_S, R'_S	= transfer coefficients
t	= time
$T(\alpha)$	= environment transfer function defined in Eq. 3
u'	= root-mean-square turbulent velocity
V	= holdup volume

Greek Letters

α	= age [time]
α_{ij}	= stoichiometric coefficient
δ	= Dirac delta function
ϵ	= turbulent energy dissipation rate per unit mass
η	= efficiency factor
λ	= residual lifetime
λ_d	= microscale of turbulence
ν	= kinematic viscosity
σ^2	= variance of concentration distribution
τ	= mean residence time
τ_m	= characteristic mixing time scales defined in Eqs. 10, 11 and 12
ϕ	= equivalence ratio

Subscripts

s	= scalar
i, j, k	= index variables
ℓ	= macroscale
λ	= microscale

Superscripts

E	= exit
L	= leaving environment
0	= initial
S	= segregated

Specific Symbols

overbar	= mean value
overhat	= per unit time interval
II, III, IV	= integrals defined in Eqs. 5, 6 and 30

APPENDIX A: PROOF OF INDEPENDENCE OF CONVERSION FROM R_S FOR FIRST-ORDER REACTION

Consider a CSTR being fed with two separate streams. For simplicity, we assume that the streams have equal flow rates and identical residence-time distributions of an ideal CSTR. Stream 1 contains reactant A and the following first-order reaction occurs in the reactor:



where

$$r = k_r C_A \quad (A2)$$

and k_r is the true kinetic constant. Thus, $N = 2$, $k = 1$, $\alpha_{11} = 1$, α_{21}

$= -1$, $A_1 = A$ and $A_2 = S$ in Eqs. 26 and 31. Using $C_{A1}^S(\alpha = 0) = C_{A1}^0$ and $C_{A2}^0(\alpha = 0) = 0$ in Eq. 32, we solve Eq. 31 to get

$$C_{A1}^S = C_{A1}^0 \exp(-k_r \alpha) \quad (A3)$$

and

$$C_{A2}^S = 0. \quad (A4)$$

With $f_i(t) = 1/\tau \exp(-t/\tau)$, we substitute Eqs. A3 and A4 in Eqs. 28–30 and obtain the following expressions:

$$II_1 = II_2 = f(\lambda) \frac{R_S \tau}{(1 + R_S \tau)}, \quad (A5)$$

$$III_1 = III_2 = \frac{f(\lambda)}{(1 + R_S \tau)}, \quad (A6)$$

$$IV_{A1} = \frac{f(\lambda) C_{A1}^0}{(1 + k_r \tau + R_S \tau)} \quad (A7)$$

and

$$IV_{A2} = 0. \quad (A8)$$

Subsequently, we employ Eq. A5 to arrive at the solution of Eqs. 33:

$$\hat{V}_1^L = \hat{V}_2^L = II_1 V_1 = II_2 V_2. \quad (A9)$$

which satisfies the boundary conditions (Eq. 34).

We set the left hand sides of Eqs. 37 to zero to satisfy the boundary conditions (cf., Eq. 38). Note that since the right hand sides of Eqs. 37 are independent of λ , the only way to obtain a bounded solution is to set the left hand sides to zero. By using the expressions A2–A9, we now write Eqs. 37 as

$$k_r C_{A1}^L = R_S \left[\frac{V_1}{\hat{V}_1^L} (IV_{A1} - III_1 C_{A1}^L) + (C_{A2}^L - C_{A1}^L) \right] \quad (A10)$$

$$k_r C_{A2}^L = R_S \left[\frac{V_2}{\hat{V}_2^L} (0 - III_2 C_{A2}^L) + (C_{A1}^L - C_{A2}^L) \right]. \quad (A11)$$

It is easy to show from Eqs. A10 and A11 that

$$(C_{A1}^L + C_{A2}^L) = \frac{C_{A1}^0 (1 + R_S \tau)}{(1 + k_r \tau)(1 + k_r \tau + R_S \tau)} \quad (A12)$$

Finally, we calculate the exit concentration of A by substituting above results in Eq. 40:

$$\begin{aligned} \bar{C}_A^E &= \frac{1}{Q_1 + Q_2} \{ [\hat{V}_1^L C_{A1}^L + \hat{V}_2^L C_{A2}^L] |_{\lambda=0} + [IV_{A1}] |_{\lambda=0} V_1 \} \\ &= \left[\frac{R_S \tau C_{A1}^0}{2(1 + k_r \tau)(1 + k_r \tau + R_S \tau)} + \frac{C_{A1}^0}{2(1 + k_r \tau + R_S \tau)} \right] \\ &= \frac{C_{A1}^0}{2(1 + k_r \tau)}, \end{aligned} \quad (A13)$$

which is independent of R_S .

In the case of a plug-flow reactor, $f_i(t) = \delta(t - \tau)$, and it is easy to verify that

$$II_1 = II_2 = \frac{1}{\tau} (1 - \exp[-R_S(\tau - \lambda)]) \quad (A14)$$

$$III_1 = III_2 = \frac{1}{\tau} \exp[-R_S(\tau - \lambda)] \quad (A15)$$

$$IV_{A1} = \frac{C_{A1}^0}{\tau} \exp[-(k_r + R_S)(\tau - \lambda)]. \quad (A16)$$

Equations A3, A4, A8 and A9 also apply to the plug-flow reactor. The exit concentration is given by

$$\begin{aligned} \bar{C}_A^E &= \frac{1}{Q_1 + Q_2} \{ (\hat{V}_1^L C_{A1}^L) |_{\lambda=0} + (\hat{V}_2^L C_{A2}^L) |_{\lambda=0} \\ &\quad + (IV_{A1}) |_{\lambda=0} V_1 \}. \end{aligned} \quad (A17)$$

The component material balances for each leaving environment (Eqs. 36) are

$$-\frac{d}{d\lambda}(\hat{V}_i^L C_{Ai}^L) = R_S[IV_{Ai}V_i + \hat{V}_k^L C_{Ak}^L - \hat{V}_i^L C_{Ai}^L] - \hat{V}_i^L k_r C_{Ai}^L;$$

$$\begin{aligned} i &= 1, 2 \\ k &= 3 - i \end{aligned} \quad (A18)$$

and it is readily verified that

$$\frac{-d(IV_{A1})}{d\lambda} = (k_r + R_S)IV_{A1}, \quad (A19)$$

By adding Eqs. A18 for $i = 1, 2$ and Eq. A19, we arrive at the following equation for \bar{C}_A^E :

$$-\frac{d}{d\lambda}\bar{C}_A^E = -k_r\bar{C}_A^E, \quad (A20)$$

which shows that \bar{C}_A^E is independent of R_S .

APPENDIX B: VARIANCE DECAY LAWS OF FOUR ENVIRONMENT MODEL

The concentration variance of an inert tracer A (which entered a two feedstream reactor via stream 1) at the reactor exit can be calculated as

$$\begin{aligned} \sigma^2 &= \frac{1}{Q_1 + Q_2} [\hat{V}_1^L(C_{A1}^L(0) - \bar{C}_A)^2 + \hat{V}_2^L(C_{A2}^L(0) - \bar{C}_A)^2 \\ &\quad + III_1(0)V_1(C_{A1}^0 - \bar{C}_A)^2 + III_2(0)V_2(0 - \bar{C}_A)^2]. \end{aligned} \quad (B1)$$

For simplicity we shall assume that both the streams have equal flow rates and identical residence-time distributions.

Stirred Tank Mixer

As in Appendix A, $f_i(t) = 1/\tau \exp(-t/\tau)$, and Eqs. A5–A9 apply. We drop the reaction terms from Eqs. 37 and obtain a bounded solution while accommodating Eqs. 38 by setting the lefthand sides of Eqs. 37 to zero. Consequently, the following two linear equations result:

$$C_{A1}^L(0) - C_{A2}^L(0) = \frac{1}{R_S\tau} (C_{A1}^0 - C_{A1}^L(0)) \quad (B2)$$

and

$$C_{A1}^L(0) - C_{A2}^L(0) = \frac{C_{A2}^L(0)}{R_S\tau}. \quad (B3)$$

We solve these equations and obtain

$$C_{A1}^L(0) = \frac{C_{A1}^0(1 + R_S\tau)}{(1 + 2R_S\tau)}; \quad (B4)$$

$$C_{A2}^L(0) = \frac{C_{A1}^0 R_S\tau}{(1 + 2R_S\tau)}. \quad (B5)$$

The variance of the feed is

$$\sigma_0^2 = (C_{A1}^0/2)^2. \quad (B6)$$

Substitution of these results in Eq. B1 yields Eq. 42.

Plug-Flow Mixer

Here $f_i(t) = \delta(t - \tau)$, which when substituted in Eqs. 28 and 29 gives the following expressions:

$$II_1 = II_2 = \frac{1}{\tau} (1 - \exp[-R_S(\tau - \lambda)]), \quad (B7)$$

$$III_1 = III_2 = \frac{1}{\tau} \exp[-R_S(\tau - \lambda)]. \quad (B8)$$

In addition, equality of flow rates yields

$$\hat{V}_1^L = \hat{V}_2^L = II_1 V_1 = II_2 V_2, \quad (B9)$$

from Eqs. 35. Since there is no chemical reaction, $C_{A1}^S(\alpha) = C_{A1}^0$ and $C_{A2}^S = 0$ (cf., Eqs. 31, 32). Consequently,

$$IV_{A1} = C_{A1}^0 III_1 \quad (B10)$$

and

$$IV_{A2} = 0, \quad (B11)$$

as can be seen from Eqs. 30. After setting the reaction terms in Eqs. 37 equal to zero, it can be shown that

$$C_{A1}^L + C_{A2}^L = C_{A1}^0, \quad (B12)$$

and the equation for C_{A1}^L becomes

$$\frac{dC_{A1}^L}{d\lambda} = R_S \left[\frac{III_1}{II_1} (C_{A1}^L - C_{A1}^0) + (2C_{A1}^L - C_{A1}^0) \right] \quad (B13)$$

subject to the boundary condition

$$C_{A1}^L(\lambda = \tau) = C_{A1}^0. \quad (B14)$$

The solution of Eqs. B13–B14 is

$$C_{A1}^L = \frac{1}{2} \left[\frac{1 - \exp[-2R_S(\tau - \lambda)]}{1 - \exp[-R_S(\tau - \lambda)]} \right] C_{A1}^0. \quad (B15)$$

Substitution of Eqs. B7–B12 and B15 into Eq. B1, along with Eq. B6, leads us to Eq. 41.

LITERATURE CITED

- Beek, Jr., J., and R. S. Miller, "Turbulent Transport in Chemical Reactors," *Chem. Eng. Prog. Symp. Ser.*, **55**, 25 (1959).
- Brtko, W. J., and R. L. Kabel, "Transfer of Gases at Natural Air-Water Interfaces," *J. of Phy. Oceanogr.*, **8**, 543 (1978).
- Corrsin, S., "Simple Theory of an Idealized Turbulent Mixer," *AIChE J.*, **3**, 329 (1957).
- Corrsin, S., "The Isotropic Turbulent Mixer: Part II. Arbitrary Schmidt Number," *AIChE J.*, **10**, 870 (1964).
- Curl, R. L., "Dispersed Phase Mixing: Part I. Theory and Effects in Simple Reactors," *AIChE J.*, **9**, 175 (1963).
- Danckwerts, P. V., "The Effect of Incomplete Mixing on Homogeneous Reactions," *Chem. Eng. Sci.*, **8**, 93 (1958).
- Evangelista, J. J., S. Katz, and R. Shinnar, "Scaleup Criteria for Stirred Tank Reactors," *AIChE J.*, **15**, 843 (1969).
- Harris, I. J., and R. D. Srivastava, "The Simulation of Single Phase Turbulent Reactors with Incomplete Reactant Mixing," *Can. J. Chem. Eng.*, **46**, 66 (1968).
- Hill, J. C., "Models for Turbulent Transport Processes," *Chem. Eng. Educ.*, **13**, No. 1, 34 (1979).
- Hinze, J. O., *Turbulence*, 2nd ed., McGraw-Hill, New York (1975).
- Kattan, A., and R. J. Adler, "A Stochastic Mixing Model for Homogeneous, Turbulent, Tubular Reactors," *AIChE J.*, **13**, 580 (1967).
- Ng, D. Y. C., and D. W. T. Rippin, "The Effect of Incomplete Mixing on Conversion in Homogeneous Reactions," Third European Symp. on Chemical Reaction Engineering, Amsterdam, Sept. 1964, Pergamon Press, Oxford, 161 (1965).
- Nishimura, Y., and M. Matsubara, "Micromixing Theory via the Two-Environment Model," *Chem. Eng. Sci.*, **25**, 1785 (1970).
- Rao, D. P., and I. J. Dunn, "A Monte Carlo Coalescence Model for Reaction with Dispersion in a Tubular Reactor," *Chem. Eng. Sci.*, **25**, 1275 (1970).
- Reith, Ir. T., "Generation and Decay of Concentration Fluctuations in a Stirred Baffled Vessel," *AIChE, I. Chem. Eng. Symp. Ser.*, No. 10, London, 14 (1965).
- Ritchie, B. W., and A. M. Tobgy, "General Population Balance Modelling of Unpremixed Feedstream Chemical Reactors: A Review," *Chem. Eng. Commun.*, **2**, 249 (1978).
- Ritchie, B. W., and A. M. Tobgy, "A Three-Environment Micromixing Model for Chemical Reactors with Arbitrary Separate Feedstreams," *Chem. Eng. J.*, **17**, 173 (1979).
- Ritchie, B. W., "Simulating the Effects of Mixing on the Performance of Unpremixed Flow Chemical Reactors," *Can. J. Chem. Eng.*, **58**, 626 (1980).
- Rosensweig, R. E., "Idealized Theory for Turbulent Mixing in Vessels," *AIChE J.*, **10**, 91 (1964).

- Rosensweig, R. E., "Isotropic Turbulent Mixing with Boundary Sources," *Can. J. Chem. Eng.*, **44**, 255 (1966).
- Shain, S. A., "Performance of Stirred Reactors with Dispersed Phase Mixing," *AIChE J.*, **12**, 806 (1966).
- Spielman, L. A., and O. A. Levenspiel, "A Monte Carlo Treatment for Reacting and Coalescing Dispersed Phase Systems," *Chem. Eng. Sci.*, **20**, 247 (1965).
- Tarbell, J. M., and C. A. Petty, "Combustion Modifications for the Control of NO_x Emissions," *Chem. Eng. Sci.*, **32**, 1177 (1977).
- Treleaven, C. R., and A. H. Tobgy, "Monte Carlo Methods of Simulating Micromixing in Chemical Reactors," *Chem. Eng. Sci.*, **27**, 1497 (1972).
- Villermaux, J., and A. Zoulalian, "Etat de mélange du fluide dans un réacteur continu. A propos d'un modèle de Weinstein et Adler," *Chem. Eng. Sci.*, **24**, 1513 (1969).
- Weinstein, H., and R. J. Adler, "Micromixing Effects in Continuous Chemical Reactors," *Chem. Eng. Sci.*, **22**, 65 (1967).
- Zwietering, Th. N., "The Degree of Mixing in Continuous Flow Systems," *Chem. Eng. Sci.*, **11**, 1 (1959).

Manuscript received June 8, 1981; revision received January 22, 1982 and accepted April 26, 1982.

Part II. Comparison with Experiments

The four environment model, which was developed in Part I, has been compared with three extensive sets of experimental data from plug-flow and stirred-tank reactors with unmixed feedstreams and a single chemical reaction. The data sets have been accurately reproduced with a single value of the micromixing parameter (R_S), and the "best fit" value of R_S for each data set was close to the value estimated from the Corrsin-Rosensweig turbulent mixing theory. This lends support to the turbulence analogy suggested in Part I. Simulations of competing reactions of the parallel-consecutive type are used to discriminate between the four and three environment models with the four environment model providing much more realistic predictions.

**R. V. MEHTA and
J. M. TARBELL**

Department of Chemical Engineering
and
Center for Air Environment Studies
The Pennsylvania State University
University Park, PA 16802

SCOPE

In Part I, we developed a general chemical reactor model (the four environment model) capable of describing industrial reactors with unmixed feedstreams, complicated large-scale mixing patterns, and competing chemical reactions all within the computationally efficient framework of ordinary differential equations. We developed a turbulence analogy which allows estimation of the model's micromixing parameter (R_S) from easily measured variables, and we suggested that the four environment model would describe reactors with competing

reactions more realistically than the three environment model (Ritchie and Tobgy, 1979).

Our objectives in this paper were: (1) to compare the predictions of the four environment model with experimental data obtained in well-characterized chemical reactors; (2) to consider the validity of the turbulence analogy suggested in Part I in light of experimental data; and (3) to discriminate between the four and three environmental models by considering a chemical reactor with competing reactions.

CONCLUSIONS AND SIGNIFICANCE

The four environment model has been compared with three extensive experimental data sets obtained in reactors with unmixed feed streams both plug-flow and stirred-tank residence-time distributions, and a wide range of (single) reaction rates. The four environmental model accurately predicts the observed performance of the reactors over a broad range of operating conditions with only a single value of the micromixing parameters (R_S). The "best fit" value of R_S for each data set was close to the value estimated from the Corrsin-Rosensweig turbulent mixing theory, and this supports the validity of the turbulence analogy suggested in Part I.

Well-defined experimental data for competing reactions were not available, so simulation of a realistic hydrocarbon combustion reactor, where the effect of micromixing on carbon monoxide emissions is known at least qualitatively, were carried out with the four and three environment models. The four environment model showed the realistic trend of increased carbon monoxide emissions with a decreased rate of micromixing. The three environment model showed essentially no effect of micromixing on carbon monoxide emissions.

We conclude that the four environment model looks promising as a general model for chemical reactors with competing reactions, unmixed feed streams and arbitrary macromixing. It is computationally efficient and compares favorably with available experimental data.