Turbulent Reactive Mixing with a Series-Parallel Reaction: Effect of Mixing on Yield

The yield of a nonpremixed series-parallel reaction at complete conversion was measured in a turbulent, tubular-flow reactor with single and multijet feeds. The yield of the intermediate decreased as mixing was slowed relative to the chemical kinetics, either by decreasing the Reynolds number, or by using a less efficient mixing device, or by increasing the feed concentration.

Four models, a modified slab model, a modified stretch model, the Harada mass transfer model, and a new closure model, adequately predict the yield when chemical and mixing kinetics are known from independent measurements of the conversion of acid-base reactions. Without modification, the original slab and stretch models are unable to account for the earlier observed invariance of conversion to Schmidt number of very rapid, single-step reactions or to satisfactorily predict the yield of the series-parallel reaction.

K. T. Li, H. L. Toor
Department of Chemical Engineering
Carnegie-Mellon University
Pittsburgh, PA 15213

Introduction

When a chemical reaction is carried out by turbulently mixing two reactants, the time-averaged convective diffusion equations usually cannot be solved because nonlinear chemical reactions introduce unknown micromixing terms; in turbulence terminology, the equations are not closed.

For the archetypical single-step reaction described by,

$$A + nB \xrightarrow{k} R \tag{1a}$$

$$r_A = -kC_AC_B \tag{1b}$$

$$\bar{r}_A = -k(\overline{C_A}\,\overline{C_B} + \overline{C'_AC'_B}) \tag{1c}$$

the equations can be closed for large and small Damköhler numbers in the sense that $\overline{C'_AC'_B}$ can be related to the intensity of segregation of a passive tracer (Toor, 1962, 1969; Keeler et al., 1965; Vassilatos and Toor, 1965; Miyawaki et al., 1974). This led to a closure hypothesis for all Damköhler numbers that makes $\overline{C'_AC'_B}$ proportional to the intensity of segregation (Toor, 1969; Mao and Toor, 1971; McKelvey et al., 1975) in a near-stoichiometric, one-dimensional reactor.

Other approaches have sidestepped the closure problem by replacing the convective diffusion equations with simplified equations that can be solved either by assuming that the simultaneous diffusion and reaction takes place in hypothetical fluid elements of simple geometry and motion, or by separating the reaction from the mass transfer with lumped parameters. These various methods, once calibrated, say with acid-base data, also satisfactorily predict the effect of stoichiometry and Damköhler number in one-dimensional systems (Harada et al., 1962; Ng and Rippin, 1964; Kattan and Adler, 1967; Mao and Toor, 1970; Ranz, 1979). They are not limited to near-stoichiometric mixtures and are readily extended to complex reactions.

All the above methods require knowledge of the intrinsic chemical kinetics and the mixing; the former can be obtained independently by measurement of conversion under chemically controlled conditions (small Damköhler number) and the latter by measurement under diffusion-controlled conditions (large Damköhler number).

In all methods a complete knowledge of the chemistry and mixing is not needed. Sufficient knowledge of the chemistry is given by knowledge of the rate-controlling step and its rate constant, and sufficient knowledge of the mixing by the variance of

---

K. T. Li is presently at the Department of Chemical Engineering, University of Detroit, Detroit, MI 48221.

a scalar tracer or its normalized form, the intensity of segregation.

Although insufficient mixing may reduce the yield of single-step reactions and make scale-up difficult, the more important problems in practice arise with complex reactions where the selectivity can be influenced by mixing. Unlike the former situation, here selectivity cannot be enhanced by overdesign and, unless reactions are slow compared to mixing, scale-up will change the selectivity.

For series-parallel reactions with separate feeds, the subject of this study,

$$A + B \xrightarrow{k_1} R \tag{2a}$$

$$R + B \xrightarrow{k_2} S \tag{2b}$$

segregation, which will occur when the intrinsic reaction speed is comparable to or greater than the mixing speed, will decrease the yield of R by slowing down the first reaction more than the second. Levenspiel (1972) and Bourne and Toor (1977) have discussed this problem qualitatively, and a number of experimental studies have been carried out (Paul and Treybal, 1971; Bourne and Kozicki, 1977; Bourne et al., 1977a, b, c, 1981b).

Bourne and coworkers measured the yield of diazo coupling reactions (whose chemistry they determined independently) in a continuous stirred-tank reactor (CSTR) and found various variants of diffusion and stretch models that were more or less in accord with their data (Bourne et al., 1981b; Bourne, 1982; Angst et al., 1982; Bolzern et al., 1983; Angst et al., 1984). However, because of the lack of experimental data describing the complex mixing in their CSTR, they had to resort to theoretical estimates of mixing parameters. This raises uncertainties, both because of the incomplete state of turbulence theory and the complex fluid mechanics in a CSTR.

Our object in this work is to measure the yield of the above well-characterized series-parallel reactions in a tubular-flow reactor where the turbulent mixing has also been experimentally well characterized, and to use the data to assess reactive mixing models with a minimum of ambiguity. To do this we will use Bourne's diazo coupling reaction where k_1 and k_2 are known, with two different jet mixing devices whose mixing characteristics have been determined with acid-base reactions.

We will assess the slab diffusion model (Mao and Toor, 1970) and the stretch model (Ranz, 1979), both of which will first be modified in light of earlier data, and the mass transfer model of Harada et al. (1962). We will also develop and test a closure model based on the instantaneous convective diffusion equations.

Experimental

We used the reaction system developed by Bourne and coworkers (1981a), the coupling of 1-naphthol (A) with diazotized sulfanilic acid (B) in dilute, alkaline solution at room temperature to produce two dyestuffs: 4-(4′-sulfophenylazo)-1-naphthol (R) and 2,4-bis(4′-sulfophenylazo)-1-naphthol (S), and synthesized reactant B immediately before use in the manner given by Kozicki (1980).

The experiments were carried out at 22°C and pH = 10, at which condition the data of Bourne et al. (1985) gives

$$5 \times 10^6 \ \text{m}^3/\text{kmol} \cdot \text{s} < k_1 < 1.1 \times 10^7 \ \text{m}^3/\text{kmol} \cdot \text{s}$$
$$k_2 = 1.8 \times 10^3 \ \text{m}^3/\text{kmol} \cdot \text{s}$$

k_1 is large enough for the first step to be essentially instantaneous in our experiments, so its precise value is not needed. (The Damköhler number for the primary reaction is effectively infinite). At this limit incomplete mixing has its largest effect. k_1/k_2 is also large enough so that at complete conversion of B with perfect mixing the yield of R is essentially 100% when the initial concentrations of A and B are equal; a decreased yield of R then signals incomplete mixing.

A schematic diagram of the flow system is shown in Figure 1. The useful capacity of each tank was 2.5×10^{-4} m^3 and compressed N_2 was the driving agent. Two mixing devices were used; their mixing characteristics are given by Singh and Toor (1974). A geometrically similar version of the single-jet device and the multiple-jet device itself were used earlier to study fast, single-step reactive mixing in gases and liquids, from which the mixing characteristics were obtained.

The single-jet device consisted of a smaller tube centered with four vanes in a larger tube. The smaller tube was 4×10^{-3} m ID and 4.8×10^{-3} m OD; the larger tube measured 6.6×10^{-3} m ID. The outer tube, where the reaction takes place, extended 1.83 m beyond the inner tube. Large-scale radial concentration gradients are gone in about 0.04 m at $Re = 2{,}300$ and 0.006 m at $Re = 7{,}000$, after which the reaction is essentially one-dimensional.

The multiple-jet device consists of 14 8.4×10^{-4} m OD tubes close-packed in a 6.6×10^{-3} m ID tube. It was followed by the same 1.83 m long tube as the former device. The reactants are fed through alternate tubes and the macromixing is essentially complete in about 2.5×10^{-3} m, after which the reaction is essentially one-dimensional. At the same tube Reynolds number the mixing in the multiple-jet device is considerably faster than in the single-jet device. With both devices the reaction is completed (B is consumed) well before the liquid leaves the reactor. The reaction takes place in an essentially one-dimensional system in which the micromixing is taking place at a known rate, which is determined independently by measuring the conver-

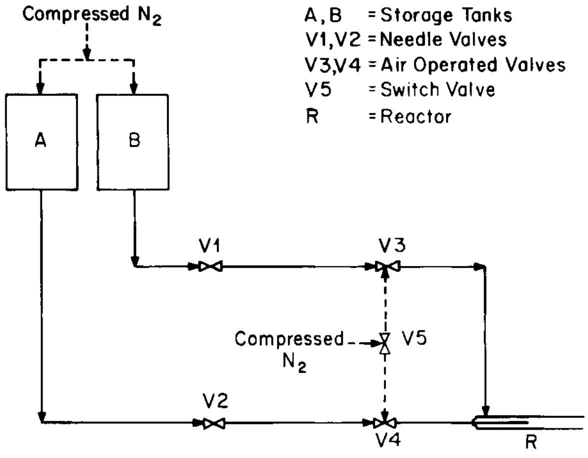

Figure 1. Flow system.

sion-distance relationship of single-step acid-base reactions whose intrinsic kinetics are so rapid that their conversion is controlled by the mixing.

The product solutions from the reactor outlet were collected after a short initial period, diluted, and then analyzed by spectrophotometry.

Results

Experiments were carried out at 22°C with equal flow rates of reactants and $\beta = 0.96$. The feed concentration of B was varied from 0.198×10^{-3} to 2.86×10^{-3} kmol/m^3 for the single jet, and from 0.244×10^{-3} to 1.92×10^{-3} kmol/m^3 for the multiple jet. The tube Reynolds numbers for the single jet were varied from 2,300 to 7,600 and for the multiple jet from 500 to 4,900. Most runs were repeated at least once and reported values are averages of replicates. Reproducibility of the yield was 0.5% for the single-jet data and 2.4% for the multijet data.

The single-jet data are shown in Table 1. We note that the yield in the single-jet reactor was usually higher when reactant A rather than reactant B was fed through the jet. This is not surprising because this system is two-dimensional before the jet expands to meet the tube wall, so there is no reason to expect the yield to be independent of feed position. Since the effect is relatively small and would require a two-dimensional model to analyze, it was not pursued further. Data for both situations are distinguished in Figure 4.

The multiple-jet data at $C_{BO} = 1.92 \times 10^{-3}$ kmol/m^3 are shown in Figure 2 up to $Re = 3{,}500$, where the yield is approaching the perfectly mixed value of one. Two single-jet data points with the same feed concentrations are also shown in the figure for comparison. Yield decreases as the Reynolds number is decreased in either device and as one goes from the multijet to the single-jet device at the same Reynolds number; in both cases poorer mixing decreases yield. Similarly, yield was found to decrease with decreasing turbine speed in a stirred tank (Bourne et al., 1981b). Yield also decreases as the reactant concentrations (at a constant β) increased: increasing intrinsic reaction speed decreases yield. All these effects represent a decrease of yield as the ratio of mixing speed to intrinsic reaction speed, a Damköhler number, increases. We now use the data to assess various models that lead to different Damköhler numbers. These are all Damköhler numbers for the secondary reaction; the Damköhler number for the primary reaction is effectively infinite in all the experiments.

Table 1. Yield of Diazo Coupling Reactions in a Single-Jet Tubular Reactor

Conc. of B gmol/m^3	Reynolds No.	% Yield when Jet is Reactant B	% Yield when Jet is Reactant A
2.86	3,530	82.05	84.92
2.86	5,150	84.85	88.87
2.86	7,552	88.33	90.68
1.92	2,385	—	76.76
1.92	3,530	—	85.74
1.92	5,149	—	89.3
0.964	3,530	88.95	91.13
0.964	5,150	91.69	93.61
0.964	7,552	93.45	94.88
0.198	2,300	93.28	91.7
0.198	3,383	98.54	98.97

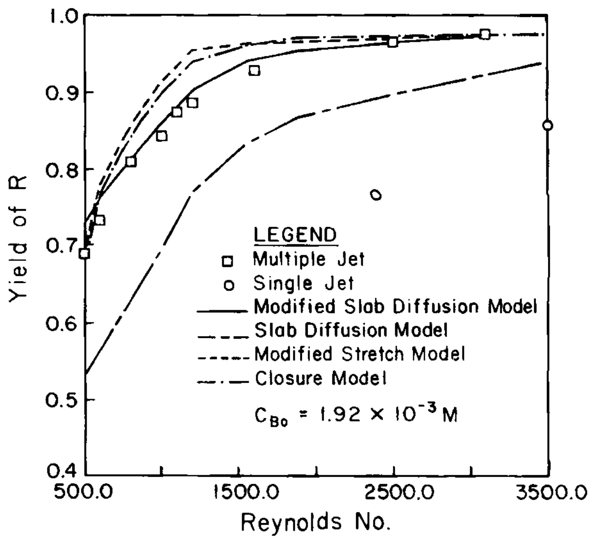

Figure 2. Yield vs. Reynolds number at a fixed feed concentration.

Diffusion Model

Mao and Toor's (1970) slab diffusion model assumed that mixing is controlled by molecular diffusion between alternate slabs of thickness δ, which depends upon fluid mechanics, and that in the case of chemical reactions a single constant Fickian diffusion coefficient can be used for all components i, so

$$\frac{\partial C_i}{\partial t} = D\frac{\partial^2 C_i}{\partial \xi^2} + r_i, \quad i = 1, 2, \ldots \tag{3}$$

The symmetry imposed by the alternate slabs makes all fluxes zero at $\zeta = 0$ and δ and with spatially uniform initial conditions the equations are easily solved. For the single-step reaction of Eq. 1a the solution gives

$$\bar{x}_A = \bar{x}_A(\theta, N_{D1}, \beta) \tag{4}$$

with

$$\theta = \frac{Dt}{\delta^2} \tag{4a}$$

Mao and Toor (1970) obtained δ by fitting Eq. 4 to acid-base conversion distance data at $\beta = 1$ with $t = z/u$ and then used this parameter to predict the measured conversion of acid-base reactions at other stoichiometric ratios as well as the conversion of slower speed reactions. Mao and Toor's (1971) measured conversion did not change as acid-base reactants were changed, although the diffusion model would predict some change, but the diffusivities did not change very much from one reactant to another. And since their values were also confounded by ionic effects, Mao and Toor in using the model ignored any changes in diffusivity, which is equivalent to assuming that $\delta^2 \alpha D$. Later, however, Ajmera et al. (1976) found that the conversion did not change even with the very large change in diffusivity in going from a liquid to a gaseous system. They found that at the same Reynolds number, N_{D1}, and β, and in the same apparatus, the conversion-distance profile for the very rapid gas phase reaction of NO and O_3 was the same as the conversion-distance profile for liquid phase acid-base reactions.

If we apply the slab diffusion model to these two situations, for the same conversion, from Eq. 4a,

$$\frac{D_\ell t_\ell}{\delta_\ell^2} = \frac{D_g t_g}{\delta_g^2} \tag{5}$$

and since at the same Reynolds number the conversion is the same in both cases at the same distance down the reactor

$$t_\ell = \frac{z}{u_\ell}; \quad t_g = \frac{z}{u_g} \tag{6}$$

$$\frac{u_\ell}{u_g} = \frac{\nu_\ell}{\nu_g} \tag{7}$$

Equations 5–7 give

$$\frac{\delta_g}{\delta_\ell} = \left(\frac{Sc_\ell}{Sc_g}\right)^{1/2} \tag{8}$$

so equality of the conversion-distance profiles in gases and liquids requires the slab thickness to vary as $Sc^{-1/2}$. With this modification the diffusion model also predicts that the conversion profile will be the same for all acid-base reactions, as observed by Vassilatos and Toor (1965) and Mao and Toor (1971) in six different systems; in liquids, $\delta^2 \alpha D$. Because the diffusivities of the reactants in the series-parallel reactions are small compared to the diffusivities of the reactants used to determine δ, the modification has a significant effect on predicted yield of the series-parallel reaction.

Thus we conclude that the slab thickness δ, originally assumed to be fixed only by hydrodynamics, also depends upon diffusivity. But since only the group Dt/δ^2 appears in Eq. 4, this means that there is no predicted effect of diffusivity on mixing or reaction—as observed experimentally—and this prediction should be independent of the chemistry.

It is of interest to note that in the multijet reactor where the energy dissipation rate, ϵ, and δ have both been measured (McKelvey et al., 1975), the diffusive length scale

$$\lambda = 2\pi(\nu^3/\epsilon)^{1/4}\left(\frac{D}{\nu}\right)^{1/2} \tag{9}$$

(The scale below which diffusion becomes important) is $\frac{2}{3}\,\delta$ after the jets coalesce.

Application of the Slab Diffusion Model to the Series-Parallel Reaction

Equation 3 can be written as the following set of nondimensional equations for the series-parallel reaction system

$$\partial X_A/\partial\theta = \partial^2 X_A/\partial Z^2 - N_{D1}X_A X_B \tag{10a}$$

$$\partial X_B/\partial\theta = \partial^2 X_B/\partial Z^2 - [N_{D1}/\beta]X_A X_B - N_{D2}X_R X_B \tag{10b}$$

$$\partial X_R/\partial\theta = \partial^2 X_R/\partial Z^2 + [N_{D1}/\beta]X_A X_B - N_{D2}X_R X_B \tag{10c}$$

$$\partial X_S/\partial\theta = \partial^2 X_S/\partial Z^2 + N_{D2}X_R X_B \tag{10d}$$

with initial conditions:

$$\theta = 0, 0 < Z < 0.5, X_A = 1, X_B = 0, X_R = 0, X_S = 0;$$
$$0.5 < Z < 1, X_A = 0, X_B = 1, X_R = 0, X_S = 0 \tag{10e}$$

and boundary conditions, at $Z = 0$ and $Z = 1$:

$$\partial X_A/\partial Z = \partial X_B/\partial Z = \partial X_R/\partial Z = \partial X_S/\partial Z = 0 \tag{10f}$$

The Galerkin method was used to transform the space domain of Eq. 10 into finite-element equations. The time derivative was written in finite-difference form by using the forward difference method, and the resulting system of simultaneous linear algebraic equations was solved by the Gaussian elimination method on a DEC-20 computer. The computation continued until the dimensionless concentration of the limiting reactant B was less than 10^{-3}. The calculation results are plotted in Figure 4 for Damköhler number (N_{D2}) from 0.1 to 28, $N_{D1}/N_{D2} = 2{,}000$, and $\beta = 0.96$.

δ^2/D was obtained as a function of Reynolds number for both devices mostly from the acid-base data of various investigators (Mao, 1969; Singh, 1973) and scaled where necessary following Toor and Singh (1973). For the lower Reynolds numbers we measured the acid-base conversion ourselves (Li, 1985). δ^2/D was determined by using $t = z/u$ in Eq. 4 and equalizing the areas of overestimation and underestimation on the conversion-distance graphs. The deviation between Eq. 4 and the data increases at the lower Re numbers, suggesting that the diffusion model does not simulate the very rapid single-step reaction very well at low (presumably transitional) Reynolds numbers. However this appears to cause little subsequent difficulty in predicting yield of the series-parallel reaction.

The values of D/δ^2 so obtained are shown in Figure 3. A data point of $D/\delta^2 = 3.25\ s^{-1}$ at $Re = 12{,}000$ for the single-jet reactor is off the graph.

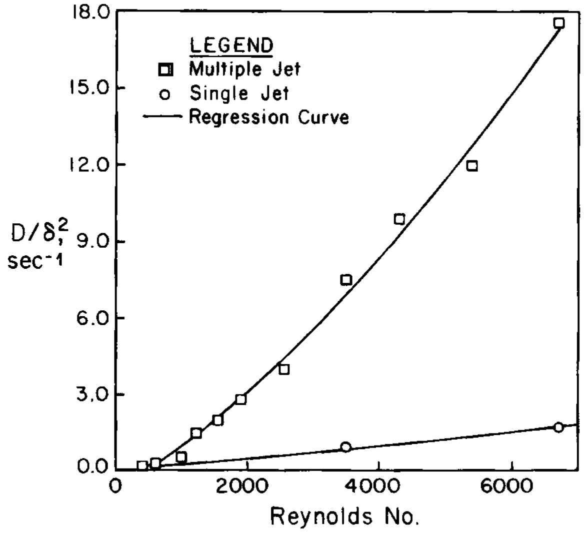

Figure 3. Mixing data, D/δ^2 vs. Re.

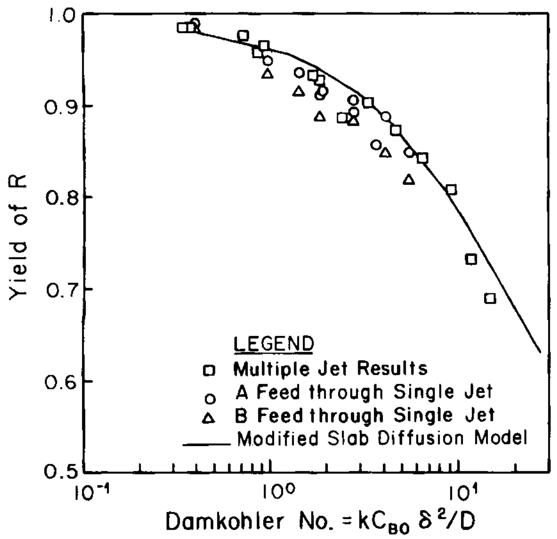

Figure 4. Yield vs. Damköhler number.

Since D/δ^2 is a function only of Reynolds number, we use the measured values of D/δ^2 in Eq. 10 without modifying for changes in diffusivity to determine the Damköhler number that corresponds to the slab diffusion model for the series-parallel reaction.

Because the mixing is slower in the single-jet reactor than in the multijet reactor at the same Reynolds number with the same feed concentrations, the yield in the two reactors was seen to differ significantly at the same Reynolds number (Figure 2). However, when compared at the same Damköhler number in Figure 4, the yield in both reactors is almost the same. Furthermore, the yield predicted by the modified slab diffusion model, which is shown in the figure, fits both sets of data reasonably well. The multijet data fit somewhat better than the single-jet data, and this good fit holds even at the lower Reynolds numbers where the diffusion model fits acid-base data most poorly. The model predictions are also compared to the data in Figures 2 and 5. We emphasize that the agreement is obtained with no adjustable parameters (although acid-base conversion measurements in the same reactor are required to determine the mixing parameter δ), which suggests that the modified slab diffusion model is robust indeed. However we shall see subsequently that other models do an equally good job.

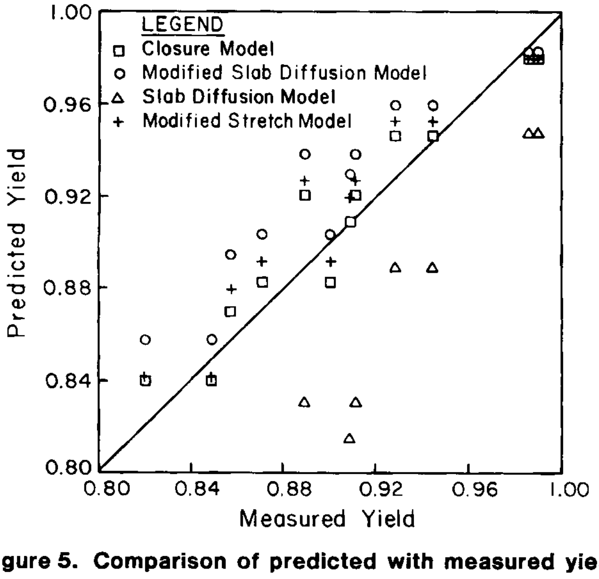

Figure 5. Comparison of predicted with measured yield in single-jet reactor.

We also plot the unmodified slab diffusion model in Figures 2 and 5 by using estimated diffusivities and observe that it predicts significantly lower yields than measured.

Stretch Model

Ranz and coworkers (Ranz, 1979; Ottino et al., 1979; Ou and Ranz, 1983) developed a stretch (or lamellar) model similar to the slab diffusion model. The major difference between these two models is that the slab thickness is independent of time (distance) in the slab diffusion model while the slab thickness (or striation thickness) varies with time in the stretch model.

The governing equation in a stretching slab is

$$\frac{\partial C_i}{\partial t} + w\frac{\partial C_i}{\partial \xi} - D\frac{\partial^2 C_i}{\partial \xi^2} = r_i, \quad i = 1, 2, \ldots \tag{11}$$

After transformation of variables, the stretch model gives the dimensionless form of Eq. 3 for the conversion for a single-step reaction with θ replaced by τ, which is given by

$$\tau = \int_0^1 [D/\delta^2(t')]\,dt' \tag{12}$$

Single-step acid-base conversion data at $\beta = 1$ can be used to relate τ and t from Eq. 4, and then $D/\delta^2(t)$ can be obtained by differentiating Eq. 12:

$$\frac{D}{\delta^2(t)} = \frac{d\tau}{dt} \tag{13}$$

The resulting values of $\delta(t)$ can then be used to predict the effect of β and k in the same apparatus at the same Reynolds number.

Not surprisingly, it is also necessary to modify this model in the same way the slab model was modified to account for the observed invariance of the conversion-distance curve with diffusivity. Thus, all the earlier single-step reaction data can be described by a modified stretch model in which we write for a given geometry:

$$\delta^2(t) = (Sc)^{-1} g(t, Re) \tag{14}$$

For the series-parallel reactions the stretch model gives Eq. 10 with θ replaced by τ so the Damköhler numbers, $[k_i C_{B0} \delta^2(t)]/D$, now vary with time. Thus, as with the slab model, this model predicts yield of the series-parallel reactions with no adjustable parameters if acid-base conversion data or comparable mixing data are available at the given Reynolds number to give $g(t, Re)$, and if k_1 and k_2 are known. Thus $\delta(t)$ was determined from the acid-base conversion data in the two reactors and the resulting predictions are compared to experiment in Figures 2 and 5. This modified stretch model does a poorer job than the modified slab diffusion model in the multijet reactor and a better job in the single-jet reactor.

Predictions of the unmodified stretch model are not shown because the estimated diffusivities are so low that the series-parallel reaction would be incomplete at the downstream distance where the acid-base reaction is essentially complete. Hence, we have no measurement of $\delta(t)$ to use after this point. It is clear, however, that for any reasonable extrapolations of $D/\delta^2(t)$ the unmodified stretch model will underpredict yield much like the unmodified slab diffusion model.

Closure Method

The alternative to using simplified models is to start with the convective diffusion equations and introduce a hypothesis to close the equations. To attempt to do this, we start with the instantaneous equation for species i in a mixture where all the diffusion coefficients are equal,

$$\mathcal{L}(C_i) = \frac{\partial C_i}{\partial t} + \underline{v} \cdot \nabla C_i - D\nabla^2 C_i = r_i, \quad i = 1, 2, \ldots \tag{15}$$

so the time-averaged equations are

$$\frac{\partial \overline{C}_i}{\partial t} + \overline{\underline{v}} \cdot \nabla \overline{C}_i - \nabla \cdot (D + \epsilon)\nabla \overline{C}_i = \overline{r}_i, \quad i = 1, 2, \ldots \tag{16}$$

If the reaction is assumed not to affect the eddy diffusivity, the lefthand side of the equation is closed. Actually ϵ plays no role in our experiment, since in the tubular reactor it is satisfactory to neglect time-averaged radial gradients and axial diffusion so that Eq. 16 becomes

$$u\frac{d\overline{C}_i}{dz} = \overline{r}_i, \quad i = 1, 2, \ldots \tag{17}$$

for the series-parallel reactions,

$$\overline{r}_A = -k_1(\overline{C}_A\overline{C}_B + \overline{C'_AC'_B}) \tag{18}$$

$$\overline{r}_S = k_2(\overline{C}_B\overline{C}_R + \overline{C'_BC'_R}) \tag{19}$$

$$\overline{r}_B = \overline{r}_A - \overline{r}_S \tag{20}$$

$$\overline{r}_R = -\overline{r}_A - \overline{r}_S \tag{21}$$

Thus, closure of the equations requires knowledge of the two terms $\overline{C'_AC'_B}$ and $\overline{C'_BC'_R}$.

Bourne and Toor (1977) argued that A and B are strongly correlated, while B and R are weakly correlated. Following this, if $\overline{C'_AC'_B}$ for the series-parallel reaction is assumed to be the same as for the single-step reaction, and if $\overline{C'_BC'_R}$ is assumed to be negligible compared to $\overline{C}_B\overline{C}_R$, then Eqs. 17–21 can be solved. However, the predicted yields by this method are in significantly poorer accord with measurements than earlier models, so we pursue this approach no further.

Brodkey and Lewalle (1985) closed the equations by assuming that $\overline{C'_AC'_B}$ is unaffected by the second reaction and used a separate hypothesis for the latter. This method gives even poorer predictions and we neglect this also.

Rather, we proceed as follows: From Eqs. 17 and 19

$$\frac{d\overline{X}_S}{dZ} = N'_{D2}(\overline{X}_B\overline{X}_R + \overline{X'_BX'_R}) \tag{22}$$

The yield of both S and R at complete conversion can be obtained if this equation can be integrated to the point where B is completely consumed.

Starting with Eq. 22, assuming that the first reaction is instantaneous so A and B are segregated and that X_S at the resulting reaction surface is small compared to one, gives (Appendix):

$$\frac{d\overline{X}_S}{dZ} = N'_{D2}\{[\hat{X}_B(Z) - \overline{X}_S][\hat{X}_R(Z) - \overline{X}_S] + \Delta\} \tag{23}$$

$$\Delta = \Delta_S[\hat{X}_R(Z) - \hat{X}_B(Z) - \Delta_S] + \overline{X'_BX'_R} \tag{24}$$

Δ_S is the amount of X_S on the A side of the reaction surface and $\hat{X}_B$ and $\hat{X}_R$ are the dimensionless time-average concentrations of B and R, respectively, when $k_2 = 0$, so they are known functions of Z. The contributions to the integration of Eq. 23 of the two separate terms in Eq. 24 are small and of opposite sign (at least in the slab diffusion model) so we close the equation by assuming $\Delta = 0$ to give

$$\frac{d\overline{X}_S}{dZ} = N'_{D2}[\hat{X}_B(Z) - \overline{X}_S][\hat{X}_R(Z) - \overline{X}_S] \tag{25}$$

Equation 25 was integrated numerically from $Z = 0$ where $\overline{X}_S = 0$ by taking $\hat{X}_B(Z)$ and $\hat{X}_R(Z)$ directly from acid-base conversion data, with the same mixing device at the same Reynolds number. Note that because $\hat{X}_B$ is independent of diffusivity the difference in diffusivities between the acid-base systems and the series-parallel system should have no effect. Conversion is complete when $\overline{X}_S = \hat{X}_B$, which, to within our approximation, is the point where B is completely consumed. The yield of R at complete conversion is defined as $\overline{C}_{Rf}/\overline{C}_{BO}$ where $\overline{C}_{BO}$ is the bulk average concentration of B in the mixed feed before reaction, and $\overline{C}_{Rf}$ is the bulk average concentration of R in the product where B is completely consumed. By stoichiometry $\overline{C}_{BO} = \overline{C}_{Rf} + 2\overline{C}_{Sf}$, and because the flow rates of the separate feed streams are equal $\overline{C}_{BO} = C_{BO}/2$, so

$$Y = \frac{\overline{C}_{Rf}}{\overline{C}_{BO}} = 1 - \frac{2\overline{C}_{Sf}}{\overline{C}_{BO}} = 1 - 4\frac{\overline{C}_{Sf}}{C_{BO}} = 1 - 4\overline{X}_{Sf} \tag{26}$$

The results are compared with measurement for both reactors in Figures 2 and 5. In the multijet reactor the model gives results very close to the modified stretch model—reasonably good agreement with data, but inferior to the modified diffusion model—while it gives the best prediction of all the models in the single-jet reactor.

Mass Transfer Model

Called by Harada et al. (1962) the coalescence-redispersion model because it was derived from this mechanism, called the IEM model by Villermax and coworkers (David and Villermax, 1975), and called the two-environment model by Bourne and Rohani (1982), this model is closely related to the coalescence-redispersion model. When applied to a flow reactor and calibrated with acid base data it satisfactorily predicts the slower speed reactions near $\beta = 1$, but fails to predict the conversion of acid-base reactions that are initially far from stoichiometric (Li, 1985). Bourne and Rohani (1982) also showed that the model could not predict the effect of varying the volume ratio in their experiments. When applied to our series-parallel experiments, the mass transfer model predicts essentially the same yield as the closure model.

Discussion

Although the modified stretch model, closure model, and mass transfer model all start from different points of view, they all predict similar yields and give a better prediction in the single-jet reactor than the modified diffusion model, which does a better job in the multijet reactor.

However all the models are probably accurate enough to serve for practical design and scale-up in reactors of the type used. The models contain no adjustable parameters and do not require explicit fluid mechanical information, but require independent knowledge of the intrinsic chemical kinetics and micromixing.

The similar predictions of the models are advantageous from a practical viewpoint, but this also means that the series-parallel reactions could not be used to distinguish among the models. However, since the series-parallel reactions appear to offer a stringent test of reactive mixing, it seems possible, if not probable, that general complex reactions can be handled by most of these models.

The closure model is specific to a series-parallel reaction so, although it comes closest to a fundamental viewpoint, it will be of less practical use for general complex reactions. The other models generalize readily to other reactions. Although it is the simplest, the mass transfer model is limited to near-stoichiometric feeds and so may be of less general utility. The modified diffusion and modified stretch models generalize readily and appear to be the models of choice, although the former is somewhat simpler to implement.

Earlier data, as well as the data of this study, make it clear that with both single-jet and multiple jet feeds, reactive mixing is not sensitive to molecular diffusion. After modification, the diffusion and stretch models still depend upon diffusion equations to predict yields. The fact that they do this quite successfully seems paradoxical in light of the above, but the additional fact that the mass transfer model gives similar predictions, even though it does not depend upon diffusion, suggests that the success is due to the relative insensitivity of reactive mixing to the details of the mixing—an observation made much earlier (Mao and Toor, 1970).

Finally, the experiments were effectively spatially one-dimensional. The models are similarly one-dimensional and do not readily extend to multidimensional systems where macromixing and micromixing are both important, as in the entrance to our reactor before the jets break up.

Notation

C = concentration
k_1 = reaction rate constant for primary reaction
k_2 = reaction rate constant for secondary reaction
$\mathcal{L}$ = operator, Eq. 15
n = stoichiometric coefficient
N_{D1} = Damköhler number $(=k_1 C_{BO}\delta^2/D)$
N_{D2} = Damköhler number $(=k_2 C_{BO}\delta^2/D)$
N'_{D2} = Damköhler number $(=k_2 C_{BO} z_m/u)$
r = rate of chemical reaction per unit volume
Re = Reynolds number based on reaction tube diameter
Sc = Schmidt number $(=\nu/D)$
t = time
u = velocity along the reactor
$\underline{v}$ = velocity vector
w = stretching velocity
X = dimensionless concentration $(X_A = C_A/C_{AO}, X_B = C_B/C_{BO}, X_R = C_R/C_{BO}, X_s = C_S/C_{BO})$
Y = yield of product R
z = distance along the reactor
z_m = half-mixing distance
Z = dimensionless distance $(=\xi/\delta$ or $z/z_m)$

Greek letters

β = initial stoichiometric ratio $(=C_{BO}/C_{AO})$
Δ = defined in Eq. 24
δ = slab thickness
ϵ = energy dissipation rate or eddy diffusivity
θ = dimensionless time $(=Dt/\delta^2)$
λ = diffusive length scale
ν = kinematic viscosity
τ = dimensionless time, Eq. 12
ξ = distance in the direction of diffusion

Subscripts and superscripts

A = species A
B = species B
f = the point where reactant B is completely consumed
g = gas phase
i = species A, B, R or S
ℓ = liquid phase
R = species R
S = species S
o = initial value or absence of reaction
1 = primary reaction or 1 inlet
2 = secondary reaction or 2 inlet
$'$ = fluctuating component of concentration
$\hat{}$ = single-step, diffusion-controlled reaction
— = time-averaged value
* = reaction surface

Appendix: Closure Model

We extract the linear combinations of reactants that are invarient to the reaction, as was done earlier with the single-step reaction. From the stoichiometry,

$$r_A + r_R + r_S = 0 \tag{A1}$$

$$r_A - r_B - r_S = 0 \tag{A2}$$

Then with Eq. 15

$$\mathcal{L}(C_A + C_R + C_S) = 0 \tag{A3}$$

$$\mathcal{L}(C_A - C_B - C_S) = 0 \tag{A4}$$

and for a nonreacting tracer,

$$\mathcal{L}(C_A^o) = 0 \tag{A5}$$

we label the jets through which A enters by 1 and the jets through which B enters by 2, and introduce the tracer through the 1 jets. Define

$$f = \frac{C_A^o - C_{A2}^o}{C_{A1}^o - C_{A2}^o} \tag{A6}$$

$$g = \frac{(C_A + C_R + C_S) - (C_A + C_R + C_S)_2}{(C_A + C_R + C_S)_1 - (C_A + C_R + C_S)_2} \tag{A7}$$

$$h = \frac{(C_A - C_B - C_S) - (C_A - C_B - C_S)_2}{(C_A - C_B - C_S)_1 - (C_A - C_B - C_S)_2} \tag{A8}$$

Then

$$\mathcal{L}(f) = \mathcal{L}(g) = \mathcal{L}(h) \tag{A9}$$

Since f, g, and h are the same on all the inlet surfaces and their normal derivatives are zero on all other surfaces,

$$f = g = h \tag{A10}$$

With the following conditions

$$\begin{gathered} C^o_{A1} = C_{A0}, C_{A1} = C_{A0}, C_{B1} = 0, C_{R1} = 0, C_{S1} = 0 \\ C^o_{A2} = 0, C_{A2} = 0, C_{B2} = C_{B0}, C_{R2} = 0, C_{S2} = 0 \end{gathered} \tag{A11}$$

Equations A6–A11 give

$$X_A - \beta(X_B + X_S) = (1 + \beta)f - \beta \tag{A12}$$

$$X_A + \beta(X_R + X_S) = f \tag{A13}$$

Since f represents the instantaneous nondimensional tracer concentration whose statistics, at least, are presumed known, we consider the above two equations to represent two relationships among the four instantaneous reactant concentrations.

Equations A12 and A13 also give

$$X_R + X_B + 2X_S = 1 - f \tag{A14}$$

Because k_1 is large the first step is almost surely diffusion-controlled in our experiments (the first Damkohler number of the slab diffusion model is the order [10^3–10^4]). Hence A and B are segregated; they cannot coexist, and like the analogous single-step reaction, A and B react on a reaction surface where A and B are both effectively zero. From Eq. A12 the value of f at this surface is given by

$$f^* = \frac{\beta}{1 + \beta}(1 - X^*_S) \tag{A15}$$

when $f > f^*$, $X_A > 0$, and $X_B = 0$, so from Eqs. A12 and A14, in the A fluid

$$X_A = \beta X_S + (1 + \beta)f - \beta \tag{A16}$$

$$X_R = (1 - f) - 2X_S \tag{A17}$$

when $f < f^*$, $X_B > 0$, and $X_A = 0$. So again from Eqs. A12 and A13, in the B fluid

$$X_B = 1 - \frac{1 + \beta}{\beta}f - X_S \tag{A18}$$

$$X_R = \frac{f}{\beta} - X_S \tag{A19}$$

If we presume that the behavior of the tracer f is known, the above equations represent two equations for the four unknown instantaneous concentrations X_A, X_B, X_S, and X_R. Because the additional conditions required to close the equations cannot be obtained from our starting equations (as usual in turbulence), we proceed as follows:

$$X_i = X_i(f) \tag{A20}$$

and if the probability density function of f is $\phi(f)$

$$\overline{X}_i = \int_0^1 X_i(f)\phi(f)\,df \tag{A21}$$

then from Eqs. A18 and A21, since B exists only for $f < f^*$,

$$\overline{X}_B = \int_0^{f^*} \left(1 - \frac{1 + \beta}{\beta}f\right)\phi(f)\,df - \int_0^{f^*} X_s(f)\phi(f)\,df \tag{A22}$$

and from Eqs. A17, A19, and A21, with some manipulation,

$$\overline{X}_R = \frac{1}{\beta}\int_0^{f^*} f\phi(f)\,df + \int_{f^*}^1 (1 - f)\phi(f)\,df - [\overline{X}_s + \Delta_s] \tag{A23}$$

where Δ_s, the amount of S in the A fluid, is given by

$$\Delta_s = \int_{f^*}^1 X_s(f)\phi(f)\,df \tag{A24}$$

When $k_2 = 0$, $X_s = 0$ and we have the single-step reaction, Eq. 1, so from Eqs. A15 and A22

$$\hat{X}_B = \int_0^{\beta/1+\beta} \left(1 - \frac{1 + \beta}{\beta}f\right)\phi(f)\,df \tag{A25}$$

$\hat{X}_B$ is the time-averaged concentration that would exist at a given position if $k_2 = 0$ and k_1 is large, a single-step, instantaneous reaction. $\hat{X}_B$ is known from acid-base measurements or can be obtained from the intensity of segregation since Eq. A25 relates $\hat{X}_B$ to the mean and variance of f. [A normal distribution for $\phi(f)$ gives results in accord with measurements, although Li (1985) showed that a more realistic Beta distribution gives similar results.] Also when $X_s = 0$, Eq. A14 gives

$$\hat{X}_R = 1 - \bar{f} - \hat{X}_B \tag{A26}$$

Since the maximum value of $\overline{X}_s$ in our experiments is 15.5% and $X^*_s < \overline{X}_s$, we now assume that X^*_s is small compared to one so we can use Eqs. A15, A21, A22, A23, A25, and A26 to write, after some manipulation,

$$\overline{X}_B = \hat{X}_B - \overline{X}_s + \Delta_s \tag{A27}$$

and

$$\overline{X}_R = \hat{X}_R - \overline{X}_s - \Delta_s \tag{A28}$$

From Eqs. 17 and 19

$$\frac{d\overline{X}_s}{dz} = \frac{k_2 C_{BO}}{u}(\overline{X}_B\overline{X}_R + \overline{X'_B X'_R}) \tag{A29}$$

and then using Eqs. A27 and A28 and nondimensionalizing the distance with the half-mixing distance, z_m,

$$\frac{d\overline{X}_s}{dZ} = N'_{D2}\{[\hat{X}_B(z) - \overline{X}_s][\hat{X}_R(z) - \overline{X}_s] + \Delta\} \tag{A30}$$

$$\Delta = \Delta_s[\hat{X}_R(Z) - \hat{X}_B(Z) - \Delta_s] + \overline{X'_B X'_R} \tag{A31}$$

Literature Cited

Ajmera, P. V., M. Singh and H. L. Toor, "Reactive Mixing in Turbulent Gases," *Chem. Eng. Commun.*, **2**, 115 (1976).

Angst, W., J. R. Bourne, and R. M. Sharma, "Mixing and Fast Chemical Reaction. V: Influence of Diffusion within the Reaction Zone on Selectivity," *Chem. Eng. Sci.*, **37**, 1259 (1982).

Angst, W., J. R. Bourne, and P. Dell'ava, "Mixing and Fast Chemical Reaction. IX: Comparison Between Models and Experiments," *Chem. Eng. Sci.*, **39**, 335 (1984).

Bolzern, O., and J. R. Bourne, "Mixing and Fast Chemical Reaction. VI: Extension of the Reaction Zone," *Chem. Eng. Sci.*, **38**, 999 (1983).

Bourne, J. R., "The Characterization of Micromixing Using Fast Multiple Reactions," *Chem. Eng. Commun.*, **16**, 79 (1982).

Bourne, J. R., and F. Kozicki, "Mixing Effects During the Bromination of 1,3,5-trimethoxybenzene," *Chem. Eng. Sci.*, **32**, 1538 (1977).

Bourne, J. R., and S. Rohani, "An Evaluation of a Two-Environment Model of Micromixing," *Proc. Eur. Conf. Mixing*, 4th, 312 (1982).

Bourne, J. R., and H. L. Toor, "Simple Criteria for Mixing Effects in Complex Reactions," *AIChE J.*, **23**, 602 (1977).

Bourne, J. R., C. Hilber, and G. Tovstiga, "Kinetics of the Azo Coupling Reactions between 1-Naphthol and Diazotized Sulphanilic Acid," *Chem. Eng. Commun.*, **37**, 293 (1985).

Bourne, J. R., F. Kozicki, and P. Rys, "Mixing and Fast Chemical Reactions. I: Test Reactions to Determine Segregation," *Chem. Eng. Sci.*, **36**, 1693 (1981a).

Bourne, J. R., F. Kozicki, U. Moergeli, and P. Rys, "Mixing and Fast Chemical Reactions. III: Model-Experiment Comparisons," *Chem. Eng. Sci.*, **36**, 1655 (1981b).

Bourne, J. R., U. Moergeli, and P. Rys, "Mixing and Fast Chemical Reaction: Influence of Viscosity on Product Distribution," *2nd Proc. Eur. Conf. Mixing*, 41 (1977a).

Bourne, J. R., F. Nabholz, and P. Rys, "Chemical Selectivities Disguised by Mass Diffusion. IV," *Hel. Chim. Acta*, **60**, 2937 (1977b).

Bourne, J. R., P. Rys, and K. Suter, "Mixing Effects in the Bromination of Resorcin," *Chem. Eng. Sci.*, **32**, 711 (1977).

Brodkey, R. S., and J. Lewalle, "Reactor Selectivity Based on First-Order Closures of the Turbulent Concentration Equations," *AIChE J.*, **31**, 111 (1985).

David, R., and Villermaux, J., "Micromixing Effects on Complex Reactions in a CSTR," *Chem. Eng. Sci.*, **30**, 1309 (1975).

Harada, M., K. Arima, W. Eguchi, and S. Nagata, "Micromixing in a Continuous-Flow Reactor," *Mem. Fac. Eng. Kyoto Univ.*, **24**, 431 (1962).

Kattan, A., and R. J. Adler, "A Stochastic Mixing Model for Homogeneous, Turbulent, Tubular Reactors," *AIChE J.*, **13**, 580 (1967).

Keeler, R. N., E. E. Petersen, and J. M. Prausnitz, "Mixing and Chemical Reaction in Turbulent-Flow Reactors," *AIChE J.*, **11**, 221 (1965).

Kozicki, F., Ph.D. Diss. No. 6618, ETH, Zurich (1980).

Levenspiel, O., *Chemical Reaction Engineering*, Wiley, New York (1972).

Li, K. T., "Turbulent Mixing with Complex Reactions in Unpremixed Tubular Reactors," Ph.D. Diss., Carnegie-Mellon Univ. (1985).

Mao, K. W., "Chemical Reactions with Turbulent Mixing," Ph.D. Diss., Carnegie-Mellon Univ. (1969).

Mao, K. W. and H. L. Toor, "A Diffusion Model for Reaction with Turbulent Mixing," *AIChE J.*, **16**, 49 (1970).

———, "Second-Order Chemical Reactions with Turbulent Mixing," *Ind. Eng. Chem. Fund.*, **10**, 192 (1971).

McKelvey, K. N., H. Yieh, S. Zakanycz, and R. S. Brodkey, "Turbulent Motion, Mixing, and Kinetics in a Chemical Reactor Configuration," *AIChE J.*, **21**, 1165 (1975).

Miyawaki, O., H. Tusjikawa, and Y. Uraguchi, "Turbulent Mixing in Multinozzle Injection Tubular Mixer," *J. Chem. Eng., Japan*, **7**, 52 (1974).

Ng, D. Y. C., and D. W. T. Rippin, "The Effect of Incomplete Mixing on Conversion in Homogeneous Reactions," *3rd Eur. Symp. Chem. Reac. Eng.*, Pergamon, Amsterdam, 161 (1964).

Ottino, J. M., W. F. Ranz, and C. W. Macosko, "A Lamellar Model for Analysis of Liquid-Liquid Mixing," *Chem. Eng. Sci.*, **34**, 877 (1979).

Ou, J. J., and W. F. Ranz, "Mixing and Chemical Reactions," *Chem. Eng. Sci.*, **38**, 1005 (1983).

Paul, E. L., and R. E. Treybal, "Mixing and Product Distribution for a Liquid-Phase, Second-Order, Competitive-Consecutive Reaction," *AIChE J.*, **17**, 718 (1971).

Ranz, W. F., "Application of a Stretch Model to Mixing, Diffusion, and Reaction in Laminar and Turbulent Flows," *AIChE J.*, **25**, 41 (1979).

Singh, M., "Chemical Reactions in One- and Two-Dimensional Turbulent Flow Systems," Ph.D. Diss., Carnegie-Mellon Univ. (1973).

Singh, M., and H. L. Toor, "Characteristics of Jet Mixers—Effect of Number of Jets and Reynolds Numbers," *AIChE J.*, **20**, 1224 (1974).

Toor, H. L., "Mass Transfer in Dilute Turbulent and Nonturbulent System with Rapid Irreversible Reactions and Equal Diffusivities," *AIChE J.*, **8**, 70 (1962).

———, "Turbulent Mixing of Two Species with and without Chemical Reactions," *Ind. Eng. Chem. Fund.*, **8**, 655 (1969).

Toor, H. L., and M. Singh, "The Effect of Scale on Turbulent Mixing and Chemical Reaction Rates During Turbulent Mixing in a Tubular Reactor," *Ind. Eng. Chem. Fund.*, **12**, 448 (1973).

Vassilatos, G., and H. L. Toor, "Second-Order Chemical Reaction in a Nonhomogeneous Turbulent Fluid," *AIChE J.*, **11**, 666 (1965).

Manuscript received Oct. 17, 1985, and revision received Feb. 6, 1986.