Effect of Partial Segregation on Conversion in Continuous Stirred-Tank Reactors

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A model is described which accounts for partial segregation in continuous stirred-tank reactors by considering packets circulating within a completely micromixed continuous regime. The packets have a nonideal residence time and concentration distribution. Mass transport occurs between these packets and the continuous phase of uniform composition in proportion to their concentration gradients. Laplace transformed tracer responses establish the diffusion and mixing parameters. Over 90% of the system is segregated in unstirred aqueous solutions. Addition of polymer increases segregation by over 40% at a 100 rev/min stirrer speed.

SCOPE

In carrying out reactions in stirred tanks, attention is being given to the dependence of the rate of reaction on the local concentration of reactants. If we assume that a significant conversion occurs, the rate and degree to which the incoming stream is mixed with the material already in the reactor affects the reaction rate. Many attempts have been made to develop a quantitative approach to the problem of the relationship between mixing and the extent of reaction in flow systems. Danckwerts (1953) presented a method for characterizing mixing patterns by means of residence time distribution diagrams and showed that these could be used to determine conversions of isothermal first-order reactions. It was pointed out that residence time distributions are based on average effluent concentrations and do not describe how well molecules are mixed on an individual basis. Hence, more information is needed to accurately predict reactor yields.

To resolve this difficulty Danckwerts (1952, 1953) defined a degree of segregation based on the variance of the ages of the molecules. His concepts were extended by Zwietering (1959), who calculated the conversion for two extreme cases which occur for an arbitrary residence time distribution, namely, complete segregation and maximum mixedness. This determines bounds between which the actual conversion must lie. Worrel and Eagleton (1964) correlated the region of maximum mixedness with power input and recirculation rate in a reactor.

Various models have been proposed which attempt to predict the effects of partial mixing. Of particular interest are the ones by Villermaux and Zoulalian (1969), Rippin (1967), Manning et al. (1965), Evangelista et al. (1969), Nauman (1975), and Ziegler et al. (1971). The latter model deals directly with one salient fact: if partial physical segregation exists inside a reactor, concentration differentials will exist between the different packets and the continuous or nonsegregated portion of the fluid. Interchange of reactants and solvent, if any, will occur by eddy and molecular diffusion, affecting the concentration and therefore the rate of reaction in each phase. The model presented here extends the previous work to the region of nonideal residence time distribution for the segregated phase. The intention of the present work is to develop a model based on the foregoing physical situation and to validate the effects of the physical and chemical variables predicted by this model. Assumptions were made to minimize the number of dimensionless parameters required to describe the reaction system. In this way, it was hoped that any relationships resulting from the model would be simple enough to be used for practical design purposes, provided that it could first be proved capable of predicting actual reaction yields. It also seemed likely that the simpler model would be easier to test experimentally without resorting to attempts at directly measuring the degree of segregation (that is, fluctuations in concentration, etc.). This is a very difficult task and often cannot yield definitive results. For example, if a probe is designed to yield average values of a parameter over a volume of 10^{-5} cm^3 (which is probably fairly close to a practical limit from a standpoint of obtaining true samples of the system), it will still be averaging over some 3.3×10^{17} molecules for an aqueous system. This type of datum is, in any case, not available in normal design circumstances.

Experimental data discussed previously by Leitman and Ziegler (1971) are used to test the partially segregated model results and to compare them with those predictions of other models.

CONCLUSIONS AND SIGNIFICANCE

1. The concept of segregated and microscopically mixed portions in a continuous reactor leads to a simple but useful model. With few assumptions made to minimize the number of independent variables, a model is derived which describes the region between total segregation and micromixing.

2. Iterative numerical integration using Simpson's rule and/or the Gaussian-Laguerre fourteen-point formula is all that is required for the computations of the model.

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The latter may be represented as a function of only three dimensionless variables, with clearly defined physical meanings: a = fraction of reacting system in segregated form, R_1 = ratio of diffusional speed to reaction rate, and R_2 = ratio of space velocity to reaction rate.

These parameters may be found if the kinetics of the system are known and the values of $\underline{a}$ and ϕ are estimated from tracer studies.

3. Insofar as the model can be tested with the sparse quantity of available data, good general agreement exists between its predictions and experimental results. For higher R_1 to R_2 ratio values, near $\underline{a} = 1$, the model or more probably the computational methods need further modifications.

Additional experiments are suggested, particularly at low R_2 values, which will establish considerable differences in conversion for the two extreme cases of segregation.

4. The data analyzed in tracer experiments often consist of recorded curves. It is therefore suggested that the Laplace transform be obtained directly from the data by attaching an integrating device (an analogue or hybrid computer) to the recorder. This would require parallel amplifiers corresponding to different S values, with the response expected to decay to small values fairly quickly.

PREVIOUS MODELS

Villermaux and Zoulalian (1969) expanded upon a model developed earlier by Weinstein and Adler (1967). They postulate that the feed divides into two streams before entering two parallel reactors, partitioned by age, corresponding to the two extreme cases of complete segregation and maximum mixedness, and no transfer between reactors occurs. This model has the advantage of relative simplicity but loses generality in its attempt to define a reasonably complex situation in terms of a single parameter.

Rippins' (1967) model is a two-environment model, the two environments corresponding to the two extreme cases, as noted in a previous model, the difference being that they are not partitioned by an age. In addition, an extra parameter R is used which determines the rate at which molecules transfer from the entering to the leaving environment. The idea of one portion of a reactor being in a state of maximum mixedness might be considered esoteric.

The model of Manning et al. (1965) imagines that the feed and the recirculating stream remain segregated until reaching the impeller, where complete micromixing is assumed. The ratio of flow rate of the recirculating stream to that of the feed stream is taken as the mixing parameter. They present two models with two extreme feed conditions.

The model by Evangelista et al. (1969) regards the reacting mass as composed of a large number of equisized blobs of material which undergo pairwise collisions, thereupon equalizing concentration, before they separate. Each blob behaves like a batch reactor between collisions. Three parameters are required in this model, and a complex analysis is necessary to use the results for nonlinear reaction. The Monte Carlo model of Spielman and Levenspiel (1965) considers coalescence between fluid elements in the reactor. These models, having truly discrete phase assumptions, are applicable primarily to two-phase systems.

Nauman's droplet diffusion model (1975) postulates that the entering fluid is immediately dispersed into spherical droplets of uniform size and diffusion between droplets occurs. By not taking into account the possibility of micromixed portions of the fluid, it loses some generality.

PARTIALLY SEGREGATED MODEL

In the model of the current study, a major concern is to allow for deviation from the limiting condition of complete mixing while recognizing that segregated neighborhoods might still be completely mixed. Thus, in this system the incoming reactant stream is distributed as segregated clusters which move through a continuous microscopically mixed phase. The clusters undergo no further change in size, but diffusional interchange may occur between them and the randomly mixed phase. The remaining portion of the inlet stream is immediately mixed into the random phase, which has everywhere the same concentration. Figure 1 indicates the makeup of such a system.

It is recognized that the foregoing represents at best an approximation of the real physical situation; on the other hand, an attempt to include all possible factors would result in a model with an undesirably high order of complexity. Furthermore, many of the parameters which would have to be accounted for in a complete model (for example, spectrum of eddy sizes, creation and disappearance of eddies, modes of mass transfer from eddies to continuous phase, etc.) are at present poorly understood even for pure mixing situations, let alone for instances in which

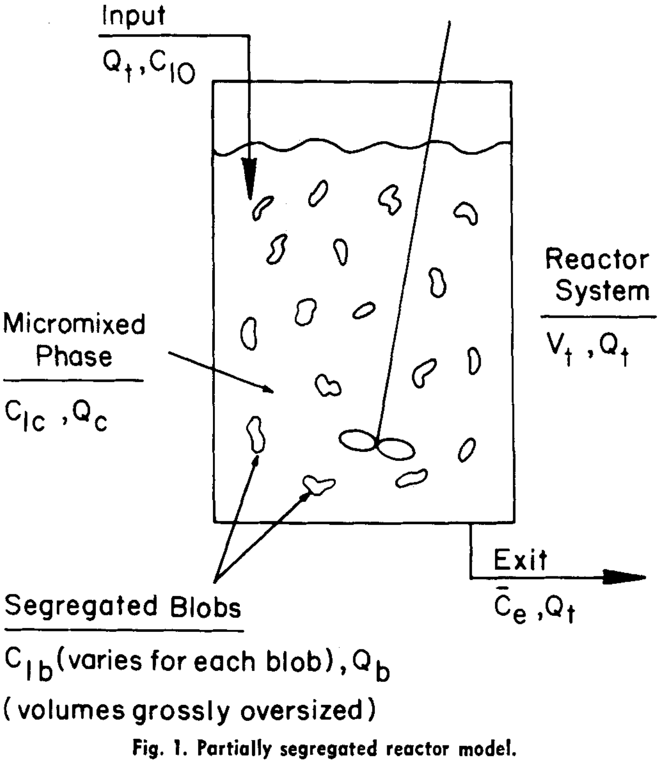

Fig. 1. Partially segregated reactor model.

nonlinear chemical reactions are involved. Finally, such a model, even if theoretically soluble, would be extremely difficult to test and/or to use.

For convenience, the case of a second-order isothermal decomposition reaction is considered (this would also apply, of course, to a system with two reactants of equal initial concentration entering as a homogeneous mixture if their effective diffusivities from clumps to continuous phase were similar). As previously mentioned, the nonlinearity of second-order reactions is sufficient to yield significant differences between segregated and microscopically mixed systems. Thus, they can be used to test the ability of the model to describe the chemical and physical interactions in reaction vessels. The model can be extended to other nonlinear cases of interest.

In order to analyze the model described above, mass balances must be generated for each phase (discrete and continuous) which incorporate the interdiffusional transport properties of the system. A dimensionless approach will be utilized because of the conciseness that frequently results, and because the parameters required for a complete system description may best be minimized when transformed to their dimensionless counterparts.

The assumptions of the model are as follows:

1. The vessel is divided into two parts, whose ratio is time invariant, one a continuous perfectly mixed portion and the other a discontinuous segregated portion.
2. The average residence time of each portion in the reactor is the same.
3. The segregated portion of the fluid consists of equisized blobs which retain their size while in the vessel; diffusional transfer between the blobs and the segregated position is, however, possible.
4. The diffusional transfer follows a Fickian relationship; namely, the rate of transfer is proportional to the concentration difference. The diffusional coefficient is not necessarily that of simple molecular diffusion.
5. The blobs are very large in number and very small compared to the size of the vessel.
6. The physical and chemical parameters are of constant value.

DISCRETE PHASE

A mass balance may be written for a single clump or blob of molecules undergoing a segregated flow, as follows:

Accum. of comp. 1		Gain of comp. 1 by reaction	Gain of comp. 1 by diffusion
$V_b \dfrac{dc_{1b}}{dt}$	$=$	$-k_2 c_{1b}^2 V_b$	$-\dfrac{D_1}{L}(c_{1b}-c_{1c})A_{bc}$

(1)

Although D_1/L is written as if for molecular diffusion, it represents a total diffusional or mass transport coefficient. This equation may be transformed to a dimensionless expression which is readily separable for integration:

$$\frac{Q_t V_b c_{10}}{V_t}\left(\frac{dY_{1b}}{d\theta}\right) = -k_2 c_{10}^2 V_b Y_{1b}^2 - \frac{D_1 c_{10} A_{bc}}{L}(Y_{1b}-Y_{1c}) \quad (2)$$

An expression for Y_{1b}, the dimensionless concentration within any single blob, as a function of Y_{1c}, θ, and several dimensionless parameters, may be obtained by integrating Equation (2) between the limits of 0 and θ, rearranging the results and utilizing the known physiochemical characteristics of the system to choose between the various acceptable mathematical solutions. Thus

$$Y_{1b} = \frac{R_1(1-M_2) - R_1(1+M_2)\left[\dfrac{2+R_1(1-M_2)}{2+R_1(1+M_2)}\right]e^{-M_1\theta}}{2\left[\left\{\dfrac{2+R_1(1-M_2)}{2+R_1(1+M_2)}\right\}e^{-M_1\theta}-1\right]} \quad (3)$$

with dimensionless parameters:

$$M_1 = \frac{R_1 M_2}{R_2}, \quad M_2 = \sqrt{1+\frac{4Y_{1c}}{R_1}},$$

$$R_1 = \frac{D_1 A_{bc}}{k_2 c_{10} L V_b}, \quad R_2 = \frac{Q_t}{k_2 c_{10} V_t}$$

Under steady state conditions, it may be assumed that the residence time distribution of the blobs in the reactor does not change; hence an average internal concentration and exit concentration can be calculated by standard methods, that is

Internal:

$$<Y_{1bi}> = \int_0^\infty Y_{1b} i(\theta)\,d\theta \quad (4)$$

Exit:

$$<Y_{1be}> = \int_0^\infty Y_{1b} e(\theta)\,d\theta \quad (5)$$

NONIDEAL RESIDENCE TIME DISTRIBUTIONS

In studying the partially segregated systems under discussion, the possibility that the segregated and perfectly mixed portions will display different residence time distributions should be considered. The latter phase is by definition in a state of maximum mixedness, but the former may undergo nonideal mixing (indeed, this might be a contributory cause to the segregation). It would, therefore, be of interest to determine the effect of moderate deviations from ideal mixing for the segregated clumps. Large deviations would not be expected because of the well-mixed nature of the continuous phase. The so-called Gamma-Distribution function was used to generate possible exit residence time distributions:

$$e(\theta) = \frac{1}{\alpha!\,\beta^{\alpha+1}}\theta^\alpha e^{-\theta/\beta} \quad (6)$$

This function was chosen because it was capable of satisfying the fundamental criteria for $e(\theta)$; that is, total area under integral from $\theta = 0$ to $\theta = \infty$ equals 1.0, and a β may be chosen for any given α such that $\overline{\theta}$ equals 1.0 also (as required by the hold time for any steady state reactor). For simplicity, only low integer values of α were considered in the present work to demonstrate the significance of such effects rather than try to analyze them exhaustively.

The required residence time distributions were generated in the following manner:

1. α was set equal to the desired integer and β computed from the relationship: $\overline{\theta} = \beta(\alpha+1) = 1$.
2. $e(\theta)$ was computed directly.
3. $i(\theta)$ was determined via the known relationship between the dimensionless residence time distributions; that is

$$1 - \int_0^\theta e(\theta)\,d\theta = i(\theta)$$

The exit distributions $e(\theta)$ obtained by this approach are very interesting in that the relations obtained using $\alpha = 1$ and 2 are $4\theta e^{-2\theta}$ and $27/2\,\theta^2 e^{-3\theta}$, respectively, and it may be inferred that the Gamma function is a generalized tanks in series distribution. These residence time distributions may be used directly in the computation of exit conversions from Equations (4) and (5).

CONTINUOUS PHASE

The continuous phase may be treated as a typical micromixed continuous stirred-tank reactor with an added input term for the diffusional interchange with the discrete phase. The following dimensionless mass balance results at steady state:

$$\underset{\text{comp. 1}}{\overset{\text{Accum. of}}{\frac{dY_{1c}}{d\theta}}} = 0 = \underset{}{\overset{\text{Input of comp. 1 by flow}}{\frac{Q_c V_t}{Q_t V_c}(1 - Y_{1c})}}$$

$$\overset{\text{Gain of comp. 1 by reaction}}{- \frac{k_2 c_{10} V_t}{Q_t} Y_{1c}^2} + \overset{\text{Gain of comp. 1 by diffusion}}{\sum \left[\frac{D_1 A_{bc} V_t}{V_c Q_t L} (Y_{1b} - Y_{1c}) \right]} \tag{7}$$

If we utilize the previously developed internal average blob concentration, the foregoing may be rearranged to obtain a simple quadratic equation which, using assumptions (2) and (5), may be solved for Y_{1c}:

$$Y_{1c} = \frac{-(R_2 + R_3) + \sqrt{(R_2 + R_3)^2 + 4(R_2 + R_3 {<}Y_{1bi}{>})}}{2} \tag{8}$$

$$R_3 = \frac{D_1 (\Sigma A_{bc})}{k_2 c_{10} L V_c}$$

CRITICAL DIMENSIONLESS VARIABLES

The relation between the total volume of the discrete phase and the total reactor volume may be described by a dimensionless parameter $\underline{a}$ which represents the fraction of the reactor taken up by the discrete phase. If the assumption (third) is made that the value of A_{bc}/V_b occurring in R_1 may be replaced without great loss of precision by $\overline{A_{bc}}/\overline{V_b}$, then R_1 becomes $\dfrac{D_1(\Sigma A_{bc})}{L k_2 c_{10} a V_t}$ and R_3 reduces to $(a/1 - a) R_1$.

The entire reactor system may thus be described by three dimensionless parameters: $\underline{a}$, R_1, and R_2 assuming the residence time distribution parameter α is known. The physical significance of the first parameter is obvious. Of the remaining two, R_1 represents essentially a ratio of a diffusional speed and a characteristic second-order reaction velocity, and R_2 the ratio of the average space velocity to the reaction velocity, the inverse of the commonly used dimensionless reaction parameter X.

A recursion solution of the two separate equations is to be used to determine the values of Y_{1c} and $<Y_{1bi}>$ for any given values of the dimensionless parameters. Once Y_{1c} is known, $<Y_{1b_e}>$ can be directly calculated, and the average conversion $<Y_e>$ across the reactor is determined:

$$<Y_e> = a<Y_{1b_e}> + (1 - a)\, Y_{1c} \tag{9}$$

With three dimensionless parameters involved, various methods of graphical presentation could be used. One approach would be to use a plot similar to the Koo-Ziegler plot (1969) (see Figure 2) for second-order reactions, except that the ordinate is $<Y_e>/R_2$ and the abscissa is $1/R_2$. The effect of $\underline{a}$ can be demonstrated by plotting a series of curves for different values of this parameter at a given value of R_1. Use of five to ten such plots at different R_1 values should cover the range of normal expectations sufficiently, depending on how sensitive the system is to changes in this variable.

For first-order reaction cases, with ideal residence time distribution, the conversion was found to be $R_2/1 + R_2$, as expected. It should be noted that

$$<Y_{1be}> = <Y_{1bi}> = Y_{1c} = \frac{R_2}{1 + R_2}$$

for all values of a and R_1.

The expression for conversion with a nonideal residence time distribution is given in the appendix.

PARAMETER ESTIMATION

In order to use the model in a practical case, it is necessary to first evaluate the mixing parameters of the system. This may be done by applying the model to tracer data of either the unit step or pulse input type. For convenience, only a step input is considered here, but it is well known that pulse results are readily related to step results. It is only necessary to solve for the tracer response in the Laplace domain, since an estimate of the parameters may be made by a comparison with data also transformed to the Laplace domain.

This procedure is often convenient when the differential equations representing the system do not have a closed form solution. Though normally a least-squares fit should be made, a slight simplification was used here in that, firstly, one of the parameters was held constant and, secondly, a sufficiently good fit, well within experimental error, was found rather than a best fit, which within this framework loses some of its meaning. Details of the method of estimating parameters in the Laplace domain may be found in Williams, Adler, and Zolner (1970).

The method outlined above for the estimation of parameters of course implies that the parameters so found are not unique. However, the parameters estimated by a nonlinear least-squares technique outlined by Box (1960) and Marquardt (1963) would also be localized by the choice of the initial point. Also, if the above parameters give a good fit for tracer data, they would probably produce an accurate value of the conversion.

Tracer test parameter equations

Taking the tracer component material balance for both the blobs and continuous portions for a step input, Chand (1971) determined the exit concentration in the Laplace (s) domain as a function of ϕ, ψ, α. The first two of these parameters may be used to determine the parameters a, R_1 when needed for second-order conversion problems of known R_2:

$$R_1 = \phi R_2 \quad \text{and} \quad a/(1 - a) = \psi/\phi \tag{10}$$

The averaged transformed exit concentration may be expressed by

$$\overline{Y_e} = a<\overline{Y}_{be}> + (1 - a)\, \overline{Y_c} \tag{11}$$

in which

$$\overline{Y}_c = \frac{\dfrac{1}{S(1 + \psi + S)} \left\{ 1 + \dfrac{\psi}{(S + \phi)} \left[1 - \left(\dfrac{\alpha + 1}{S + \phi + \alpha + 1} \right)^{\alpha + 1} \right] \right\}}{1 - \dfrac{\phi\psi}{(S + \phi)(S + 1 + \psi)} \left[1 - \dfrac{1}{(S + \phi)} \left\{ 1 - \left(\dfrac{\alpha + 1}{\alpha + 1 + S + \phi} \right)^{\alpha + 1} \right\} \right]} \tag{12}$$

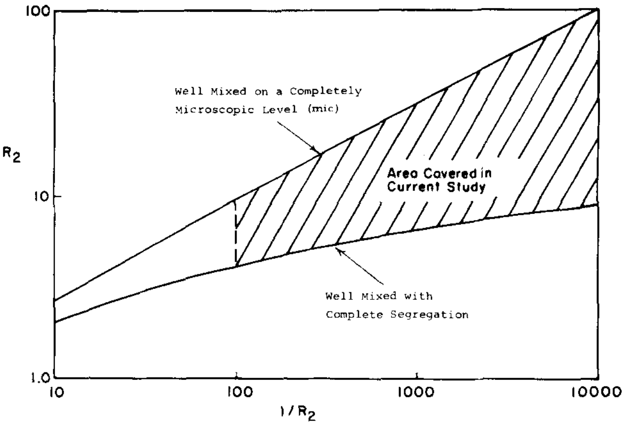

Fig. 2. Modified Koo-Ziegler (1969) plot for second-order reaction.

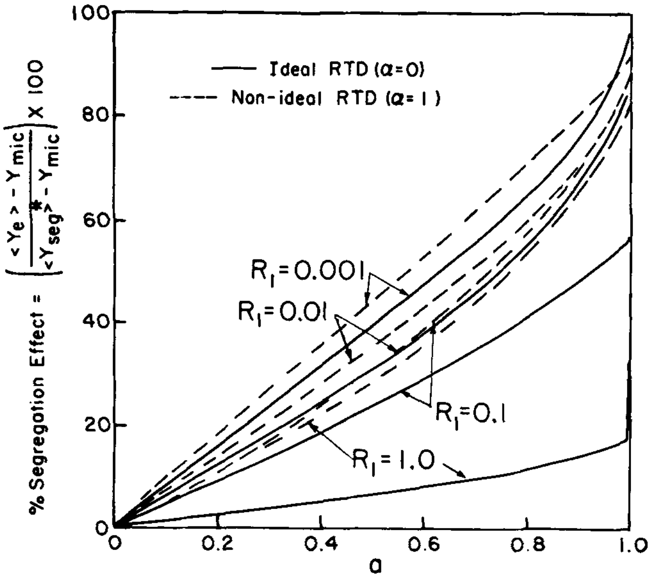

Fig. 3 (a). Effect of variation in diffusion/reaction rate ratio (R_1) asd fraction in discrete phase (*a*). Moderate throughput/reaction rate ratio, $R_2 = 0.01$. $^*\langle Y_{seg}\rangle$ is different for a different α value.

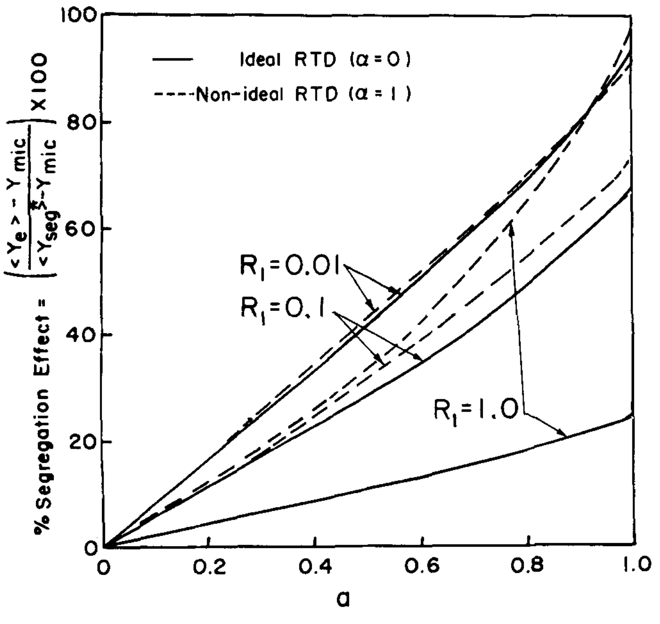

Fig. 3 (b). Effect of variation in diffusion/reaction rate ratio (R_1) asd fraction in discrete phase (*a*). Very low throughput/reaction rate ratio, $R_2 = 0.001$. $^*\langle Y_{seg}\rangle$ is different for different α value.

and

$$\langle \overline{Y}_{be}\rangle = \frac{1}{S}\left[\frac{\alpha+1}{\alpha+1+S+\phi}\right]^{\alpha+1} + \frac{\phi\overline{Y}_c}{(S+\phi)}\left[1-\left(\frac{\alpha+1}{\alpha+1+S+\phi}\right)^{\alpha+1}\right] \qquad (13)$$

For a pulse test transform $\overline{Y}_e$, it is necessary only to multiply the transformed $\overline{Y}_e(s)$ value of Equation (11) by s. Similarly, response data from a pulse test may be transformed at a particular s value into a step response form by multiplying the numerically or graphically integrated value (pulse transform) by s.

Evaluation of the model

The best measure of any mathematical model is, of course, the accuracy with which it fits actual cases from a predictive standpoint. However, it is of qualitative importance to evaluate the theoretical response to $\underline{a}$, R_1, and R_2 that would be predicted by the current model. In this way, any obvious deficiencies leading to inconsistent or unrealistic behavior in the model could be detected.

The cases of $\alpha = 0$ and $\alpha = 1$ for the proposed model were tested. Simpson's rule and Gaussian-Laguerre fourteen-point formula were juxtaposed for computation of integrals (4) and (5).

The results of the computations discussed are presented in Figures 3 and 4, in which the effects of varying a and R_1 at different values of R_2 are summarized. To simplify comparisons, all results have been converted to a percentage of segregation effect (%S.E.), so that the degree of approach to fully segregated conditions can be observed directly:

$$\%\text{S.E.} = \frac{\langle Y_e\rangle - Y_{\text{mic}}}{\langle Y_{\text{seg}}\rangle - Y_{\text{mic}}}\,(100\%)$$

Note that zero %S.E. represents perfect microscopic mixing and 100% S.E. completely segregated mixing. Also note that 100% S.E. has different values for $\alpha = 0$ and $\alpha = 1$.

The following characteristics of the model can be readily seen:

1. As $\underline{a}$ increases, %S.E. (that is, conversion) increases (see Figures 3 and 4).

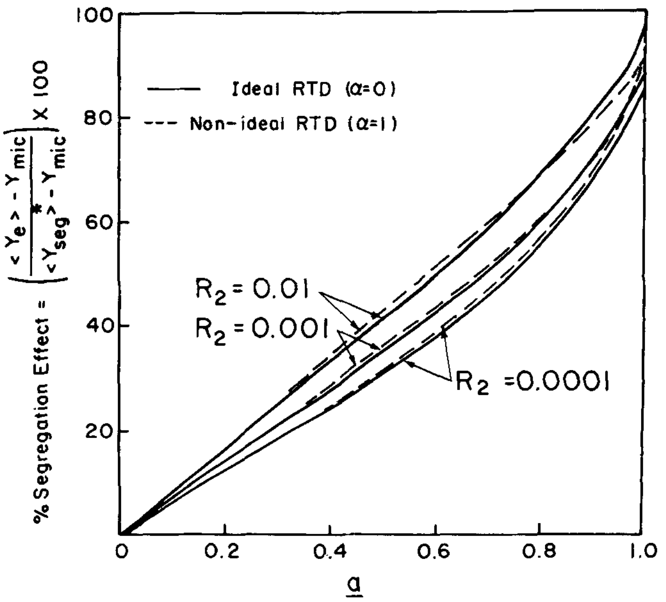

Fig. 4. Effect of mixing parameters on % S.E. at diffusion/reaction rate ratio, $R_1 = 0.01$. $^*\langle Y_{seg}\rangle$ is different for different α value.

Table 1. Parameter Estimates for Typical Data Leitman (1970)

	Water			Polyox		
Rev/min	$\underline{a}$	ϕ	Coef.	$\underline{a}$	ϕ	Coef.
0	0.939	10.0	0.007	0.990	0.001	0.037
100	0.492	10.1	0.027	0.721	10.0	0.003

2. For ideal residence time distribution, as R_1 increases (that is, diffusion increases relative to reaction rate), %S.E. decreases for any given value of $\underline{a}$ and R_2 (see Figure 3). In case of nonideal residence time distribution, %S.E. passes through a minima (see Figure 3$\underline{a}$). The fact that an incomplete mixing residence time distribution passes through a maximum at non zero time might influence this behavior.

3. For an increase in R_1 and R_2 in equal proportion, %S.E. decreases for any value of $\underline{a}$ in the case of an ideal (completely mixed) residence time distribution.

4. Except when the ratio of R_1 and R_2 is very high, both residence time distributions give almost the same value of %S.E. for a given $\underline{a}$, R_1, R_2.

5. Near $\underline{a} = 1$, the %S.E. curve becomes more discontinuous in the case of a micromixed residence time distribution than a comparable curve for nonideal residence time distribution. This may be interpreted as the micromixed residence time distribution being less compatible and probably less realistic in that region.

The data of LaRosa and Manning (1964) on the reaction of methyl bromide, tert-butyl acetate, and ethyl acetate with sodium hydroxide satisfy essentially all of the criteria of the current model except that the inlet concentrations are not equimolar. The experimental data show an increase in %S.E. for increasing reaction rate at any given mixing condition. For the model, increasing reaction rate causes an equal relative decrease in R_1 and R_2. This will increase %S.E. (for example, in case of ideal residence time distribution, consider $R_1 = 0.1$, $R_2 = 0.01$ and $R_1 = 0.01$, $R_2 = 0.001$ for any given value of $\underline{a}$). The experimental increase in %S.E. with decrease in impeller speed is essentially linear. This is consistent with the linear effects of changes in $\underline{a}$ at relatively low %S.E. at a given R_1 and R_2.

To carry out the estimation of the parameters, it was decided to simplify the procedure by setting $\alpha = 1$ in Equations (12) and (13). This takes into account the fact that a maximum residence time occurs at nonzero time. The error involved in conversion calculations probably will be smallest when the same α value is used.

Table 1 contains local best fit values of $\underline{a}$ and ϕ, with the coefficient of variation for the transformed data (that is, standard deviation divided by the mean).

The value of $\underline{a}$ appears to decrease from a nearly completely segregated value of unity as the revolution per minute value is increased in both systems. The dimensionless diffusivity ϕ increases with increase in revolutions per minute.

Figure 5 depicts the effect of ϕ at low, intermediate, and high values of the segregated fraction. These curves may be used for approximate estimation by first plotting the transformed concentration data at various s values on transparent paper using the logarithmic axes as a background and then comparing with the characteristic curves of Figure 5. The effect of ϕ is much more pronounced at higher values of a, that is, at more segregated conditions. In Figure 5a, in fact, the values for $\phi = 10$, 100, and the

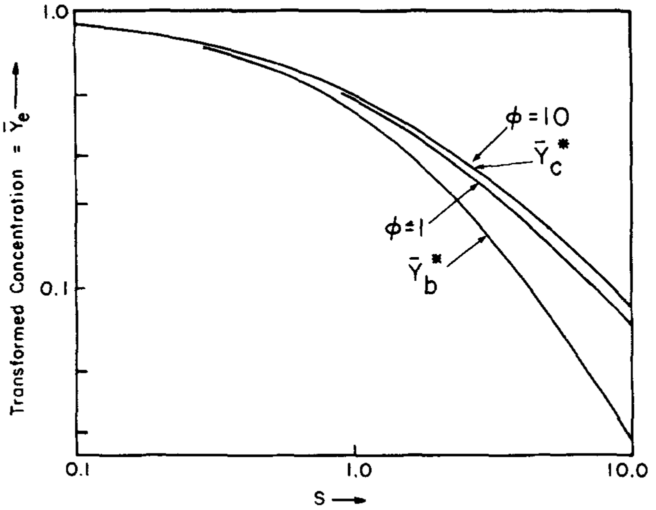

Fig. 5 (a). The influence of ϕ on the transformed response to a pulse input. Low segregated fraction value, $a = 0.25$.

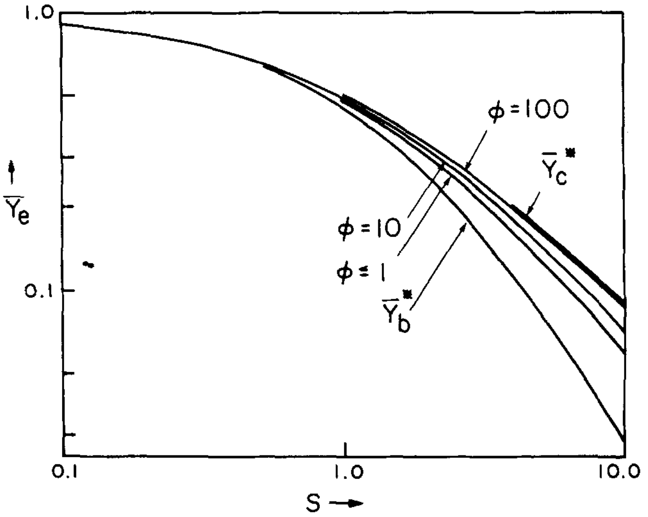

Fig. 5 (b). The influence of ϕ on the transformed response to a pulse input. Intermediate segregated fraction, $a = 0.5$.

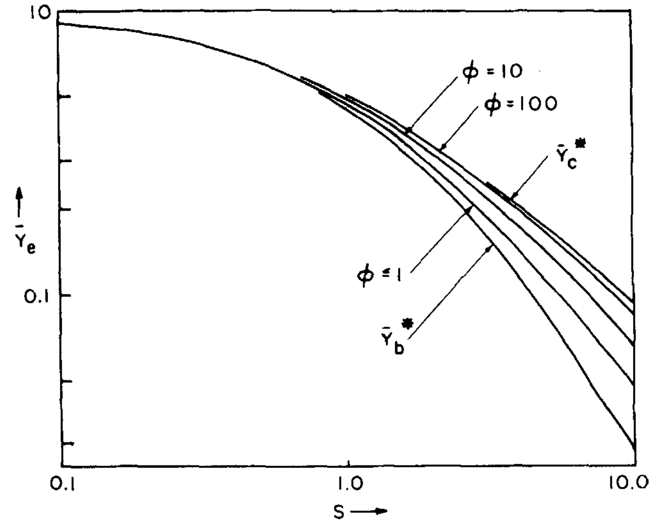

Fig. 5 (c). The influence of ϕ on the transformed response to a pulse input. High segregated fraction, $a = 0.75$.

TABLE 2. PERCENT DIFFERENCE OF RESULTS FOR VARIOUS MODELS

Models	0 rev/min	100 rev/min	Polymer 0 rev/min	Polymer 100 rev/min
CSTR	6.30	5.11	5.12	4.12
Plug	−24.90	−27.00	−26.50	−27.50
Segregated	−5.37	−0.67	−6.73	−6.87
Segregated dispersion	−3.77	4.71	−3.89	−3.36
Maximum mixedness	14.72	10.09	17.17	14.81
Recycle*	0.19	1.76	−1.89	−0.11
Unsegregated dispersion	7.22	7.39	2.97	4.65
Current model ($\alpha = 1$)	−1.99	2.29	−13.70	0.50

* Although the recycle model of Gillespie and Carberry (1966) does well in these tests, Rippin (1967) describes some of the dangers encountered using such models in regions where the effects of micromixing are significant. Leitman (1970) has found errors of greater than 3 to 4% in the recycle model at 200 rev/min in aqueous solution. Unfortunately, the range of variation in Leitman's conversions was small (44 to 53%).

ideally mixed portion almost coincide. Also the values for $\phi = 1$ and 0 are not very different in any of the figures; thus the denotation $\phi \leqq 1$ is used. If we consider the function $\overline{Y}(s)$ with parameter ϕ, holding $\underline{\alpha}$ and $\underline{a}$ constant, a determines the bounds on the value of $\overline{Y}(s)$ between $[\overline{Y}_c^*]$ and $[(1-a)\overline{Y}_c^* + a\overline{Y}_b^*]$. Thus the smaller the segregated portion $\underline{a}$, the narrower the region in which $Y(s)$ can vary with ϕ as a parameter.

Comparison with Conversion Data

For comparison of current model with various other models, experimental data of Leitman (1970) were used. Using the a and ϕ values of Table 1, conversion was calculated for $\alpha = 1$, using numerical methods. Using residence time curves, the expected conversion was calculated for various other models.

The difference between these and the actual experimental conversions were expressed as the relative percent difference

$$\%\ \text{diff.} = \frac{X_{\text{exp}} - X_{\text{calc}}}{X_{\text{exp}}}\ (100\%) \qquad (14)$$

where X_{exp} is the experimentally determined conversion, and X_{calc} is the conversion calculated using the chosen model.

A comparison of the percent difference is presented in Table 2.

Except for 0 rev/min polymer case, the model shows very low percent difference. It gives better prediction than both completely micromixed and completely segregated models in cases of 0 rev/min water and 100 rev/min polymer.

In the case of 0 rev/min polymer, it shows a high percent difference. For this case, $\underline{a} = 0.99$, and, as noted during the parametric study, there is some discontinuity found near $\underline{a} = 1$, which is unrealistic.

The nonideality of a residence time distribution is influenced by the degree of segregation. Deviations are observable, provided that the tracer technique is precise. This sensitivity to tracer concentration resolution will improve as instrument response is enhanced, for example, by using low lag time measurement techniques such as fiber optics, Leitman and Ziegler (1971).

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NOTATION

Dimensions: M = mass, L = length, T = time

$\underline{a}$, a = fraction of system in segregated phase (dimensionless, see text)
A_{bc} = area of surface between segregated blob and continuous phase (L^2)
c_{10} = initial concentration of component 1 (M/L^3)
c_{1b} = instantaneous concentration of component 1 in segregated blob (M/L^3)
c_{1c} = concentration of component 1 in continuous micromixed phase (M/L^3)
D_1 = total pseudo diffusional coefficient of component 1 (L^2/T)
$e(\theta)$ = exit residence time distribution (dimensionless)
$i(\theta)$ = internal residence time distribution (dimensionless)
k_2 = second-order reaction constant (L^3/MT)
L = length of diffusional path from segregated blob to continuous phase (L)
Q_t = flow rate through reactor (L^3/T)
Q_c = flow rate in continuous phase (L^3/T)
R_1 = (diffusion/reaction) rate parameter $D_1A_{bc}/k_2c_{10}LV_b$
R_2 = flow/reaction rate parameter $Q_t/k_2c_{10}V_t$
S = Laplace transform parameter (dimensionless)
V_b = volume of segregated blob (L^3)
V_c = volume of continuous phase (L^3)
V_t = total volume of reactor (L^3)
x = $(c_{10} - \langle c_1 \rangle_e)/c_{10}$
Y_{1b} = dimensionless concentration in segregated blob (c_{1b}/c_{10})
Y_{1c} = dimensionless concentration in segregated blob (c_{1c}/c_{10})
$\langle Y_{1bi} \rangle$ = dimensionless average internal concentration in segregated portion
$\langle Y_{1be} \rangle$ = dimensionless average exit concentration in segregated portion
Y_c^*, Y_b^* = limiting values for given tracer test if $a = 0$ and $a = 1$, respectively
Y_{mic} = theoretical dimensionless exit concentration perfect molecular mixing
$\langle Y_{\text{seg}} \rangle$ = theoretical dimensionless average exit concentration perfect segregated mixing
$\overline{Y}$ = Laplace transform of Y

Greek Letters

α = parameter in Gamma distribution function
β = parameter in Gamma distribution function
θ = dimensionless reactor hold time (Q_tt/V_t)
ϕ = $D_1A_{bc}V_t/LV_bQ_t$
ψ = $a\phi/(1-a)$

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APPENDIX

For first-order reaction with nonideal residence time distribution

$$<Y_{e_{\text{seg}}}> = 4\left(\frac{R_2}{1 + 2R_2}\right)^2$$

which is less than $<Y_{e_{\text{mic}}}> = \dfrac{R_2}{1 + R_2}$

$$<Y_e> = \left[\frac{a\,R_1(1 + R_1 + 4R_2)}{(1 + R_1 + 2R_2)^2} + (1 - a)\right] Y_{1c} + \frac{4\,a\,R_2^2}{(1 + R_1 + 2R_2)^2}$$

where

$$Y_{1c} = \frac{R_2\,[(1 + R_1 + 2R_2)^2 - a(1 + R_1 + 4R_2 + 4R_2^2)]}{[(1 + R_2)(1 + R_1 + 2R_2)^2 - a(1 + 8R_2^2 + R_1 + 2R_1R_2 + 5R_2 + 4R_2^3)]}$$

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Nonisothermal Nip Flow in Calendering Operations

An efficient and simple numerical technique is presented for analyzing nonisothermal nip flow of viscous liquids. It has been applied on calendering to calculate the design parameters as well as the interaction effects between roller characteristics, operation conditions, and material properties. Viscous heating is shown to drastically change the mechanics near the nip exit if the rollers rotate at different speeds. Consequences for scaling-up and model experiments are indicated.

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During their processing, many viscous fluids, including polymer melts, are subjected to flow between rotating rollers. Nip flow can be used to homogenize material with respect to either composition or temperature, for kneading, or to produce continuous layers and sheets. Design, selection of operating conditions, and scaling-up of equipment require an adequate knowledge of the fluid mechanics during the process.

Early analyses assumed isothermal conditions and fluids with constant viscosity (Gaskell, 1950; Torner and Dobroljubov, 1958). McKelvey (1962) and Torner (1972) introduced power law liquids. An analytical solution for asymmetric nip flow of Newtonian liquids was recently obtained by Takserman-Krozer et al. (1975). Non-

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