Performance of Stirred Reactors with Dispersed Phase Mixing

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Theoretical studies have shown that coalescence and redispersion of drops in a two-phase system can have a pronounced influence on the average reaction rate of non-first-order reactions. An extensive review and discussion of the literature for such systems has appeared (*3*) and certain of these effects have been summarized previously (*1*) in which results were obtained for zero-order reactions and for mass transfer controlled reactions. These results have now been extended to include some other reaction schemes. To aid the calculations, the drop mixing computer program (*1*) was modified by the inclusion of an exponential extrapolation procedure. This modification permitted reduction of the computation time required to generate the steady state concentration distribution in a reacting two-phase system by a factor of 20 to 40. This permits calculation in a practical period of time of conversions for a wide range of reaction rate moduli and drop interaction moduli.

With this change, the program has been used to calculate the effect of coalescence and redispersion of drops on the conversion achieved in a stirred vessel when a second-order reaction ($A + A \rightarrow B$) is proceeding in the dispersed phase. Several limiting cases have been computed for parallel reactions for a variety of competing reactions with differing reaction orders. Slight modifications to the computer program allow calculation for the general case of two competing parallel reaction paths with a single reactant species.

MODIFICATIONS TO THE DISPERSED PHASE MIXING PROGRAM

The dispersed phase mixing program solves the drop mixing equation

$$\frac{\partial p(c)}{\omega_r \partial t} = p_o(c) - p(c) + I\left[4\int_o^c p(c+\alpha)p(c-\alpha)\,d\alpha - p(c) \right] + \frac{K\partial c^s p(c)}{\partial c} \tag{1}$$

where*

$$K = \frac{k{C_o}^{s-1}}{\omega_r}$$

and

$$I = \frac{\omega_i}{\omega_r}$$

by an unsteady state computational procedure. The terms contributing to the change in concentration distribution among drops, $p(c)$, are feed flow into the reactor with distribution $p_o(c)$, flow of reactor contents out with distribution $p(c)$, the effect of coalescence and redispersion of drops of different concentration (drop interaction term), and loss of material due to chemical reaction (reaction term). The equation is limited to the situation in which all drops are of the same size and the effluent of the reactor is a well-mixed sample of the reactor contents. The probability density function, $p(c)$, is calculated at succeeding intervals of time from Equation (1) until the left-hand side of Equation (1) is within a specified tolerance of zero, yielding a steady state solution. The computer program (*1*) has been modified to provide a more rapid generation of the steady state probability distribution.

Examination of the variation with time of the probability density function generated by the computer program, $Y_n = p\,[c_o(n - \frac{1}{2})/N]\Delta c$, indicates that the approach to steady state is very slow. An extrapolation routine has now been incorporated in the program which results in a time saving of typically a factor of 20 to 40. The extrapolation program is based on the following, admittedly crude, representation of the variations of the individual values of the probability density. It is assumed that the solution at any particular value of the concentration is approached in a more or less exponential manner.

$$Y_n(\omega_r t) = [Y_n(o) - Y_n(\infty)]\exp(-A_n\omega_r t) + Y_n(\infty) \tag{2}$$

This equation can be extrapolated out to the steady state value, that is, infinite time. The exponential decay is equivalent to the decay law

$$\frac{dY_n(\omega_r t)}{\omega_r dt} = -A_n[Y_n(\omega_r t) - Y_n(\infty)]$$

For a small value of the time step $\omega_r\Delta t$, the three successive values $Y_{1,n}$, $Y_{2,n}$ and $Y_{3,n}$ are related by the following equations:

$$Y_{2,n} - Y_{\infty,n} = (Y_{1,n} - Y_{\infty,n})(1 - A_n\omega_r\Delta t_1) \tag{3}$$

$$Y_{3,n} - Y_{\infty,n} = (Y_{2,n} - Y_{\infty,n})(1 - A_n\omega_r\Delta t_2) \tag{4}$$

These equations may be solved for estimates of the decay constants A_n and extrapolated values $Y_{\infty,n}$:

$$A_n \cong -\left(\frac{Y_{3,n} - Y_{2,n}}{Y_{2,n} - Y_{1,n}}\right)\frac{1}{\omega_r\Delta t_2} + \frac{1}{\omega_r\Delta t_1} \tag{5}$$

and

$$Y_{\infty,n} \cong Y_{1,n} + \frac{(Y_{2,n} - Y_{1,n})}{A_n\omega_r\Delta t_1} \tag{6}$$

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* The reader is cautioned that the rate parameter or rate modulus, K, used here has been normalized with the initial concentration to an appropriate power and therefore differs from the rate modulus of reference *1*.

The original expression may then be extrapolated to an infinite time. However, if the value of A_n is negative, it indicates that the function is diverging from rather than approaching a steady state value. This apparent growth is a temporary condition. The program will not make the extrapolation in this case but will instead retain the last value of this variable. For a value of A_n between 0 and ln 10, the last value is also retained. This last procedure tends to filter out random fluctuations in the values of the variables and insures that only large, and therefore significant, values of the decay constant A_n are used in the extrapolation procedure. For values of A_n between ln 10 and $1/\omega_r\Delta t$, the value of $Y_{1,n}$ is extrapolated according to Equation (6). Values of A_n greater than $1/\omega_r\Delta t$ indicate that the function is representable by an oscillatory function contained in an exponentially decaying envelope. For this situation, the value of the probability function is smoothed according to Equation (7).

$$Y_{\infty,n} \cong (1/3)(Y_{1,n} + Y_{2,n} + Y_{3,n}) \tag{7}$$

The choice of the cutoff value of A_n at ln 10 corresponds to the argument which follows: Consider the value of Y from Equation (2) after a residence time of one unit. This value of the probability density is

$$Y_n(1) = [Y_n(o) - Y_n(\infty)] \exp(-A_n) + Y_n(\infty) \tag{8}$$

which may be rearranged to give

$$Y_n(1) = Y_n(o) \exp(-A_n) + Y_n(\infty)[1 - \exp(-A_n)] \tag{9}$$

If the coefficients of $Y_n(o)$ and $Y_n(\infty)$ are thought of as weighting factors, a value of A_n greater than ln 10 insures a weighting factor of at least 9/10 for the extrapolated value of the probability $Y_n(\infty)$ after one residence time unit. The criterion serves to filter out noise due to rounding errors and to the contributions of the other terms representing interactions of variables which would appear in a more exact linearization of an expression for the derivative of the probability densities.

It was found empirically that the solutions were stable if

$$\omega_r\Delta t \leqq \frac{1}{2}\left(\frac{I}{1 + I + K(N + s)}\right)$$

The tolerance limit for a criterion of convergence of the iterative calculations is chosen to correspond to a bound on deviation of the average concentration of 0.5%.

Conversion as a function of reaction rate modulus for a second-order reaction at intermediate values of the drop mixing rate modulus I ranging from 5 to 500 and for the limiting cases of $I = 0$ and $I = \infty$ are summarized graphically in Figure 1. Twenty-five concentration increments have been used for most of the calculations. These calculations were based on the exponential extrapolation procedure previously outlined. The results have been slightly modified in order to get an exact overall material balance with a unit feed concentration, rather than the 0.98 concentration represented by the finite concentration increment.

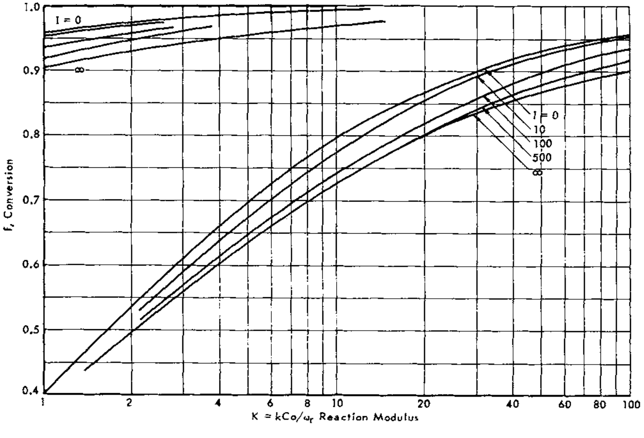

Fig. 1. Conversion for a second-order reaction.

As would be expected for a reaction rate higher than first order, the effect of drop interaction is to retard the progress of the reaction. For example, at conversion levels below 40%, the conversions for limiting cases of no drop interaction and an infinite rate of drop interaction differ by only a small amount. For conversion levels between 40 and 60% and with a drop interaction rate corresponding to a power input of approximately 10 h.p./1,000 gal. (*2*), residence times greater than 10 min. are required to bring the conversion to within 1% of that for an infinite rate of drop interaction (well-mixed reactor). It should be noted that the drop interaction parameter I involves both the frequency of interaction (for example, as given in reference 2) and the residence time. For conversion levels between 60 and 80% and at this same power input, residence times greater than 1 hr. are required to approach the limiting case of an infinite rate of drop interaction. For conversion levels greater than 80%, a reaction rate constant calculated on the basis of an ideally mixed reaction system may be typically incorrect by a factor of 2 or greater. Conversely, a reactor design on the basis of a well-stirred vessel at conversion levels between 80 and 90% will be overdesigned by a factor of from 2 to 4 if the rate of drop interaction is in fact negligible. For conversion levels above 90%, this factor of error increases rapidly.

The results of the methods presented here are in substantial agreement with the published results of Spielman and Levenspiel (*4*), which are based on a Monte Carlo simulation, if compared at conversion levels below 90%. At higher conversion levels there are significant differences which result primarily from representing small concentrations with an equal number of finite width concentration cells. In addition, part of the difference is a result of the use of a fixed time interval between coalescences in the Monte Carlo simulation. These differences are probably not critical, since both approaches are model approximations to a more complex physical situation. In this regard it is easier to incorporate extensions to the model in a Monte Carlo simulation, particularly with regard to reaction schemes which involve several reactants.

The above effects for a second-order reaction are similar to those observed for a zero-order or mass transfer controlled reaction but are opposite in direction. They can lead to two related types of errors in the design of a reactor system. First, laboratory data in a system which does not have a sufficiently high mixing rate for the well-mixed reactor assumption to be valid can lead to estimates of kinetic rate constants which are in error by a factor of 2 or more if that assumption is made. Second, the use of laboratory kinetic data obtained in well-mixed systems may easily lead to the oversizing of less well-mixed large-scale equipment by a similar factor if the scale-up is based on a well-mixed reactor assumption. Overdesign may be particularly detrimental if the reaction sequence includes an undesirable side reaction, for example, polymerization.

COMPETING PARALLEL REACTIONS

A problem of practical interest is the case of a *single reactant species* which may react in *more than one parallel reactant path.*

For example, consider

$$A \rightarrow B \quad \text{(first order)}$$
$$2A \rightarrow C \quad \text{(second order)}$$

where the second reaction may represent an undesirable side reaction (polymerization). The equation for the distribution of drops of a given concentration, Equation (1), must now be supplemented with an additional reaction term, that is

$$\frac{\partial p(c)}{\omega_r \partial t} = p_o - p(c) + I\left[4\int_o^c p(c+\alpha)p(c-\alpha)d\alpha - p(c)\right] + K_1\frac{\partial cp(c)}{\partial c} + K_2\frac{\partial c^2 p(c)}{\partial c} \quad (10)$$

Because of the nonlinear form of the equations, there is no simple relation between the solution of Equation (10) for two reactions and the corresponding solutions to Equation (1) for two reactions considered separately. Solutions for the limiting cases of infinite and for zero rate of drop interaction are presented below. These are an extension of examples presented by Rietema (3).

For the limiting case of an infinite rate of drop interaction ($I = \infty$) the first moment of Equation (10) is equivalent to the material balance

$$1 - \bar{c} - K_1\bar{c} - K_2\bar{c}^2 = 0 \quad (11)$$

from which

$$\bar{c} = -\frac{(K_1+1) \pm \sqrt{(K_1+1)^2 + 4K_2}}{2K_2} \quad (12)$$

and since the average concentration $\bar{c}$ is greater than zero, the positive square root is appropriate. The conversion is then

$$f = 1 - \frac{(K_1+1)}{2K_2}\left(\sqrt{1 + \frac{4K_2}{(K_1+1)^2}} - 1\right) \quad (13)$$

and the selectivity for the first-order reaction path is

$$S_1 = K_1\,\bar{c}/f$$
$$= K_1\,(1-f)/f \quad (14)$$

For the limiting case of a zero rate of drop interaction, the drops may be visualized as batch reaction systems with a distribution of life times $\omega_r e^{-\omega_r t}$. For each drop

$$\frac{dc}{\omega_r dt} = -K_1 c - K_2 c^2 \quad (15)$$

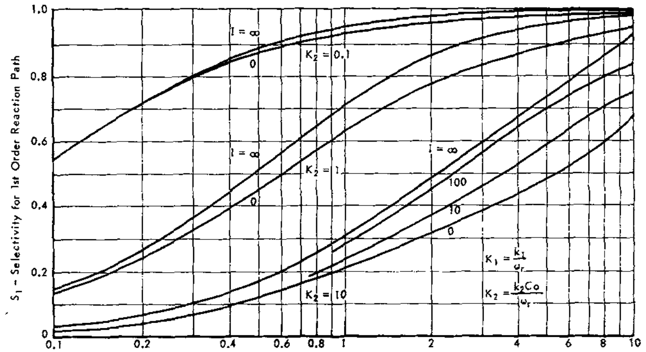

Fig. 2. Selectivity in competing reaction paths.

TABLE 1. CONVERSION AND SELECTIVITIES FOR PARALLEL COMPETING REACTION PATHS FOR ZERO AND FOR INFINITE DROP INTERACTION RATES

Reaction orders	$I = 0$	$I = \infty$
0 vs. 1	$f = \frac{K_1+K_o}{K_1+1} - \frac{K_o}{K_1+1}\left(\frac{K_o}{K_1+K_o}\right)^{\frac{1}{K_1}}$ $S_1 = K_1(1-f)/f$ $S_o = 1 - S_1$	$f = \frac{K_1+K_o}{K_1+1}\ (K_o < 1)$ $f = 1(K_o \geqq 1)$ $S_1 = K_1(1-f)/f$ $S_o = K_o/f$
1 vs. 2	$f = 1 - K_1\int_0^1 \frac{u^{K_1}}{K_1 + K_2 - K_2 u^{K_1}}du$ $S_1 = K_1(1-f)/f$ $S_2 = 1 - S_1$	$f = 1 - \frac{(K_1+1)}{2K_2}\left(\sqrt{1+\frac{4K_2}{(K_1+1)^2}} - 1\right)$ $S_1 = K_1(1-f)/f$ $S_2 = K_2(1-f)^2/f$
0 vs. 2	$f = 1 - \frac{\tan^{-1}\left(\sqrt{\frac{K_2}{K_o}}\right)}{\sqrt{K_oK_2}}\exp\left[-\frac{\tan^{-1}\left(\sqrt{\frac{K_2}{K_o}}\right)}{\sqrt{K_oK_2}}\right]\cdot$ $\int_0^1 \tan\left[\tan^{-1}\left(\sqrt{\frac{K_2}{K_o}}\right)u\right]\exp\left[+\frac{\tan^{-1}\left(\sqrt{\frac{K_2}{K_o}}\right)u}{\sqrt{K_oK_2}}\right]du$ $S_o = K_o\left\{1 = \exp\left[-\frac{\tan^{-1}\left(\sqrt{\frac{K_2}{K_o}}\right)}{\sqrt{K_oK_2}}\right]\right\}$ $S_2 = 1 - S_o$	$f = 1 - \frac{1}{2K_2}(\sqrt{1 + 4K_2(1-K_o)} - 1)(K_o < 1)$ $f = 1(K_o \geqq 1)$ $S_o = K_o/f$ $S_2 = K_2(1-f)^2/f$

the solution of which is

$$c(t) = \frac{K_1 e^{-K_1 \omega_r t}}{K_1 + K_2 - K_2 e^{-K_1 \omega_r t}} \qquad (16)$$

The average concentration is

$$\bar{c} = \int_0^\infty c(t) e^{-\omega_r t} d\omega_r t \qquad (17)$$

The substitution of $u = e^{-\omega_r t}$ transforms Equation (17) into a convenient form for numerical integration

$$c = \int_0^1 \frac{K_1 \, u^{K_1} \, du}{K_1 + K_2 - K_2 \, u^{K_1}} \qquad (18)$$

Figure 2 presents calculated results for the selectivity of the first-order reaction path based on Equations (13) and (18). Equation (18) was numerically integrated by using Simpson's rule with equal step sizes of 0.01 for Δu. For values of the second-order rate modulus K_2 of the same order of magnitude or greater than K_1, there is a significant difference in the selectivity of the first-order reaction path for zero and for infinite drop interaction rates. The effect indicated is an increase in selectivity for a high rate of drop interaction. This is the trend which would be expected, based on the solutions for a single reaction path, since the first-order reaction is unaffected by the drop interaction, while the second-order reaction is suppressed by it. The effects become more pronounced at large values of both K_1 and K_2.

A convenient summary of analytic results for zero-order–first-order, zero-order–second-order, and the above case of first-order–second-order parallel competing reaction paths is presented in Table 1 for the limiting cases of zero and infinite drop interaction rates. The computer program for dispersed phase mixing is easily modified to include the general case of competing parallel reaction with an arbitrary drop interaction rate. Selected results for $K_2 = 10$, $I = 10$, and $I = 100$ appear in Figure 2. It is evident from the figure that the influence of the coalescence and redispersion is slight for this example unless both reactions have sizable values for reaction rate moduli.

While the most general problem of reaction of several reactant species has not been solved, the solutions presented here in conjunction with those of references *1* and *4* should provide guidance for design in situations involving competitive reactions.

NOTATION

A_n = apparent decay constant
c = concentration variable
f = conversion
I = drop interaction modulus
k = reaction rate constant
K = reaction rate modulus
n = discrete concentration variable
N = number of concentration intervals
$p(c)$ = density function for drops
s = reaction order
S = selectivity
t = time, hr.
ω_i = drop interaction frequency, hr.$^{-1}$
ω_r = reciprocal residence time, hr.$^{-1}$

LITERATURE CITED

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Drag Augmentation by Polymer Addition

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A considerable body of recent literature (*1* to *7*) has demonstrated that the addition of small quantities of very high molecular weight polymers can lead to a drastic reduction in the skin friction associated with a given turbulent flow. An obvious application of this phenomenon is in the field of torpedo technology, and the experiments reported here were so motivated.

The experimental equipment was exceedingly simple and consisted of an open column, 17 ft. high and 8.5 in. in diameter, which could be filled with a suitable solution. Test bodies were placed on the bottom of this tank and then accelerated to terminal velocity by a system of counterweights. An arrangement employing photocells was used to determine the terminal velocity thus attained. The polymer chosen for addition was one well known for its drag-reducing capability, polyethylene oxide, [Union Carbide Polyox (code WSR 301)] with a molecular weight of about 4.5×10^{-6}. The concentrations investigated were 0, 20, 50, and 100 p.p.m. The solutions were essentially Newtonian with an intrinsic viscosity of 16.5 dl./g. Even for the most concentrated solution, the relative viscosity was less than 1.2. Two test bodies actually employed were a flat plate and a scale model of a torpedo. In both cases, calculations indicated that for pure solvent, the boundary layer on the bodies would be turbulent, but that approximately half of the drag experienced by the torpedo would be due to form drag.

As expected, the polymer addition led to a substantial increase in the terminal velocity achieved by the flat plate, that is, the drag on the plate was significantly reduced. At 20 p.p.m. the terminal velocity of the torpedo was also increased, but at higher concentrations, it had