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Reactor Selectivity Based on First-Order Closures of the Turbulent Concentration Equations

Toor's (1969) hypothesis is extended to the second-order, series-parallel reaction. A second closure relates the mixing for the second reaction to the first. The equations are solved for conversion and selectivity for a turbulent reactor configuration. The analysis is extended to incorporate concepts of residence time distribution, segregation, and maximum mixedness.

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SCOPE

A basic understanding of turbulent motion, mixing, and kinetics in context with reactor modeling and design is not yet available to the profession. A model based on meaningful and independently measurable parameters would be helpful in reactor optimization and modification for improved performance. There have been two approaches to modeling for selectivity in chemical reactors for the second-order, series-parallel reaction. The more classic approach is to utilize single-stream residence time distribution concepts coupled with the limits of segregation and maximum mixedness and a micromixing parameter that will in some way account for the multiplicity of real effects not considered by the model, such as turbulent mixing between the inlet streams. Such models have been reviewed by Nauman (1981). The second approach, taken here, is to build a solution based on the concepts of turbulent mixing between streams, extending these concepts to the reaction in question, and utilizing them as a basis to solve the reactor performance problem. In this approach certain closure hypotheses must be made. Our goal is to further the basic understanding of reactor engineering by putting model analysis on a firmer basis.

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CONCLUSIONS AND SIGNIFICANCE

Chemical reactors can be modeled on the basis of turbulent motion, mixing, and kinetics. In the modeling it is necessary to formulate closure hypothesis. Toor (1969) suggested that mixing is independent of the speed of the reaction when the reactants are fed in stoichiometric proportion. This hypothesis, shown adequate for the single, second-order reaction by McKelvey et al. (1975), has been extended here to apply to the second reaction of the second-order, series-parallel reaction sequence. A second hypothesis for mixing closure has been developed to relate the mixing for the second reaction to that for the first. The closure relates $\overline{ab}$ of the first reaction to $\overline{pb}$ of the second. The now closed set of turbulent mixing and kinetics equations can easily be solved for the course of the chemical reaction in a typical reactor, such as the tubular reactor used by Mao and Toor (1971) and McKelvey et al. (1975). The results are illustrated, but actual experimental data for the specific cases are not yet available for comparison.

Of importance to chemical engineering is the ability to model chemical reactors such as mixing tanks, tubular reactors, and variations and permutations thereof. Based on the concepts developed in the first part, such reactors are modeled as combinations of a completely segregated reactor (CSR) and a maximum mixedness reactor (MMR) together with a general formula for the actual turbulent mixing in such reactors. The selectivity for the second-order, simultaneous-consecutive reaction is investigated in enough detail to illustrate the modeling concept and to show that nothing unusual occurs, in contrast to some modeling attempts using the more conventional approach and a micromixing parameter.

INTRODUCTION

In our previous work we utilized Toor's (1969) hypothesis that mixing is independent of the speed of the reaction when the reactants are fed in stoichiometric proportion, and showed that the hypothesis could be extended to the highest stoichiometric rate (3.88) for which data was available for the second-order reaction of $A + B \rightarrow P$. The analysis involved using the mass balance equation for an individual species (A), reduced to a one-dimensional (axial) form, and estimating that the velocity-scalar covariance term is negligible (i.e., an initially well-dispersed system). The actual axial velocity as measured in the reactor as a function of axial distance was used in the calculation. Toor's hypothesis above was used so that the mixing term (involving $\overline{ab}$) from pure mixing experiments could be used.

For the series-parallel reaction (and for other complex reactions), Toor's hypothesis can be extended to apply to the second reaction, and a second hypothesis (mixing closure) can be made to relate the mixing for the second reaction to that for the first. For the series-parallel reaction of $A + B \rightarrow P$ and $B + P \rightarrow S$, the mixing for the first reaction involves $\overline{ab}$ and that for the second involves $\overline{pb}$. The mixing closure hypothesis, which allows solution of the equations, is $\overline{pb} = \overline{ab}(\overline{P}/\overline{A})$.

Results of using this hypothesis will be illustrated; in particular, the effect on selectivity will be discussed. Because of the potential usefulness of the solution, the analysis has been extended to the treatment of the mixing characteristics of reactors.

BACKGROUND AND SCOPE

Toor's Hypothesis

Turbulent mixing and chemical reactions are often closely intertwined in the analysis of industrial reactors. In such cases, chemicals react only to the extent that turbulent stretching and mixing bring the components close enough for diffusion to ensure contact of the individual molecules and subsequent reaction. These ideas are quite familiar and have been discussed in detail in a number of papers (e.g. Brodkey, 1975, 1981). In many respects one of the most useful qualities is the intensity of segregation I_s, but it has limitations. The parameter is reputed to be adequate, (i) for the overall description of material interface smearing, with or without reaction, (ii) for substitution in the averaged mass balance equations for contaminants, (iii) for easy measurability of the statistics involved in the definition, and (iv) for flexibility of use where there is mixing of streams. The strongest limitation is the implicit assumption of an initially well-dispersed system but one that is not well mixed by molecular diffusion effects. In other words, there is a large scale homogeneity such that no matter where in the system one selects, the contents of that subarea will not vary from selection to selection. Different combinations of the variances and averages of concentrations have been used in the definition of I_s (e.g., Rao and Brodkey, 1972). The most widely encountered definition

$$I_s = -\overline{ab}/\overline{A}_0\overline{B}_0 \tag{1}$$

has been used in this work for its convenience. The 0 subscript refers to some initial concentration, as discussed in the later section on the law for the combination of I_s terms.

When the mass balance equation for the well-dispersed system for the reaction

$$A + B \xrightarrow{k} P \tag{2}$$

is averaged by Reynolds method, its approximate one-dimensional form is

$$\overline{U}_x \frac{d\overline{A}}{dx} = -k(\overline{A}\,\overline{B} + \overline{ab}) + D\frac{d^2\overline{A}}{dx^2} \tag{3}$$

(see McKelvey et al., 1975).

This equation can be rewritten in terms of the intensity of segregation, Eq. 1, as

$$\frac{1}{\overline{A}_0}\frac{d\overline{A}}{dx} = -\frac{k\overline{B}_0}{\overline{A}_0\overline{U}_x}\left(\frac{\overline{A}\,\overline{B}}{\overline{A}_0\overline{B}_0} - I_s\right) + \frac{D}{\overline{A}_0\overline{U}_x}\frac{d^2\overline{A}}{dx^2} \tag{4}$$

where $\overline{A}_0/\overline{B}_0$ could be replaced by β, the stoichiometric ratio. Equation 4 is easily solved (Yieh, 1970), if I_s is known as a function of x. This suggests writing the evolution equation for $\overline{ab}$. Under the same approximations as above, the resulting equation is

$$U_x\frac{d\overline{ab}}{dx} = D\frac{d^2\overline{ab}}{dx^2} - 2D\overline{\frac{da}{dx}\frac{db}{dx}} - k[\overline{ab^2} + \overline{a^2b} + \overline{A}\,\overline{b^2} + \overline{B}\,\overline{a^2} + \overline{ab}(\overline{A} + \overline{B})] \tag{5}$$

Toor's hypothesis results from the consideration of the two extreme cases of $k \rightarrow 0$ and $k \rightarrow \infty$. In the latter situation, the term in brackets in Eq. 5 must vanish because it is not balanced by any other term. In the former case, $\overline{ab}$ decreases only by the action of diffusion. Thus, in the two limits, we have

$$k[\overline{ab^2} + \overline{a^2b} + \overline{A}\,\overline{b^2} + \overline{B}\,\overline{a^2} + \overline{ab}(\overline{A} + \overline{B})] = 0 \tag{6}$$

Toor conjectured that Eq. 6 holds at least approximately for all values of k. The consequences are far reaching: $\overline{ab}$ and consequently I_s are now independent of whether or not there is a reaction in the flow, and thus can be determined independently from pure mixing experiments, or equivalently from fast reaction experiments. The hypothesis was utilized by Yieh (1970) and McKelvey et al. (1975), and the agreement with experimental data was very good. More recently, Hill (1979) tested the hypothesis by a two-dimensional numerical simulation and although there were numerical limitations, the results were also encouraging. Thus, Toor's hypothesis can be accepted as a powerful working tool.

Series-Parallel Reactions: A Further Mixing Closure Hypothesis

Toor's conjecture, Eq. 6, provides a closure of the averaged equations for a simple reaction, Eq. 2. More complicated situations are of greater interest, involving competitive reactions in series or parallel, or catalytic effects. The variety of effects that can be encountered in those cases (Bourne and Toor, 1977) has resisted a comprehensive treatment, but progress is being made in that direction, as reviewed by Patterson (1981). We concentrated our efforts on the series-parallel reactions as one example

$$A + B \xrightarrow{k_1} P$$

$$B + P \xrightarrow{k_2} S \tag{7}$$

In this case the mass balance equation will involve not only the $\overline{ab}$ covariance, but also a $\overline{bp}$ term. Other moments can be expressed in terms of $\overline{ab}$ and $\overline{bp}$ through conservation requirements. Toor's hypothesis applied to both reactions, can help to simplify the expressions, but an additional closure is still required. It is, of course, an extension of Toor's hypothesis to apply it independently to the second reaction and thus further assume that the consumption of B in the second reaction has no effect on $\overline{ab}$ that appears in the first equation. Note, however, that a parallel equation to Eq. 5 can be written for the second reaction and that an identical argument can be applied to this equation also. The generalized form of the rate equations corresponding to Eq. 7 is considerably simplified if the covariances obey

$$\overline{bp} = \overline{ab}(\overline{P}/\overline{A}) \tag{8}$$

We endeavored to examine the plausibility and limits of accuracy of Eq. 8. A simplistic reaction cell model confirmed exactly that the relation might be valid. Further calculations based on simulating the reactions between cells with random concentrations show that the closure equation (Eq. 8) is valid to at least within a few percent when the kinetic coefficients k_1 and k_2 are equal. More elaborate work is under way, studying the possible influence of the kinetics and the mutual diffusion of all species involved. In the meanwhile, we had sufficient confidence in Eq. 8 to explore the possibilities it opened. It should be noted that if the closures have eventually to be modified to accommodate, say, weak dependence on β, k_1, k_2, etc., the resulting expressions can be introduced into the equations to follow. The generality of the analysis is not limited by particular closures used.

MULTIJET TUBULAR REACTOR

Predictions for Series-Parallel Reactions Using the Mixing Closure Hypothesis

We decided to test the closure using the tubular reactor because of its conceptual simplicity, and because we were familiar with the limiting case of $k_2 = 0$ previously investigated (Vassilatos and Toor, 1965; Mao and Toor, 1971; Yieh, 1970; etc.).

We take the reactions to be as given in Eq. 7 with initial conditions $\overline{A}_0/\overline{B}_0 = \beta$, $\overline{P}_0 = 0$, $\overline{S}_0 = 0$, where β is the stoichiometric ratio. The definitions for the mass fractions are $F_a = \overline{A}/\overline{A}_0$, $F_B = \beta\overline{B}/\overline{A}_0$, $F_P = \overline{P}/\overline{A}_0$, and the resulting equations (neglecting the diffusion terms, as in McKelvey et al., 1975) are:

$$\dot{F}_A = -\frac{k_1\overline{A}_0}{\beta}(F_AF_B - I_s)$$

$$\dot{F}_B = -k_1\overline{A}_0(F_AF_B - I_s) - k_2\overline{A}_0(F_BF_P - I_sF_P/F_A)$$

$$\dot{F}_P = +\frac{k_1\overline{A}_0}{\beta}(F_AF_B - I_s) - \frac{k_2\overline{A}_0}{\beta}(F_BF_P - I_sF_P/F_A)$$

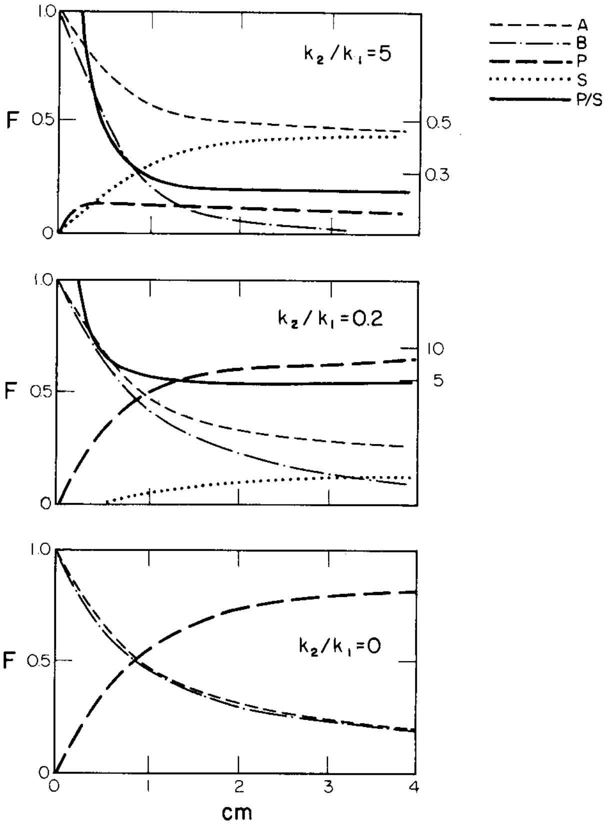

Figure 1. Evolution of concentrations in tubular reactor for several combinations of kinetics coefficients.

$$\dot{F}_S = +\frac{k_2\overline{A}_0}{\beta}(F_BF_P - I_sF_P/F_A) \tag{9}$$

when I_s is defined as

$$I_s = \overline{ab}/\overline{A}_0\overline{B}_0 \tag{1}$$

and we substitute the closure for $\overline{bp}$, as given in Eq. 8. In preliminary calculations, the parameters $\overline{A}_0$, β, and k_1 were chosen to reproduce the calculations of Yieh when $k_2 = 0$. Thus, we satisfied ourselves that the basic program worked properly (Figure 1).

Results

We have assumed that I_s is unaffected by either chemical reaction, i.e., that $\overline{ab}/\overline{A}_0\overline{B}_0$ remains unchanged also when k_2 varies. This sets I_s as that for pure mixing as measured either by mixing or by fast reactions. The integration of the four coupled equations in Eq. 9 presents no difficulty. The conditions (velocity variation and I_s decay) used to produce the results shown in Figure 1 are the same as used by McKelvey et al. (1975) in calculating the results for the reaction $A + B \rightarrow P$ as measured by Mao and Toor (1971). The results for $I_s = 0$ (kinetically controlled) would fall off extremely fast (in less than 1 cm) to the asymptotic values. Until actual measurements are available to compare with these predictions, we can only remark that nothing unexpected or puzzling happens. The $\overline{P}/\overline{S}$ curves are monotone as expected for all combinations of the parameters that were considered.

There are, however, some interesting points that warrant further comment. First, the closure approximation for the absolute plug flow case (completely segregated in time) with no backmixing whatsoever gives the same results for long times for fixed initial conditions (i.e., fixed β, $\overline{A}_0$, initial I_s, and ratio of k's) regardless of the history as long as $I_s < 1$. Thus, given enough time, the yield of P and selectivity is independent of I_s as long as $I_s < 1$. If I_s remains at 1, there is complete segregation and therefore no reaction. It is important to note that this independence of the final conversion on the history of mixing is restricted to the plug flow reactor. As will be seen later, for other reactor configurations, the yield of P

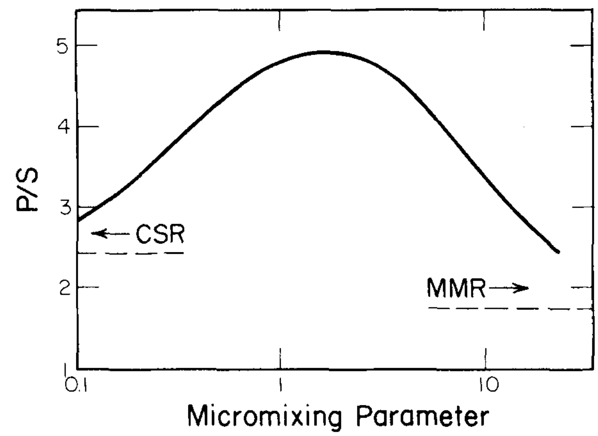

Figure 2. Micromixing parameter prediction of the selectivity curve after Apostolopoulos and Smith (1976).

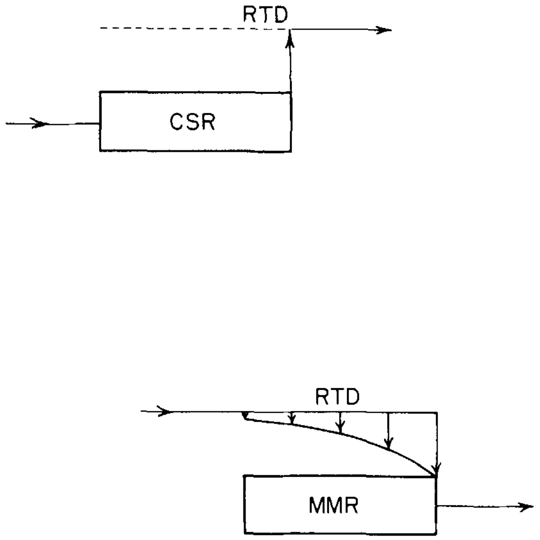

Figure 3. Residence time distribution with complete segregation reactor (CSR) and with maximum mixedness reactor (MMR).

and selectivity is a function of the history of mixing. Furthermore, the time-dependent conversion to P and the selectivity along the reactor is a strong function of I_s.

We should mention that the experimental mixing tank results of Paul and Treybal (1971) cannot be used for comparison because of the reactor configuration difference and, more important, because their experiment involved the continuous injection of B into a tank of A. This procedure violates our basic premise of initially gross mixed components as stated in the earlier section on Toor's hypothesis.

The generally satisfactory nature of our results answers some questions but clearly stimulates others. The mixing closure and the independence of I_s on the reactions (Toor's extended hypothesis) appear to be good working tools. We are, however, investigating those issues further.

MIXING CHARACTERISTICS OF REACTORS

Using simple situations, one can show that non-linear effects in the reaction scheme will result in the final concentrations depending on the residence time in the reactor and the efficiency of mixing (Nabholz et al., 1977). As one example, Apostolopoulos and Smith (1976) devised a model for several reaction schemes where the nature of the mixing is described by a micromixing parameter. They showed that selectivity was larger for a reactor of characteristics intermediate between the maximum mixedness and the complete segregation types (Figure 2) for the series-parallel reactions. Considering the potential generality of our extension of Toor's hypothesis and of the additional mixing closure, we felt it of value to attempt to extend the analysis to consider variations in residence time distribution (RTD) and the concepts of segregation and maximum mixedness. In this analysis, a full coupling is envisioned between basic turbulence modeling and the concepts normally used in reaction kinetics.

Basic Models

Two extreme cases of the mixing characteristics provide well-known basic models for the reactor: the complete segregation reactor (CSR) and the maximum mixedness reactor (MMR). The respective concepts involved were reviewed recently by Nauman (1981). The two elementary types of reactors are illustrated in Figure 3 together with their idealized residence time distribution. We assume, as is usually done, that the reaction does not affect the RTD.

The output of the CSR and the input to the MMR at any position is governed by the RTD. In all of the following, the RTD for the CSR is taken as a single spike function. Thus, the CSR is of plug-flow type for simplicity and is the same as the tubular reactor just considered in the section on the multijet tubular reactor. In the MMR, where a simplification of the RTD similar to that for the CSR would make the model trivial, we used an exponential model

$$RTD(t) = (1/\tau)\exp(t/\tau) \text{ for } t_{-\infty} < t < 0 \tag{10}$$

with an effective residence time $T_M = \tau$ independent of the cutoff $t_{-\infty}$. Note that t is negative in Eq. 10. We examined the class of real-life reactors that can be modeled by a small number of such CSR and MMR in series, in any order. The flexibility of the model is governed by two parameters for each of the basic modules: the maximum residence time (T_M or T_S) in that unit, and the decay parameter of I_s between two successive stations in the discretized version of the input and output.

In the CSR, rather than using the experimental I_s as measured in the multijet tubular reactor, the simpler exponential $I_s = I_{s,0}\exp(-zt)$ was adopted (Corrsin, 1964; Lee and Brodkey, 1964). For the MMR an incremental form between the feeding stations was used:

$$\left(\frac{dI_s}{dt}\right)_{\text{decay}} = -zI_s \tag{11}$$

The interpretation of the parameter z is the same for both types of reactors and can be considered as a measure of the turbulent mixing strength. Since the idea is to combine a CSR and MMR to model a single real reactor, z was taken as identical in the two successive units.

In order to implement the model, all that is needed is the law for the combination of the I_s factors in the reactor and the input stream of the MMR. The following section discusses the problem.

Law for the Combination of I_s Factors

Of course, the average concentrations from the two streams superimpose linearly according to the weights of the respective samples. The definition of I_s as in Eq. 1 would have us combine the covariances from two samples with different weights and averages. For the sake of the notations, we can sketch the calculations as follows: we denote by S_1 and S_2, two independent samples. The introduction of the probability measure W defines the weights and averages as,

$$W_1 = \int_{S_1} dW \qquad \bar{A}_1 = \int_{S_1} A\,dW \tag{12}$$

for sample 1 and a similar set of equations for sample 2. For the composite (subscript c), we have

$$W_c = W_1 + W_2 = \int_{S_1 \cup S_2} dW \tag{13}$$

Simple manipulations of the integrals yield

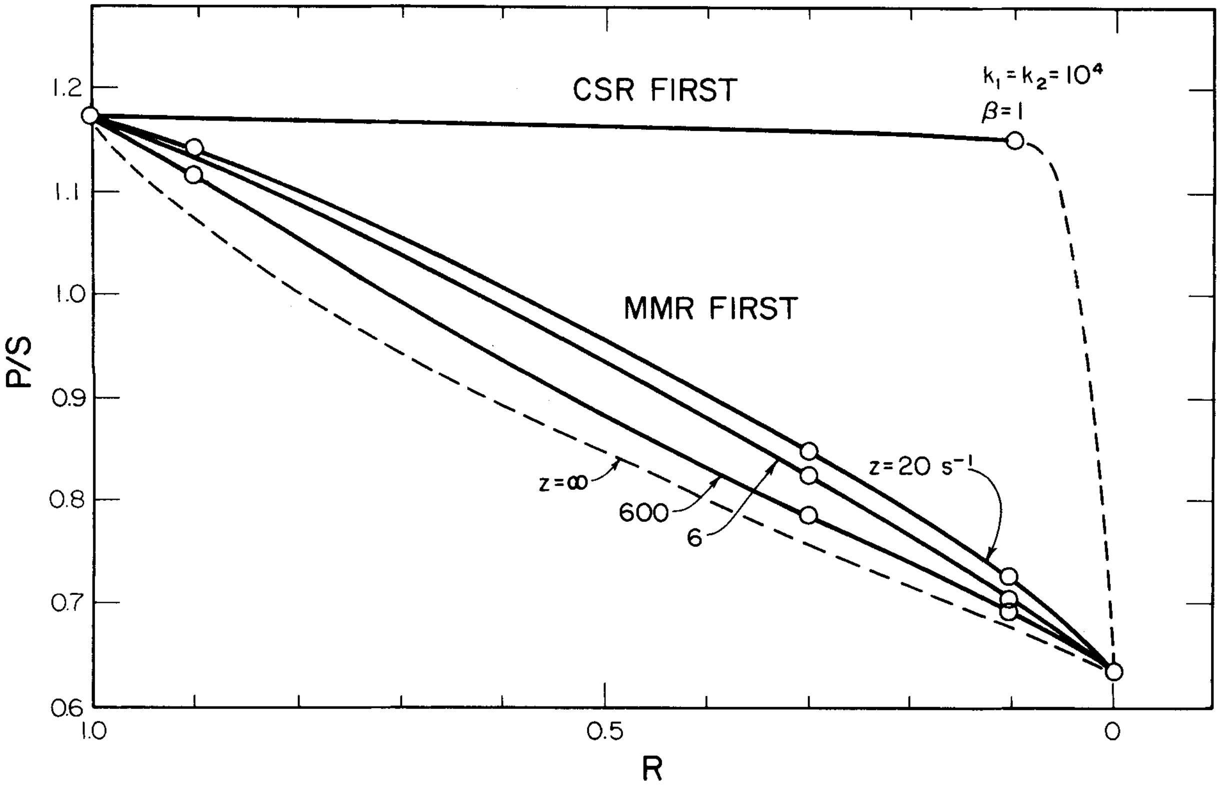

Figure 4. Selectivity curves for various reactor configurations.

$$\overline{ab}_c = \overline{ab}_1(W_1/W_c) + \overline{ab}_2(W_2/W_c) + (\overline{A}_1 - \overline{A}_2)(\overline{B}_1 - \overline{B}_2)(W_1W_2/W_c^2) \quad (14)$$

When we express $I_s = -\overline{ab}/\overline{A}_0\overline{B}_0$, it follows that

$$I_{s,c} = [(W_1/W_c)I_{s,1}\overline{A}_{1,0}\overline{B}_{1,0} + (W_2/W_c)I_{s,2}\overline{A}_{2,0}\overline{B}_{2,0} - (W_1W_2/W_c^2)(\overline{A}_1 - \overline{A}_2)(\overline{B}_1 - \overline{B}_2)]/\overline{A}_{c,0}\overline{B}_{c,0} \quad (15)$$

where $\overline{A}_{c,0}$ denotes the initial value of $\overline{A}_c$, and $\overline{A}_c$ is given by $A_c = (W_1/W_c)A_1 + (W_2/W_c)A_2$.

Equation 15 can be written as

$$I_{s,c} = (I_{s,L} + I_{s,M})/\overline{A}_{c,0}\overline{B}_{c,0} \quad (16)$$

where the subscript L stands for the linear combination of the two streams, and the subscript M refers to the combination from mixing.

In our analysis, we have assumed Toor's hypothesis so as to be able to determine I_s from pure mixing, i.e., no chemical reaction. For this case and the simple reactors being considered here, neither $\overline{A}$ or $\overline{B}$ change, consequently both $(\overline{A}_1 - \overline{A}_2)$ and $(\overline{B}_1 - \overline{B}_2)$ are identically zero, which is consistent with Toor's hypothesis. Thus, from Eq. 15, $I_{s,M}$ is zero under our assumption. With this, Eq. 16 reduces to

$$I_{s,c} = \frac{W_1}{W_c} I_{s,1} + \frac{W_2}{W_c} I_{s,2} \quad (17)$$

as a consequence of constant regime and Toor's hypothesis.

I_s in a Maximum Mixedness Reactor

Clearly, in an MMR $I_{s,2}$ (the constant input) and $I_{s,1}$ (in the reactor) will be different due to the effect of decay and mixing on $I_{s,1}$. Let us call $W_2 = RTD(t)dt$, $W_1 = \int_{t-\infty}^{t} RTD\, dt$. Combining Eqs. 10, 11, and 17 yields an equation for I_s (in the internal time of the reactor)

$$\frac{dI_s}{dt} = -zI_s + \frac{1}{\tau}(I_s - I_{s,2}) \qquad t_{-\infty} < t < 0 \quad (18)$$

with the initial condition $I_s = I_{s,2}$ at the cut-off time $t_{-\infty}$. Note, that the "internal reaction time" is negative and constitutes a simple convenient change of variables from "life expectation" as used by Zwietering (1959). Equation 18 is easily solved:

$$I_s = \frac{I_{s,2}}{\tau z + 1}\left[\tau z \exp\left\{-(t - t_{-\infty})\left(z + \frac{1}{\tau}\right)\right\} + 1\right] \quad (19)$$

and it reduces exactly to the classical results as given by Zwietering. This relation expresses in two ways the balance between the decay of the intensity of segregation and its increase due to the advection of segregated materials. First the asymptote is determined by a matching of the time constants of the mixing and the residence time distribution in addition to the input segregation. Also the exponential drop-off to that asymptote is somewhat more surprising in that the drop-off constants z and $1/\tau$ add up. The asymptote is reached in a time shorter than the residence time. For more tur-

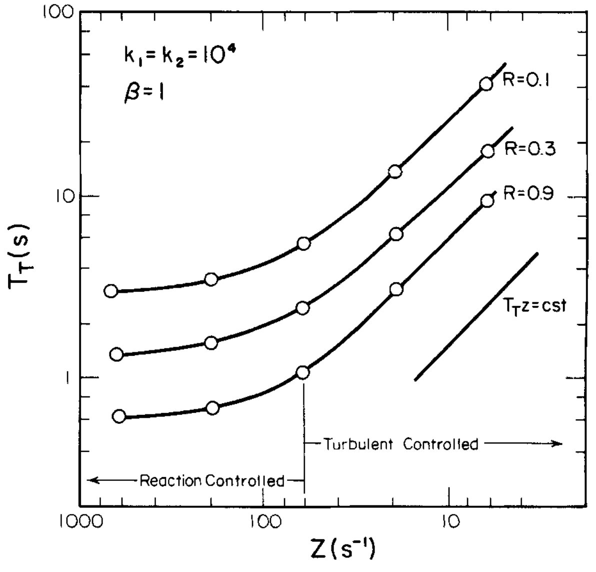

Figure 5. Residence time vs. mixing intensity for several configurations.

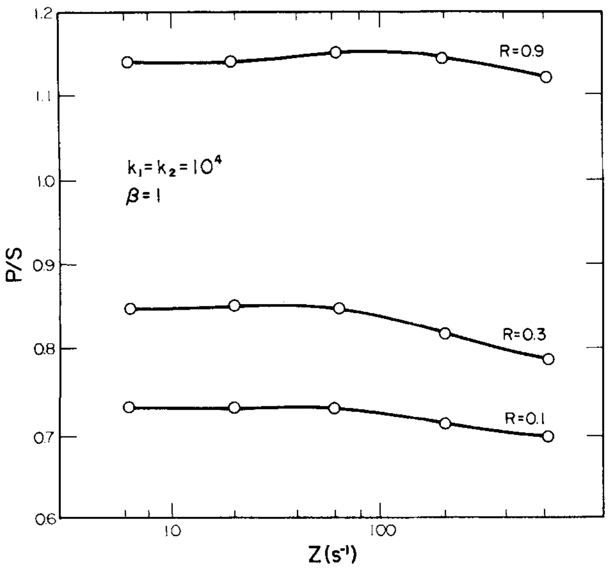

Figure 6. Selectivity as a function of mixing intensity.

bulence intensities, the actual value of I_s in the rector is accounted for by the most aged 5% of the mixture kept frozen by subsequent mixing.

Concentrations in a Maximum Mixedness Reactor

The evolution equation for the concentrations must also reflect the introduction of fresh mixture. With C as a generic symbol for A, B, P, or S, a reasoning similar to that leading to Eq. 18 yields

$$\dot{F}_C = \dot{F}|_{\text{Reaction}} + \frac{1}{\tau}(F_{C,0} - F) \qquad (20)$$

with $\dot{F}|_{\text{Reaction}}$ given by Eq. 9. From Eq. 20 we can see that the effect of pouring fresh A and B is to keep their concentrations high, while P and S are diluted in the process.

COMPOSITE REACTOR PROPERTIES

The flexibility of our model was explored using one MMR followed by one CSR using Eqs. 19, 20, 11 and 9, respectively. This particular application has more than illustrative interest: Suppose that reactions such as in Eq. 7 are given. It is a fact of observation that the final concentrations will depend on the type of reactor and on the intensity of the mixing. Therefore, it becomes important to be able to design a reactor according to the desired output. This study brings us one step closer to that goal while allowing us to test the unusual results of Apostolopoulos and Smith (1976) shown in Figure 2.

For most of the analysis, the stoichiometric ratio, β, and the ratio, k_2/k_1, were fixed at unity. Some results with different values of the ratios will be presented for comparison.

A ratio $R = T_S/(T_S + T_M)$ was chosen to describe the fraction of total time spent in the CSR. Therefore, $R = 1$ describes a plug flow reactor and $R = 0$ corresponds to a pure mixing tank. The limitations of the interpretation of R as a design parameter appear clearly when we use the CSR first, feeding its output into the MMR. It is found that the selectivity for $0 < R < 0.9$ depends on the order of the reactors; in the case of CSR leading, the output concentrations are nearly independent of R and equal to that in a CSR alone. This result is consistent with previous views that in such reactions as are considered here, the later the mixing, the larger the selectivity. Sensitivity was consequently explored on the reactor configuration with MMR leading.

For values of the final concentrations to be comparable, all reactions were carried until 1% ± 0.03% of B was left. This was done by adjusting the total reaction time $T_T = T_M + T_S$ and keeping R, k_1, k_2, β, and z fixed. Convergence to the desired level of burnout was fast using a Newton algorithm with only 3 to 8 iterations necessary. A first series of runs was made for a fast reaction $k_1 = k_2 = 10^4$, varying the parameters R and z. The results are reproduced in Figure 4. Selectivity $\overline{P}/\overline{S}$ was chosen as being of practical interest. The figure shows that for reactors of a pure type, selectivity is independent of turbulence intensity z, and lower for the maximum mixedness reactor. For mixed type reactors (R given), selectivity is found to depend on z within certain bounds:

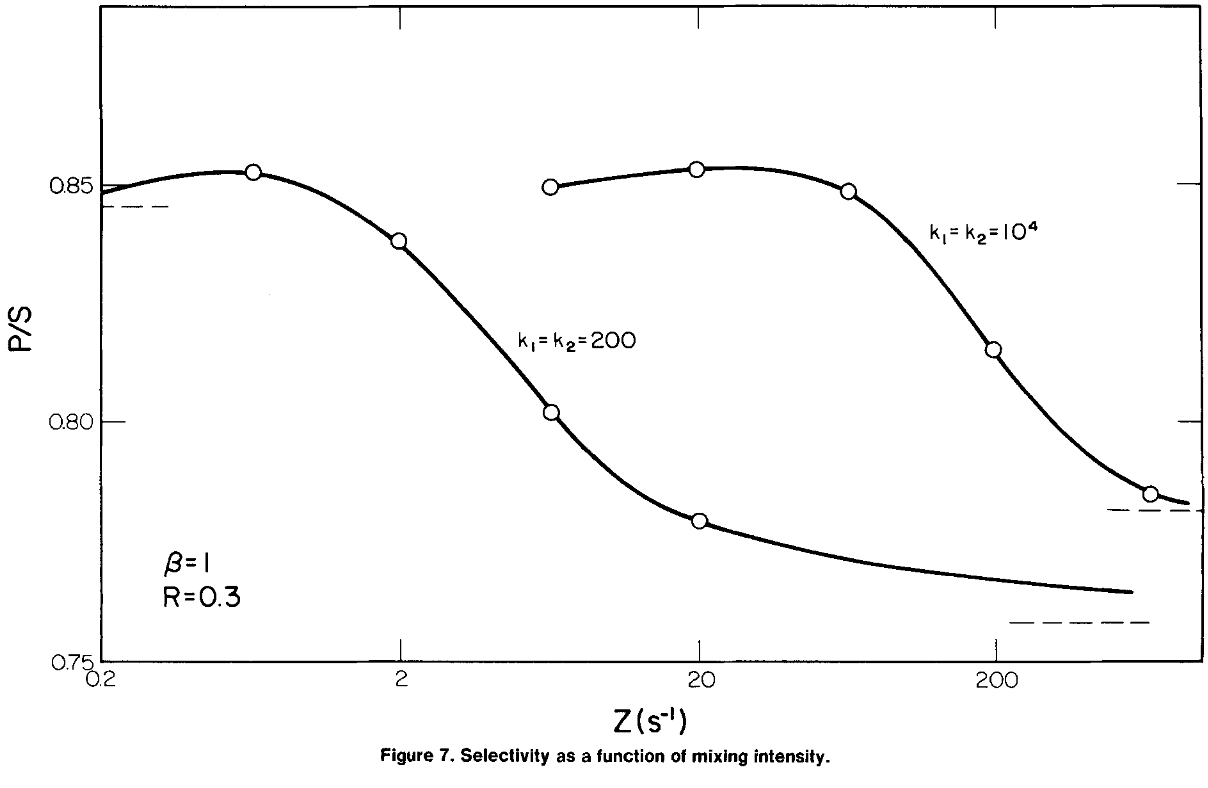

Figure 7. Selectivity as a function of mixing intensity.

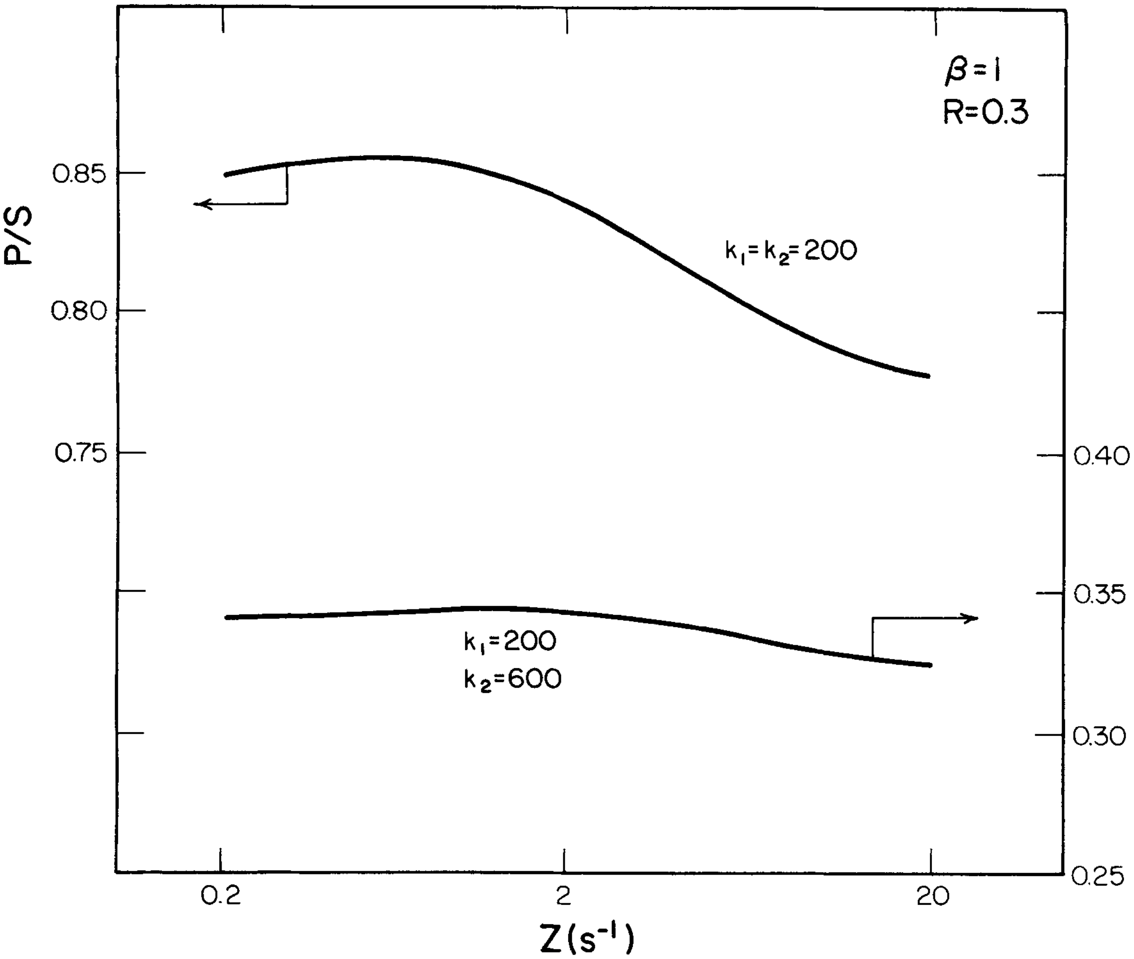

Figure 8. Selectivity as a function of mixing intensity.

the lower $\overline{P}/\overline{S}$ is obtained for unrealistically strong turbulence; the upper limit will be analyzed below. Therefore, for a desired selectivity, some flexibility exists for either turbulence intensity or reactor type. The limiting curves for $\overline{P}/\overline{S}$ vs. R were found to be independent of the reaction rates (provided, of course, $k_2 = k_1$). The cases $k_1 = 200$ and $k_1 = 2$ yield the same limits, although the curves for a given intermediate z do not coincide. No maximum of the $\overline{P}/\overline{S}$ curve other than $R = 1$ was found for any values of the parameters. This is in contrast to the results of Apostolopoulos and Smith shown in Figure 2.

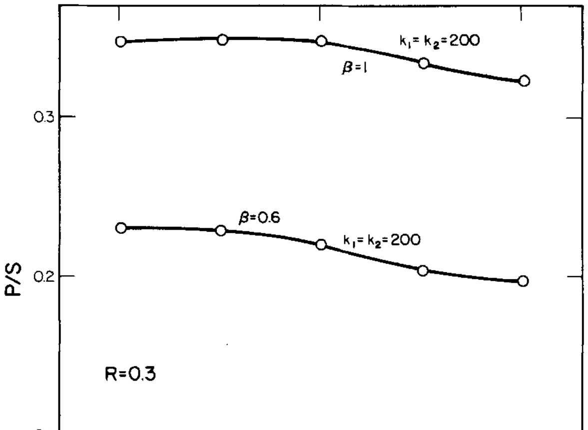

Figure 9. Selectivity as a function of mixing intensity.

Also as a matter of economic interest, in Figure 5 the total reaction times are plotted versus turbulence intensity z for several reactor configurations. The log-log plot reveals two regions. In one area, $T_T \cdot z$ is constant, expressing the fact that turbulence governs the reaction; in other words, the reaction is fast compared to the micromixing. In the other area, for much larger values of z, reaction time becomes independent of the turbulence. The transition between the two regions could be of particular interest, as the matching of the time scales of reaction and micromixing could produce new effects.

This possibility is explored in more detail in Figures 6–9. Selectivity is plotted vs. z at fixed R. Clearly the information is the same as in Figure 4, being just a cross-plot, but new elements are enhanced. Various combinations of k factors and β were examined at $R = 0.3$, where the flexibility is larger. Generally, we see that $k_1 \neq k_2$ or $\beta < 1$, favoring one reaction at the expense of the other, reduces the range of values of $\overline{P}/\overline{S}$.

Interestingly, all curves exhibit a very weak but perceptible maximum in the matching time scale region and undergo a transition on the stronger turbulence side of that maximum. The maximum location depends on the turbulence level for any given reactor combination. That phenomenon calls for a separate analysis beyond the scope of this paper. Suffice it to keep in mind that, whereas the lower limit curve of $\overline{P}/\overline{S}$ in Figure 4 is an asymptote for very strong turbulence, the upper limit reflects a weak maximum. The maximum observed in these cross-plots of selectivity versus the mixing time constant, z, cannot be compared to the maximum in Figure 2 of selectivity versus a micromixing parameter. In Figure 2, that parameter incorporates in an unknown manner both our time ratio, R, and our mixing time constant, z. The maximum location reported here depends on the turbulence level for any given reactor combination.

CONCLUSIONS

The above results are clearly only the tip of the iceberg of applications accessible with this type of model. We are encouraged to ascertain more precisely the limits of validity of our assumptions. However, verification of their accuracy for any conditions of reactions, either by analytical or numerical arguments, would be prohibitively expensive. Some questions might be settled more easily by a few key experiments, e.g., reactions in a system that follows Eq. 7 in a plug flow reactor like that of Mao and Toor (1971). Further experiments on more complex reactor configurations of the same system would be useful in checking the results of the simulation proposed in the latter part of this paper.

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NOTATION

$\overline{A},\overline{B},\overline{S},\overline{P}$ = average concentration of components of the reactions
a,b,s,p = fluctuations in concentration of the components of the reaction
$a^2,b^2,\overline{ab},\overline{pb}$ = concentration variances and crossvariances
D = molecular diffusivity
F_A = mass fraction of $A(\overline{A}/\overline{A}_0)$
F_B = mass fraction of $B(\beta\overline{B}/\overline{A}_0)$
F_P = mass fraction of $P(P/\overline{A}_0)$
F_S = mass fraction of $S(S/\overline{A}_0)$
k,k_1,k_2 = specific rate constants
I_s = intensity of segregation
$\overline{P}/\overline{S}$ = selectivity (ratio of concentration of P to S)
R = time ratio (time in CSR to MMR)
RTD = residence time distribution
S = stream sample
t = time
$t_{-\infty}$ = cut-off time of the RTD
T = total residence time
T_M = residence time in MMR
T_S = residence time in CSR
$\overline{U}_x$ = axial velocity
W = stream weight
z = mixing time constant

Greek Letters

β = stoichiometric ratio $(\overline{A}_0/\overline{B}_0)$
τ = time constant of RTD in MMR

Subscripts

0 = initial
1 = stream 1, first reaction
2 = stream 2, second reaction
c = composite stream

Other Symbols

— = (overbar) time average
· = (overdot) time derivative

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