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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.

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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.

1. INTRODUCTION

In Part I, we proposed a new model—the four environment model—to describe imperfectly-mixed turbulent-flow chemical reactors. In this paper, we present results of numerical simulations of published experimental data employing both the four environment model and the three environment model (Ritchie and Tobgy, 1979). The ability of these models to correlate experimental data over a broad range of operating variables with a single micromixing parameter is evaluated. And, the turbulence analogy established in Part I, which suggests use of the Corrsin-Rosensweig (Corrsin, 1964; Rosensweig, 1964) isotropic turbulent mixing theory to *a priori* estimate the micromixing parameter, is considered in light of the experimental data. Finally, numerical simulations of a hypothetical, yet realistic, combustion process involving competing chemical reactions are used to clearly discriminate between the four and three environment models.

2. SELECTION OF EXPERIMENTAL DATA

Very few published experimental data sets provide an adequate basis for evaluation of the four environment model. Most experimental results have been obtained in premixed feed reactors with a single, irreversible, second-order reaction under isothermal conditions. Under these conditions, the maximum difference between the extremes of micromixing (i.e., maximum mixedness and total segregation) is on the order of ±7% in terms of limiting reactant conversion (Aris, 1965).

Considering the errors involved when specific values of kinetic constants are employed in model calculations on the one hand, and the errors inherent in experimental measurements on the other, it is clear that such data are hardly suited to our purpose of model evaluation.

Greater sensitivity to micromixing in premixed feed reactors can be obtained with complex kinetics because a wide variation in selectivity and product distribution is possible. A few experimental studies of this type have been reported (O'Brien and Ross, 1966; Zoulalian and Villermaux, 1974; and Truong and Methot, 1976), but none is entirely satisfactory. Either too little data have been presented to provide a statistically significant basis for evaluation, or parameters required as input for model calculations have not been reported.

We are left with reported data from separate feedstream reactors with simple (one reaction) kinetics. We have evaluated the data sets of: (1) Vassilatos and Toor (1965); (2) Treleaven and Tobgy (1972, 1973); and (3) Plasari, David and Villermaux (1978). These studies embrace a broad range of hydrodynamic conditions (macromixing states), diverse reactor geometries and a large variation in the relative magnitudes of pertinent characteristic time scales (i.e., micromixing, reaction, and mean residence-time scales). The first two studies were conducted under macromixing conditions approximately described by a plug-flow residence-time distribution (RTD), while the conditions of the third study correspond to an ideal stirred tank RTD. Estimates of the microscale Reynolds numbers (Re_ℓ) given in Table 1, which are based on methods outlined in Part I, suggest that the experimental turbulent flow fields may be approximately described as isotropic (i.e., $Re_\ell^{3/8} \gg 1$). Thus, the data should be suitable for evaluation of the isotropic turbulence analogy suggested in Part I.

TABLE 1. MICROSCALE REYNOLDS NUMBER ESTIMATES

Source	Re_ℓ (Estimated*)
Vassilatos and Toor (1965)	400
Treleaven and Tobgy (1973)	1,100–4,700
Plasari, David and Villermaux (1978)	2,200–15,500

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* Only half of the input power per unit mass is assumed to enter the turbulence field.

3. EXPERIMENTS OF VASSILATOS AND TOOR

Vassilatos and Toor (1965) studied, single irreversible, second-order reactions in an isothermal, turbulent-flow tubular reactor. The hydrodynamics were maintained constant while the reaction rate was varied over nine orders of magnitude. The two aqueous reactant solutions were separately introduced through many alternate jets, and the reaction proceeded in the resulting microscale inhomogeneous mixture. The experimental setup is shown schematically in Figure 1 and the range of operating conditions is listed in Table 2. 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 widely used for the validation of models of mixing and chemical reaction (e.g., Kattan and Adler, 1967; Harris and Srivastava, 1968; Mao and Toor, 1970; and Rao and Dunn, 1970).

Since no RTD measurements were reported, we must assume a suitable form. We choose an ideal plug-flow RTD because it is simple and seems physically appropriate in view of the reactor geometry and the mode of operation. However, McKelvey et al. (1975) have reported that the flow in this type of reactor exhibits some peculiar nonideal features which may be attributed to complicated interactions among jets in the region immediately downstream from the injector plane. Upstream of the position where the jets merge, the flow is quite complex and unlikely to be described by a plug-flow RTD. In fact, Vassilatos and Toor observed that the jets were indistinguishable only beyond 2 cm from the inlet. Consequently, in cases where significant chemical reaction occurred in this region (i.e., very rapid reactions), we should anticipate inaccuracy in our model's predictions.

The kinetics of the various reactions employed by Vassilatos and Toor are known and the RTD has been assumed to be plug flow. The four environment model (and the three environment) will be completely specified once the micromixing parameter, R_s, is fixed. For this we turn to the Corrsin-Rosensweig turbulent mixing theory, as outlined in Part I, to arrive at the following estimate:

$$R_s^{-1} = \tau_m \simeq \frac{1}{2}[4(L_s^2/\epsilon)^{1/3} + (\nu/\epsilon)^{1/2} \ln N_{sc}]. \qquad (1)$$

For the range of conditions employed by Vassilatos and Toor, the viscosity-dependent second term in Eq. 1 contributes less than 5% of the total. Neglecting this term and relating ϵ to the measur-

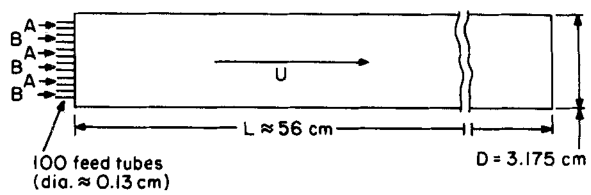


Figure 1. Schematic of the reactor used by Vassilatos and Toor (1965).

TABLE 2. EXPERIMENTAL CONDITIONS OF VASSILATOS AND TOOR (1965)
$Q_1 \simeq Q_2 \simeq 164$ cm^3/s; $L/D \simeq 17.6$

Reactants	$Da = k\overline{C}^o\tau$	$\beta = (\overline{C}_B^o/n\overline{C}_A^o)$	$\overline{C}^o \cdot 10^2$ gmol/L	Nature of Chemical Reaction
HCl-NaOH HCl-LiOH $C_2H_4O_4$-LiOH CH_2O_2-LiOH	~10^9	1.00–10.00	1.4–2.5	Very Rapid
CO_2-NaOH	109–142	1.26–3.88	0.6–0.8	Moderately Rapid
$HCOOCH_3$-NaOH	0.66–2.36	1.05–7.61	1.2–3.6	Slow

able power input per unit mass of fluid P through an efficiency parameter η ($\epsilon = \eta P$) we have:

$$\tau_m = \xi (L_s^2/P)^{1/3} \tag{2}$$

where

$$\xi = 2/\eta^{1/3}. \tag{3}$$

We will assume that the mean flow, characterized by the average velocity U, supplies the turbulent kinetic energy. Any excess kinetic energy associated with the feed jets will have been dissipated within the 2-cm jet mixing region (cf., Pompei and Heywood, 1972). Therefore, we write

$$P = \frac{U}{L_s}\frac{U^2}{2}, \tag{4}$$

and take the characteristic length as the feed tube diameter (i.e., $L_s = 0.13$ cm).

We will use ξ (Eq. 3) as an adjustable parameter to obtain a best fit to the experimental data. Based on Corrsin's estimate of η for pipe flow ($\eta = 0.5$; Corrsin, 1957) we expect to find

$$\xi = 2.5 \tag{5}$$

if the turbulence analogy is valid.

The four environment model equations are developed below. A similar development for the three environment model will not be presented. The general equations were presented in Part I (Eqs. 1, 2 and 28–40).

The RTD is assumed to be plug flow,

$$f_i(t) = \delta(t - \tau), \quad i = 1,2. \tag{6}$$

The reactions were of the simple type

$$A + nB \rightarrow P + E\ (n = 1 \text{ or } 2) \tag{7}$$

and the rate law is given by

$$r_A = r_B/n = -kC_A C_B. \tag{8}$$

Since it is desirable to use a dimensionless form of the equations, we define scaled time and concentration variables,

$$C_{ji}^* = C_{ji}/\overline{C}^o$$
$$\lambda^* = \lambda/\tau, \quad j = A,B; \quad i = 1,2. \tag{9}$$

The characteristic concentration, $\overline{C}^o$, is calculated as

$$\overline{C}^o = Q_i C_j^o/(Q_1 + Q_2), \tag{10}$$

where C_j^o is the inlet concentration of the limiting reactant j, and i is 1 or 2 according to which stream contained the limiting reactant. Assuming further that the reactants A and B are contained in stream 1 and 2 respectively, we also define β, the feed stoichiometric ratio, as

$$\beta \equiv \overline{C}_A^o/n\overline{C}_B^o \tag{11}$$

where $\overline{C}_A^o$ and $\overline{C}_B^o$ are the flow-weighted concentrations (cf., Eq. 10).

With the above definitions in hand, we now present the specific model equations (Note: Eqs. 28–40 referred to below are the corresponding equations in Part I). The ideal form of the RTD (i.e., Eq. 6) permits an analytical solution of Eqs. 33 and yields

$$\hat{V}_i^L = Q_i[1 - \left(1 - \frac{Q_k}{Q_i}\right) \exp[-2R_s\tau(1 - \lambda^*)]$$
$$+ \frac{Q_k}{Q_i}(1 - 2\exp[-2R_s\tau(1 - \lambda^*)])], \quad i = 1,2; \quad k = 3 - i, \tag{12}$$

while Eqs. 37 reduce to

$$-\frac{dC_{ji}^{L*}}{d\lambda^*} = R_s\tau\left[\frac{V_i}{\hat{V}_i^L\tau}(C_{ji}^{o*} - C_{ji}^{L*})\exp[-R_s\tau(1 - \lambda^*)]\right.$$
$$\left. + \frac{\hat{V}_k^L}{\hat{V}_i^L}(C_{jk}^{L*} - C_{ji}^{L*})\right] + (Da)C_{ji}^{L*}C_{hi}^{L*},$$
$$\begin{matrix} j,h = A,B \\ j \neq h \\ i = 1,2 \\ k = 3 - i \end{matrix} \tag{13}$$

The term Da denotes the Damkohler number of the system,

$$Da = k\overline{C^o}\tau. \tag{14}$$

Equations 13, which are a set of four coupled nonlinear ordinary differential equations, can be solved with the initial conditions (cf., Eq. 39)

$$C_{ji}^{L*}(\lambda^* = 1) = C_{ji}^{o*}. \tag{15}$$

The dimensionless feed concentrations, C_{ji}^{o*}, are calculated as follows:

If $\beta < 1$ (i.e., A-limiting)

$$C_{A1}^{o*} = (1 + Q_2/Q_1)$$
$$C_{B2}^{o*} = \frac{1}{\beta}(1 + Q_1/Q_2)$$

and

$$C_{A2}^{o*} = C_{B1}^{o*} = 0; \tag{16a}$$

If $\beta > 1$ (i.e., B-limiting)

$$C_{A1}^{o*} = \beta(1 + Q_2/Q_1)$$
$$C_{B2}^{o*} = (1 + Q_1/Q_2)$$
$$C_{A2}^{o*} = C_{B1}^{o*} = 0. \tag{16b}$$

Finally, the yield of the product (P), at the reactor exit may be computed from the dimensionless form of Eq. 40 as

$$\overline{C}_p^{E*} = 1 - \frac{1}{Q_1 + Q_2}\left[\sum_{i=1}^{2}\left([\hat{V}_i^L C_{ji}^{L*}]|\lambda^* = 0\right.\right.$$
$$\left.\left. + \frac{V_i}{\tau}\exp(-R_s\tau)C_{ji}^{o*}\right)\right]. \tag{17}$$

j = limiting reactant.

The standard International Mathematical and Statistical Library (IMSL) subroutine DVOGER (Gear's method for solving "stiff" equations) was employed for the numerical integration of Eqs. 13 from $\lambda^* = 1$ to $\lambda^* = 0$. The concentration as a function of residence time (axial position) as predicted by the three and four environment models was compared to the experimental data for many values of the adjustable micromixing parameter ξ (Eq. 3). The best fit, determined by minimizing the square of the error between the model and experimental predictions of the conversion for the entire data set, was obtained with a model parameter of $\xi = 2.0$ for both models. Representative results for $\xi = 2.0$ are displayed in Figures 2–4. The complete set of simulated results is available in Mehta (1981).

For slow and moderately fast reactions (Figures 2 and 3), the predictions of both models are in excellent agreement with the data. The comparison is not so favorable in the case of very rapid reactions (Figure 4). We attribute this discrepancy in large measure to unaccounted for backmixing in the jet region—within 2 cm of the feed plane—where most of the very rapid reaction occurs.

Inspite of this imperfection in our modeling, we begin to discriminate between the three and four environment models. We find that for very rapid reactions, the three environment model fails to display any sensitivity to the stoichiometric ratio, β, while the four environment model shows trends with β which are qualitatively consistent with data (Figure 5).

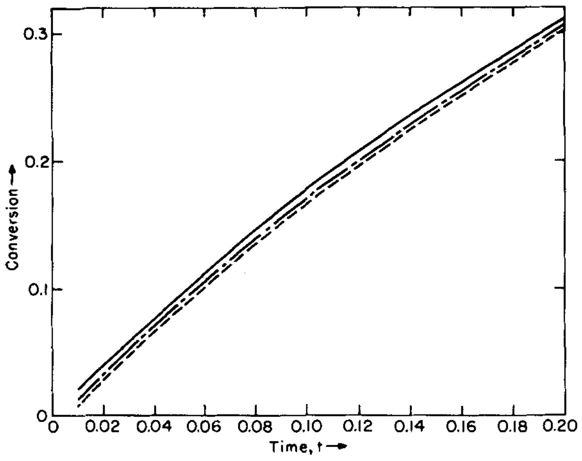


Figure 2. Slow reactions of Vassilatos and Toor (1965): — - — three environment model ($\xi = 2.0$) - - - - four environment model ($\xi = 2.0$), — experimental data and maximum mixedness ($Da = 0.88$, $\beta = 2.27$).

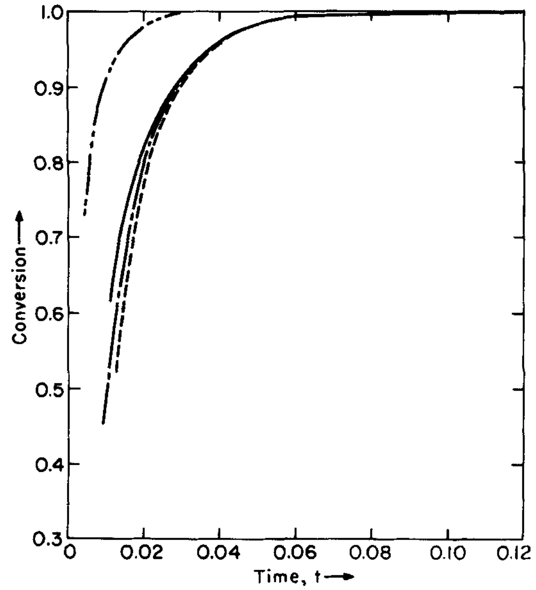
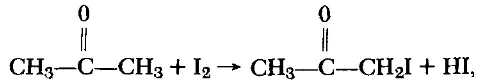


Figure 3. Moderately fast reactions of Vassilatos and Toor (1965): — — — three environment model ($\xi = 2.0$), - - - - four environment model ($\xi = 2.0$), — experimental data, — - - — maximum mixedness ($Da = 118$, $\beta = 1.71$).

The ability of the four environment model to correlate data over such a broad range of reaction-time scales with a single micromixing parameter is encouraging. Particularly since the best fit parameter value ($\xi = 2.0$) is quite close to the *a priori* turbulence estimate ($\xi = 2.5$).

4. EXPERIMENTS OF PLASARI ET AL.

Plasari et al. (1978) studied the iodination of acetone in a baffled CSTR (Figure 6). The two aqueous reactant streams were fed separately into the reactor as jets which provided considerable stirring in addition to that supplied by the six-bladed turbine. The overall reaction may be described as



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + I_2 \rightarrow CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2I + HI}, \tag{18}$$

and the global kinetic rate expression is of the Michaelis-Menten type:

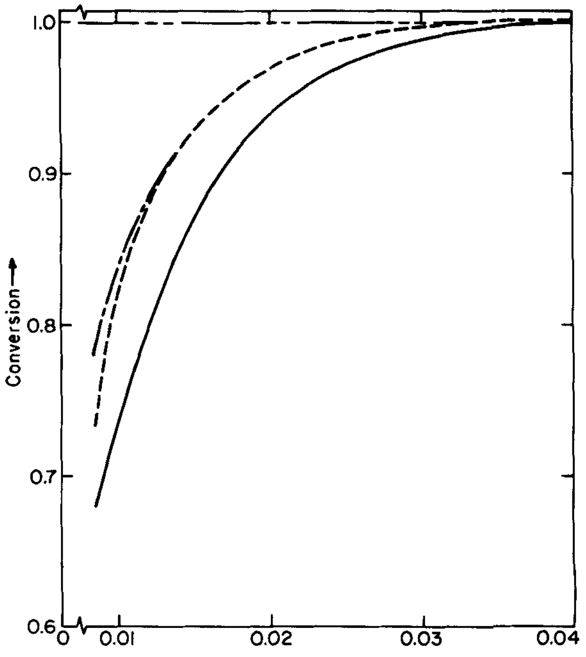


Figure 4. Very fast reactions of Vassilatos and Toor (1965): — — — three environment model ($\xi = 2.0$), - - - - four environment model ($\xi = 2.0$), — experimental data, — - - — maximum mixedness ($Da \sim 10^9$, $\beta = 1.4$).

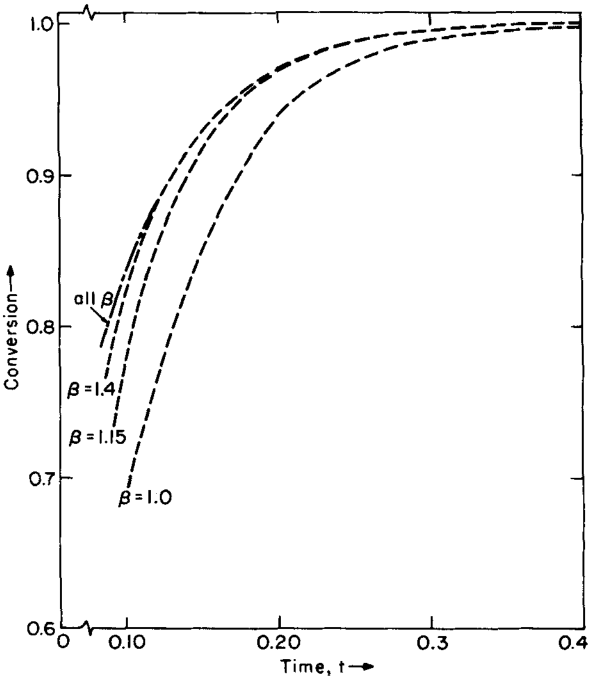


Figure 5. Effect of β on model predictions for very fast reactions of Vassilatos and Toor (1965): — — — three environment model ($\xi = 2.0$), - - - - four environment model ($\xi = 2.0$).

$$r = \frac{k_0 C_{I_2}}{k_m + C_{I_2}} \tag{19}$$

where

$$k_o = k C_{\mathrm{CH_3COCH_3}} C_{\mathrm{H^+}} \tag{20}$$

and

$$k_m = k' C_{H^+} \left(\frac{1 + K C_{\mathrm{I^-}}}{1 + \alpha K C_{\mathrm{I^-}}} \right). \tag{21}$$

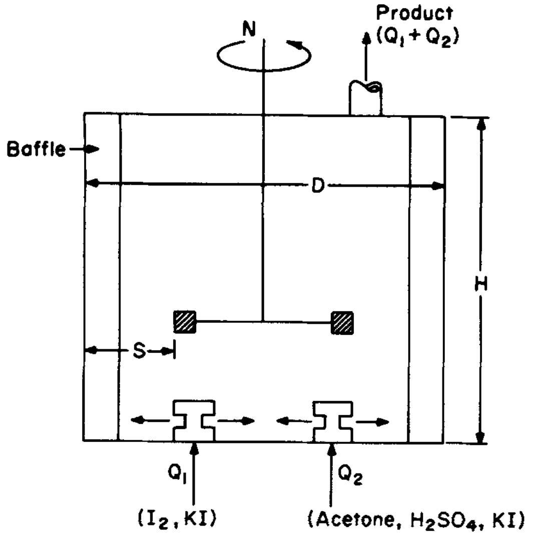


Figure 6. Schematic of Plasari's reactor (Plasari, 1976): V_R = 196 cm^3, H = 5.9 cm, D = 6.5 cm, S = 1.85 cm.

TABLE 3. EXPERIMENTAL CONDITIONS FROM PLASARI et al. (1978)

Concentration ranges:	
Acetone	0.25–0.5 M
H_2SO_4	0.15–0.3 M
KI	5×10^{-4} M
I_2:C°	1.7×10^{-5}:5×10^{-5} M
Temperature:	20–32°C
Mean Residence Time: τ	1.2–8 s
Characteristic Reaction Time: C_o/k_o	1.2–10 s
Viscosity:	0.8–6.7 cp
Stirring Speed: N	0–3,000 RPM
Flow Rate Ratio: $m = \left(\frac{Q_1}{Q_1+Q_2}\right)$	0.1–0.9

k, k', K and α are known functions of rate constants associated with the intermediate steps of a proposed reaction mechanism. However, the reactor was operated so that $k_m \ll C_{I_2}$, and thus pseudozero-order kinetics were obtained. Under such conditions, it was possible to observe the effect of imperfect micromixing through measurement of the exit concentration of iodine, $\overline{C}^E_{I_2}$. The range of operating conditions is summarized in Table 3.

It should be noted that these experiments are quite complicated—both in terms of kinetics and hydrodynamics, although no heat effects are involved and the microscale Reynolds numbers are high enough (Table 1) to suggest applicability of the turbulence analogy underlying the four environment model. Consequently, we do not confine ourselves to the limited set of data published in the literature (10 experiments; Plasari et al., 1978), but consider a much larger set obtained from the original source (101 experiments; Plasari, 1976). However, for the reasons cited later, we do not include experiments at high viscosities ($N_{Sc} > 850$).

The four environment model equations for the reactor of Plasari et al. (1978) are developed below. Since it was reported that perfect macromixing existed in the reactor, we use a perfectly stirred reactor RTD for each feed stream,

$$f_i(t) = \frac{1}{\tau}\exp(-t/\tau), \quad i = 1,2, \tag{22}$$

and obtain analytical solutions for $\hat{V}_{L_i}$ from Eqs. 33 of Part I:

$$\hat{V}_{L_i} = \frac{[R_s\tau(Q_1 + Q_2) + Q_i]R_s\tau^2 f_i(\lambda)}{(1 + R_s\tau)(1 + 2R_s\tau)} \quad i = 1,2. \tag{23}$$

The only bounded solutions of the leaving environment material balance equations (Eqs. 37 of Part I) which satisfy the condition

$$\left.\frac{dC^L_{ji}}{d\lambda}\right|_{\lambda=\infty} = 0 \quad \text{(cf. Eq. 38, Part I)} \tag{24}$$

are obtained when $dC^L_{ji}/d\theta = 0$ for all $0 \le \lambda \le \infty$. In solving these algebraic material balance equations, we neglect the reaction terms in the equations for both (H^+) and (CH_3COCH_3) since

$$C_{H^+}, \quad C_{CH_3COCH_3} \ggg C_{I_2}. \tag{25}$$

The latter then become linear algebraic equations and are readily solved for the local concentrations of (H^+) and (CH_3COCH_3) in each leaving environment:

$$C^L_{ji}(0) = \left[\frac{\mathrm{III}_k V_k + \hat{V}^L_i}{\mathrm{III}_k V_k + \hat{V}^L_i + \left(\frac{V_k}{V_i}\right)\hat{V}^L_k}\right] C^o_{ji} + \left[\frac{\hat{V}^L_k}{\mathrm{III}_i V_i + \hat{V}^L_k + \left(\frac{V_i}{V_k}\right)\hat{V}^L_i}\right] C^o_{jk};$$

$$j = H^+, \quad CH_3COCH_3 \tag{26}$$
$$i = 1,2$$
$$k = 3 - i$$

These, when substituted in Eqs. 20 and 21, yield local values of kinetic constants (k_o and k_m) for each of the reacting environments. Thus, we are left with two nonlinear algebraic material balance equations for the I_2 concentration in the leaving environments, namely,

$$\frac{k_{oi}C^L_{ji}(0)}{k_{mi} + C^L_{ji}(0)} - R_s\left[\frac{1 + 2R_s\tau}{R_s\tau[1 + (1 + Q_j/Q_i)R_s\tau]}(C^L_{ji} - C^o_{ji}) + \frac{[1 + (1 + Q_i/Q_j)R_s\tau]}{[Q_i/Q_j + (1 + Q_i/Q_j)R_s\tau]}(C^L_{ji} - C^L_{jk})\right] = 0;$$

$$j = I_2 \tag{27}$$
$$i = 1,2$$
$$k = 3 - i,$$

which are solved by using the standard Marquardt's algorithm. Finally, the exit concentration of I_2 is computed from Eq. 40 of Part I in a straightforward manner.

We now estimate the micromixing parameter, R_s, starting with the basic equation of the turbulence analogy (Eq. 1). Since both the feed jets and the turbine supply kinetic energy to the reaction mixture, we write

$$\epsilon = \eta_1 P_{\text{jet}} + \eta_2 P_{\text{turbine}}. \tag{28}$$

However, since a high level of turbulence is always maintained during the experiments, we consider it reasonable to assume that $\eta_1/\eta_2 \simeq 1$, to arrive at

$$\epsilon = \eta(P_{\text{jet}} + P_{\text{turbine}}). \tag{29}$$

We can neglect the logarithmic term in Eq. 1 for low Schmidt numbers ($N_{Sc} < 850$) and introduce less than 2% error in the estimate of τ_m. Using a typical value of 0.2 for η in stirred tanks (Zoulalian et al., 1974), we obtain an *a priori* estimate of ξ (Eq. 3):

$$\xi = 3.4. \tag{30}$$

The input kinetic energies, P_{jet} and P_{turbine}, were determined experimentally. The characteristic mixing length is taken as L_s = 1.85 cm which is the distance S in Figure 8. S is the distance between the jet nozzle and the reactor wall which is the same as the distance between the tip of the turbine blade and the reactor wall.

A data set based on 101 experiments was fit with the single adjustable parameter ξ (Eq. 3). The best fit value, arrived at by minimizing the mean relative error between experimental and model values of the I_2 exit concentration, was ξ = 3.2. This value is in excellent agreement with our estimated value of 3.4.

TABLE 4. SIMULATION OF PLASARI'S EXPERIMENTS
($\xi = 3.2$; $L_s = 1.85$ cm)

Input Parameters													
m	$(\overline{C}_{actone})^o$	$(\overline{C}H_2SO_4)^o$	$(\overline{C}_{I_2})^o$	k_o	k_m	τ	P_{jet}	$P_{turbine}$				$\overline{y}_{model}$	
	mol/L	mol/L	× 10^5 mol/L	× 10^5 mol/L·s	× 10^5 mol/L	s	m^2/s^3	m^2/s^3	N_{Sc}	rpm	$\overline{y}_{expt.}$	$(\overline{C}^E_{I_2})/(\overline{C}^o_{I_2})$	$\overline{y}_{max\text{-}mix}$
0.5	0.5	0.3	2.97	0.871	0.258	8.17	0.065	0.73	704	1,000	0.079	0.086	0.056 ± 0.007
0.5	0.5	0.3	2.97	0.871	0.258	3.92	0.59	0.00	704	0	0.254	0.256	0.199 ± 0.021
0.5	0.5	0.3	2.97	0.871	0.258	3.12	0.91	0.08	704	500	0.334	0.345	0.294 ± 0.021
0.5	0.5	0.3	4.98	0.932	0.274	3.87	0.59	0.00	672	0	0.457	0.413	0.370 ± 0.024
0.5	0.5	0.3	3.21	0.813	0.235	2.18	2.40	0.00	704	0	0.582	0.552	0.516 ± 0.020
0.5	0.5	0.3	3.21	0.813	0.235	1.57	6.90	0.00	704	0	0.771	0.669	0.643 ± 0.015
0.5	0.5	0.3	4.98	0.700	0.234	2.07	2.40	0.00	767	0	0.880	0.748	0.727 ± 0.005
0.5	0.5	0.3	4.98	0.481	0.106	1.51	6.90	0.00	828	0	0.980	0.868	0.858 ± 0.011
0.5	0.5	0.15	3.24	0.548	0.067	3.09	0.91	0.00	672	0	0.532	0.534	0.498 ± 0.019
0.5	0.5	0.15	3.24	0.548	0.067	3.09	0.91	0.08	672	500	0.525	0.533	0.498 ± 0.019
0.5	0.5	0.15	3.24	0.548	0.067	3.09	0.91	0.73	672	1,000	0.518	0.528	0.498 ± 0.019
0.5	0.5	0.15	3.24	0.548	0.067	3.09	0.91	6.20	672	2,000	0.513	0.517	0.498 ± 0.019
0.5	0.25	0.3	3.23	1.032	0.277	5.20	0.23	0.00	537	0	0.163	0.169	0.101 ± 0.012
0.5	0.25	0.3	3.23	0.776	0.251	3.87	0.59	0.08	586	500	0.328	0.324	0.275 ± 0.024
0.5	0.25	0.3	3.23	0.776	0.251	3.87	0.59	0.73	586	1,000	0.318	0.314	0.275 ± 0.024
0.1	0.5	0.3	3.07	0.843	0.362	3.93	1.40	20.80	760	3,000	0.306	0.274	0.259 ± 0.024
0.1	0.5	0.3	3.07	0.789	0.294	3.07	2.64	0.00	780	0	0.555	0.406	0.372 ± 0.024
0.2	0.5	0.3	3.22	1.350	0.375	6.20	0.35	0.73	659	1,000	0.097	0.100	0.065 ± 0.008
0.2	0.5	0.3	3.22	0.998	0.250	4.92	0.57	0.08	704	500	0.204	0.159	0.109 ± 0.013
0.8	0.5	0.3	2.53	1.025	0.379	6.20	0.23	6.20	718	2,000	0.096	0.104	0.086 ± 0.010
0.8	0.5	0.3	2.53	0.758	0.310	4.92	0.35	20.80	809	3,000	0.162	0.176	0.162 ± 0.018
0.9	0.5	0.3	3.10	0.800	0.343	3.96	1.40	0.00	809	0	0.327	0.310	0.273 ± 0.024
0.9	0.5	0.3	3.10	0.800	0.343	3.96	1.40	0.73	809	1,000	0.318	0.305	0.273 ± 0.024

For brevity, we present only a representative subset of the results in Table 4. The complete set can be found elsewhere (Mehta, 1981). The same data set was simulated with the three environment model for an identical value of ξ, and nearly identical results were obtained. The mean absolute deviation of four environment model predictions from the experimental data for the entire set of 101 points is 0.039, which is equivalent to a mean relative deviation of 11.6%. Considering the inherent errors in kinetic constants (±4% and ±7% in k_o and k_m, respectively), concentrations (reportedly negligible) and reproducibility (not reported) of the experiments, we feel that the four (and three) environment model compares very well with the experiments.

However, a few questions remain, particularly regarding the experiments at high viscosities. The experimentors varied viscosity by the addition of up to 15% polyethylene glycol (mol wt = 6,000) to the aqueous reaction mixture and obtained a range of Schmidt numbers ($537 \leq N_{Sc} \leq 10{,}060$). Equation 1 accounts for variations in N_{Sc}, but our simulations of the higher viscosity experiments led to a best fit value of ξ that was lower than the estimated value by a factor of 3, and the overall data fit was poor. The fit could be improved by using different values of ξ to fit various subsets of the data. However, this is an *ad hoc* procedure.

A closer look at the way Corrsin (1964) derived Eq. 2 is revealing. The two terms contributing to τ_m stem directly from Corrsin's approximate description of the concentration fluctuation spectrum at high wave numbers. Corrsin employed a two segment power law approximation with the segments being matched at a characteristic wave number $k_k = (\epsilon/\nu^3)^{1/4}$. The matching is not smooth and could lead to inaccuracy in the overlap region of the two power law approximations. Although several experimental studies have supported Eq. 1 (e.g., Gibson and Schwarz, 1983; Lee and Brodkey, 1964, Keeler et al., 1965, Evangelista et al., 1969; Pompei and Heywood, 1972; Lu et al., 1979), none has directly investigated Eq. 1 over a broad range of N_{Sc}. Consequently, for the purpose of the present paper, which is to evaluate the four environment model, we have not included high viscosity experiments in our simulations.

Plasari et al. (1978) simulated this entire data set with a diffusion type model—Interaction by Exchange with Mean (IEM)—due to Villermaux and Devillon (1972). The micromixing parameter of the IEM model, t_m, was believed to be analogous to Corrsin's τ_m in Eq. 1 (i.e., $t_m = {}^3\!/_8\, \tau_m$ for a zero-order reaction; Plasari, 1976). However, they found that for experiments with jet stirring only,

$$t_m \alpha \tau^{-5/3}, \tag{31}$$

while

$$\tau_m \alpha \tau \tag{32}$$

is expected from Corrsin's theory. Consquently, they rejected Corrsin's theory and proposed an alternative explanation—based on the second stage of Beek and Miller's picture of turbulent mixing (Beek and Miller, 1959)—in terms of a shrinking aggregate (SA) model. In view of the excellent agreement of the four environment model simulations with the same data, we are inclined to embrace rather than reject Corrsin's theory.

On the other hand, it can be shown that the IEM model also has a rigorous analogy to turbulence (Aubry, 1975), based on variance matching, which leads to the following relation:

$$t_m = 2\tau_m. \tag{33}$$

However, we feel that the disagreeable dependence of t_m on τ (Eq. 31) observed by Plasari et al. (1978) should be attributed to some intrinsic limitation of the IEM model, rather than Corrsin's theory.

5. EXPERIMENTS OF TRELEAVEN AND TOBGY

Treleaven and Tobgy (1973) studied single, second-order, liquid-phase chemical reactions in an unpremixed feed, confined (single) jet reactor, for which individual feed stream RTD data had been obtained previously (Treleaven and Tobgy, 1972b). A variety of feed stoichiometric ratios ($0.1 < \beta < 15.0$) were employed for a relatively narrow range of Damköhler numbers ($0.1 < Da < 18$) and several values of flow rate ratio ($1 \leq Q_2/Q_1 \leq 3$). The reactions may be considered moderately rapid relative to the mean residence time as the exit conversion ranged from 15 to 95%.

In previous studies, the data have been successfully simulated using three very different models: Treleaven and Tobgy, 1972a—coalescence-redispersion model; Ritchie and Tobgy, 1975—slab-diffusion model; Ritchie and Tobgy, 1979—three

TABLE 5. COMPARISON OF ξ (EQ. 3) FOR COALESCENCE-REDISPERSION AND THREE ENVIRONMENT MODELS

Q_1 $cm^3 \cdot s^{-1}$	Q_2 $cm^3 \cdot s^{-1}$	Coalescence-Redispersion	Three Environment*
25	25	2.4	—
50	50	2.4	—
100	100	2.5	2.6
25	50	3.0	—
50	100	2.6	—
25	75	3.4	—
50	150	3.0	3.4

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* Only two subset simulations were reported.

environment model. Thus, the data set does not provide a good basis for model discrimination. Furthermore, based on the comparisons presented in Sections 3 and 4 of this paper, we do not expect any significant difference between the three and four environment models since these experiments again involve only a single reaction. Therefore, we have not simulated this data set with the four environment model. Instead, we have considered the published results for the three environment model and the coalescence-redispersion model as a basis for further evaluation of the turbulence analogy suggested in Part I.

Treleaven and Tobgy (1972a) used experimental RTD's in a coalescence-redispersion model to simulate these experiments and found that for fixed hydrodynamic conditions (Q_1/Q_2 fixed), a single value of their micromixing parameter (I) was sufficient to predict experimental conversions quite accurately. Similarly, Ritchie and Tobgy (1979) used the same RTD data in three environment model simulations and found that with a single value of micromixing parameter (R_s), experimental conversions could be predicted with comparable accuracy.

Since an analogy has been established between isotropic turbulent mixing and both the coalescence-redispersion model (Evangelista et al., 1969) and the three environment model (Part I), it will be of interest to compare the experimentally-based mixing parameters for each model with those expected from turbulence theory. The mixing parameters of the two models are related by

$$I = 2R_s \tau \tag{34}$$

with the turbulence analogy given by Eq. 1. As in the case of Vassilatos and Toor's reactor, we consider the mean flow to be the turbulence generator with $\eta = 0.5$. We choose the characteristic mixing length equal to the reactor diameter ($L_s = 4.3$ cm) rather than the jet diameter because there was only a single jet (d = 1.3 cm) and much of the flow entered the reactor through the annulus surrounding the jet. Incorporating these assumptions into Eqs. 1–4 we are able to calculate a value of the adjustable mixing parameter ξ (Eqs. 2, 3) for each value of I reported by Treleaven and Tobgy (1972a) and each value of R_s reported by Ritchie and Tobgy (1979). The results are presented in Table 5. For comparison, the *a priori* estimate of ξ based on turbulence theory (Eqs. 1–4) is $\xi = 2.5$.

The close agreement between the values in Table 5 and the turbulence estimate seems to provide additional strong support for the turbulence analogy developed in Part I and for the underlying physical picture shown in Figure 3 of Part I. This seemingly pleasant circumstance is, in certain respects, puzzling because large-scale inhomogeneities in the flow and concentration fields were present in the upstream end of Treleaven and Tobgy's reactor where the central feed jet was expanding to fill the reactor cross section. In fact, in many experiments, this jet expansion region occupied as much as 50% of the reactor length. The turbulence theory underlying the analogies discussed in this section is based on homogeneous, isotropic turbulent fields (fine structure of turbulence) as in stages 2 and 3 of Beek and Miller's (1959) picture of turbulent mixing. The jet expansion region of Treleaven and Tobgy's reactor was neither homogeneous nor isotropic and might more realistically be categorized as stage 1 in Beek and Miller's picture. Then why the success of the models and the turbulence analogy? One answer might be that most of the chemical reaction took place beyond the point where the central jet filled the reactor (axial composition data has not been reported) where a fine structure description of turbulent mixing would be appropriate. However, if significant reaction took place in the jet expansion region, a second answer might be that the mixing models (three environment, four environment, coalescence-redispersion) possess an appropriate structure for the description of stage 1 mixing. In the absence of conclusive evidence, this remains an open question.

6. NUMERICAL SIMULATIONS FOR COMPLEX KINETICS

In all of the experiments we have simulated, except for the very rapid reactions of Vassilatos and Toor, the predictions of the three and four environment models have been very close—essentially identical. However, only simple (one reaction) kinetics were involved in these experiments. It is expected that a significant difference in the predictions of the three and four environment models should be apparent for unmixed-feed reactors with complex kinetics. Unfortunately, we have been unable to find well-defined experimental data for this type of system. Thus, we resort to numerical simulation with known kinetics in a hypothetical, yet plausible, chemical reactor. In particular, we consider methane combustion.

The gas-phase combustion of CH_4 in atmospheric air is often modeled by two kinetically significant reaction steps of the parallel-consecutive type:

$$\begin{aligned} CH_4 + 3/2\, O_2 &\rightarrow CO + 2H_2O \\ CO + 1/2\, O_2 &\rightarrow CO_2 \end{aligned} \tag{35}$$

We imagine that these reactions occur in an unmixed-feed, plug-flow type of reactor (combustor) to which the following conditions apply:

a) $\dfrac{L}{D} = 7.$

b) Mean residence time, $\tau = 0.1$ s.

c) The combustor is maintained at $T = 1{,}600$ K.

d) Turbulent kinetic energy is supplied by the mean flow.

e) $N_{Sc} = 1.$

We use the kinetic rate expressions reported by Williams et al. (1969) and estimate ξ, the micromixing parameter of Eq. 2 to be 1.7. (Actually, Eq. 10b of Part I was used to arrive at this estimate.) The details of the model development and numerical procedures are similar to those described earlier (Section 3) and will not be presented here.

Results of the simulations are shown in Figure 7 where it is evident that the predictions of the three environment model are relatively close to maximum-mixedness predictions while the four environment model shows significant deviations from the latter. There is a striking difference between the two models in their predictions of the CO dependence on fuel-air equivalence ratio (ϕ). The four environment model prediction shows the expected presence of significant CO in an unmixed, fuel-lean ($\phi < 1$) system; the three environment model does not.

Indirect experimental support for the four environment model can be found in the experiments of Pompei and Heywood (1972), who burned a kerosene/air mixture under overall fuel-lean conditions in an atmospheric-pressure, plug-flow burner. The typical experimental conditions were:

a) $\dfrac{L}{D} \simeq 8.4.$

b) $\tau \simeq 0.065$ s.

c) Temperature: 1,700–2,300 K.

d) Turbulent kinetic energy supplied by atomizing air pressure [69–207 kPa (10–30 psig)].

The most important feature of these experiments was the variation of atomizing air pressure which resulted in different rates of

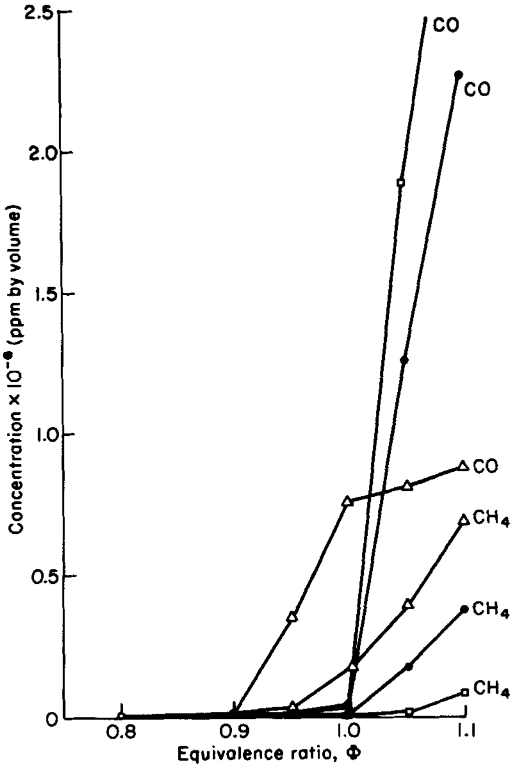

Figure 7. Simulation of methane combustion: □ maximum mixedness model, ● three environment model, △ four environment model.

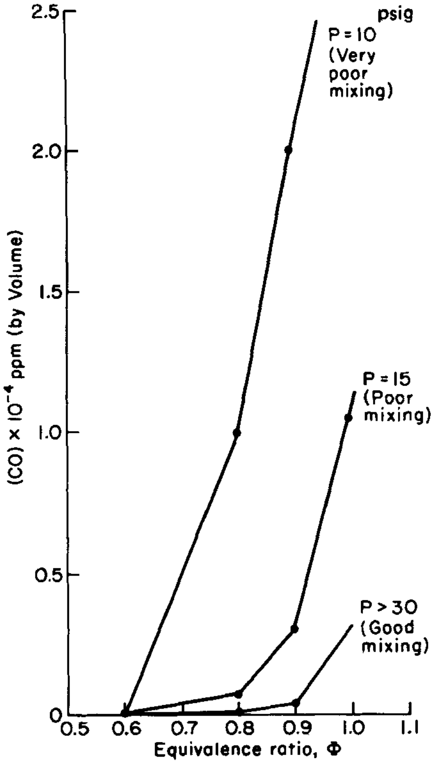

Figure 8. Experimental data of Pompei and Heywood (1972) for a kerosene burner.

microscale mixing which affected the CO concentrations, Figure 8. This micromixing effect on CO concentrations is pronounced and should be predicted by an acceptable model of mixing and chemical reaction.

We simulated the effect of varying the atomizing air pressure by varying the micromixing parameter ξ. In these simulations, we used the same methane kinetics and reactor parameters which led to the results of Figure 7. Kinetics for kerosene combustion were not available; although kerosene is not methane, it is a hydrocarbon and may be roughly modeled as burning according to a two-step (hydrocarbon partial oxidation, CO oxidation) mechanism similar to that for methane. The results of the simulations are shown in Figure 9. The solid lines are the four environment model predictions for various rates of micromixing while the single dashed line is the three environment model prediction for the same set of micromixing rates. The three environment model predictions are insensitive to micromixing and nearly identical to the maximum mixedness result. On the other hand, the four environment model displays significant sensitivity to micromixing—quite in accord with the experiments of Pompei and Heywood.

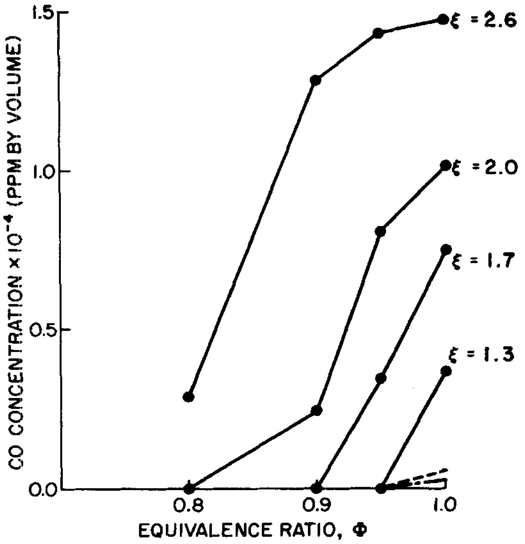

Figure 9. Simulation of experiments of Pompei and Heywood (1972): —— four environment model, - - - - three environment model, — — — maximum mixedness model.

Simulations of the competing reactions in a system containing N_2, O_2, NO and NH_3 using experimentally-based kinetics have also been carried out with the three and four environment models. Differences between the model predictions of the NO/N_2 selectivity of several orders of magnitude were observed (Mehta, 1981).

7. CONCLUDING REMARKS

The four and three environment models have accurately simulated several extensive sets of experimental reactor data (single reaction) covering a broad range of operating variables. For each reactor, the values of the micromixing parameter (ξ) which provided the best fit of the models to experimental data were very close to the *a priori* estimates provided by direct turbulence theory. This finding constitutes experimental support for the analytical turbulence analogy developed in Part I. Although it is difficult to distinguish between the three and four environment models when considering single-reaction systems, they may provide markedly different predictions of selectivity in the case of competing reactions. Our methane combustion simulations with the four environment model are in qualitative agreement with observations while similar simulations with the three environment model are not. Thus, the four environment model is proposed as a more general chemical reactor model.

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NOTATION

A,B,C,D,P,E = chemical species
C_{ji} = concentration of species j in ith environment
D,H,S = geometrical dimension
D = molecular diffusivity
Da = Damköhler number
f = residence-time frequency function
k,k' = kinetic rate constants
L = length
L_s = scalar macroscale
m = flow rate ratio, $Q_1/(Q_1 + Q_2)$
N = stirrer speed
N_{Sc} = Schmidt number = ψ/D
n = stoichiometric coefficient
P = power input per unit mass
Q = flow rate
r = chemical reaction rate
Re_ℓ = Reynolds number defined by Eq. 44 of Part I
R_s = micromixing parameter
t,t' = time
t_m = micromixing parameter
U = average velocity
V = holdup volume
V_R = total volume of the reactor
Z^* = axial distance of interest in Section 4

Greek Letters

β = feed stoichiometric ratio
δ = dirac-delta function
ϵ = turbulent energy dissipation rate per unit mass
η = efficiency factor
λ = residual lifetime
ν = kinematic viscosity
τ = mean residence time
τ_m = characteristic mixing time defined in Eq. 1
ϕ,ϕ^* = equivalence ratios
ξ,ξ' = adjustable parameters defined in Eqs. 31 and 5b respectively

Subscripts

m = micromixing
i,j,k,h = index variables
s = scalar

Superscripts

• = dimensionless quantity
o = feed
E = exit
L = leaving environment

Specific Symbols

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

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