$|V|$ = absolute value (magnitude) of oscillation in vapor boilup
X_B = bottoms composition, mole fraction water
X_D = distillate composition, mole fraction water
X_F = feed composition, mole fraction water
τ_N = nonlinear time constant, min.
τ_L = linear time constant, min.
β = slope of T_c versus V line between limits on T_c of $\pm\Delta T/2$, °F./(moles)(min.)
ω = frequency, rad./min.
$-$ = total steady state values of variables

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Mixing and Product Distribution for a Liquid-Phase, Second-Order, Competitive-Consecutive Reaction

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Mixing effects for the homogeneous, liquid-phase, second-order, competitive-consecutive reaction of iodine (B) with L-tyrosine (A) to form 3-iodo-L-tyrosine (R) and 3,5-diiodo-L-tyrosine (S) were determined for the following conditions: vessel volume, 5 and 36 liters (baffled and unbaffled); turbine diameter (2 to 6 in.) and speed (95 to 1,600 r.p.m.); feed inlet locations (3), addition rate (0.25 to 18 min.), and distribution; temperature (11° to 43°C.); initial A concentration (0.1 to 0.4 g.-mole/liter); and kinematic viscosity (0.765 to 6.35 centistokes). A was initially charged to the reactor and an equimolar quantity of feed B was added over a time period. Yields of R are less than that expected for perfect mixing owing to local regions of excess B concentration that exist for time periods during which R over-reacts to S.

Agitation power for a given yield is less in unbaffled vessels without an air-liquid interface than for baffled vessels. The local fluctuating velocity u' where feed is introduced correlates the mixing variables and predicts mixing requirements for maintaining yields of R on scale-up. Regions of excess B concentration are related to a concept of partial segregation. The extent of reaction occurring under this condition is correlated by the dimensionless group $(k_1 b \tau)(a_0/b)$, where τ is a microtime scale of mixing related to u' and the characteristic length of a microscale eddy. The magnitude of this group provides a criterion for predicting the importance of mixing effects on other reaction systems.

INTRODUCTION

The method of bringing together reactants that are to undergo reaction can have an influence on the course of the reaction for certain types of systems. If the reaction can result in only one product, the method can only influence the reaction rate. If more than one product is possible, contacting can influence the product distribution as well. These considerations apply to both homogeneous and heterogeneous reaction systems. This study is limited to homogeneous liquid-phase systems. The reactions studied form a system of the type

$$A + B \xrightarrow{k_1} R \qquad (1)$$

$$B + R \xrightarrow{k_2} S \qquad (2)$$

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carried out under semibatch conditions as follows:

1. A is initially charged to a stirred vessel as a solution.
2. B is added as a solution (hereinafter referred to as feed) through a feed pipe in a continuous manner until a stoichiometric amount for reaction (1) has been added.
3. The yield of R is determined and related to the prevailing mixing conditions.

R is considered as the desired product. The objective is to determine how mixing conditions can affect the yield of R. Both agitation environment and the manner of adding B are studied with the object of maximizing R, if possible, to the value that would be achieved by instantaneous perfect mixing to a molecular level. Once having studied the characteristics of the system on a small scale, the problem is extended to projecting the results to a larger scale.

We are concerned with the time period during which the reactants are first contacted and when they are completely mixed to a molecular scale. During this time, zones of local B concentration can vary from an upper limit equal to the feed concentration to a lower limit equal to the final, completely mixed concentration. The course of any reaction that is influenced by concentration can be influenced by mixing. The effect can be on the reaction rate, the product distribution, or both.

The rate can be reduced below that predicted by the conventional chemical rate constant because of limitations imposed by diffusional effects. The time required for mixing can add to the time for a given degree of conversion calculated on the basis of instantaneous mixing. This effect will be important only for extremely rapid reactions, and can be compensated for by an appropriate increase of contact time.

Mixing effects are of far greater importance on product distribution in multiple reactions because the impact on design and economics is more profound. In such reactions the desired product is one of two or more possible products. The selectivity of a reacting system is defined as the ratio of the amount of limiting reagent reacting to produce the desired product to the total amount actually reacted. The yield Y is the ratio of the amount of limiting reagent reacting to produce the desired product to the total amount charged.

Scale-up of mixing requirements for a multiple reaction requires knowledge of the dependency of the reaction on mixing conditions. For the majority of reactions, the effect of mixing will be negligible, assuming that turbulent mixing-impeller Reynolds numbers are used on all scales of operation. For some types of rapid multiple reactions, however, selectivity can be seriously reduced by inadequate mixing. In large-scale operation, this leads to increased raw material requirements as well as increased separation and purification costs.

REACTION TYPES

Multiple reactions occur in a wide variety of combinations, each of which must be examined individually to determine whether mixing can affect selectivity. Two major types are generally recognized as the basis of most combinations:

Competitive parallel reactions are of the type

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

$$A + B \xrightarrow{k_2} S$$

with B added to A. In this case, mixing can affect selectivity only if the reactions are of different order. Consider a local B-rich zone with some A present. The relative amounts of R and S made in this zone will not be affected if both reactions are first or second order, since the product ratio will be determined only by the ratio of the reaction rate constants k_1/k_2 independent of concentration. If the reactions are of different order, however, the second-order reaction will be accelerated while the first-order reaction (in A) will be unchanged by a B-rich zone. The magnitude of the effects will depend on the absolute values of the rate constants and the magnitude of the local concentration variations. This case has apparently not been experimentally investigated.

Competitive consecutive reactions, with B added to A, are of the type shown in Equations (1) and (2). If both reactions are first order, mixing will not affect selectivity since the concentration of only one component is involved. If both reactions are second order, mixing can affect selectivity because of local excess B concentrations, which can result in local overreaction of R to S. This type is referred to as second order, competitive-consecutive since it is competing with respect to B and consecutive with respect to A and R. Subsequent discussion is limited to this case. It is readily seen that other combinations of multiple reactions could be subject to the effects of mixing since they can be analyzed as combinations of the two basic types.

Provided reactant B is instantaneously mixed to a molecular level with the vessel contents, the maximum selectivity in a competing-consecutive reaction system is a function of the rate constants k_1 and k_2, the overall molar charge ratio of A to B, and the degree of conversion of A. The degree of conversion of A can depend on the charge ratio and the residence time. This discussion is limited to the case of sufficient residence time such that all of the B charged will react, provided B is not charged in excess for complete reaction to S. The degree of conversion of A is then only a function of the molar charge ratio of A to B. The maximum selectivity of R, in the absence of mixing effects, then becomes a function only of k_1/k_2 and the molar charge ratio. For purposes of the present study, it is convenient to establish a fixed molar charge ratio. The ratio chosen is not necessarily intended to give the maximum selectivity. For a particular reaction system (fixed k_1/k_2), a fixed molar charge ratio, and conditions of perfect mixing, the selectivity is also fixed, as is the yield and the degree of conversion of A.

At this point it is convenient to discuss the yield of R rather than the selectivity. The term "expected yield" is used to denote the yield that would be obtained under conditions of perfect mixing, as derived by van de Vusse (*18*) and Levenspiel (*10*):

$$Y_{\exp} = \frac{R}{A_0} = \frac{1}{(k_2/k_1 - 1)}\left[\frac{A}{A_0} - \left(\frac{A}{A_0}\right)^{k_2/k_1}\right] \tag{3}$$

where capital letters denote molar quantities. This equation applies to both batch and semibatch operations, provided both reaction rates depend on B in the same way and provided B is added to A in the semibatch case. The molar charge ratio used throughout the experimental work is $A_0/B_0 = 1$.

Mixing effects, exclusive of residence-time distribution effects, can only reduce the yield. The primary concern of this study is the magnitude of the yield reduction attributable to deviation from instantaneous, perfect mixing to a molecular level. The magnitude will be determined by the following major factors:

1. The elapsed time from initial contact of the reactants to final homogeneity on a molecular scale. Any overreaction of R to S must occur during this time because once the reactants are molecularly mixed, the relative amounts of R and S obtained are fixed by k_2/k_1 according to Equation (3).
2. The absolute value of k_1. The magnitude of this rate

constant will determine how much A can be converted during the time required to achieve molecular mixing. The extent of the conversion will determine the amount of R that is subject to excess B concentration and hence overreaction to S.

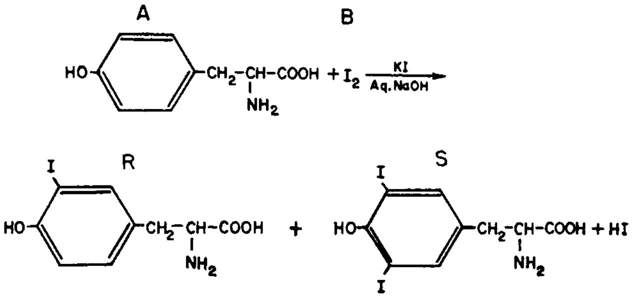
3. The relative speeds of the second reaction (k_2) and local diffusion. R is converted to S depending on the probability of a molecule of R reacting with a molecule of B. In the B-rich zone this probability is greater than in the perfectly mixed zone and the extent to which it occurs will depend on the rate at which R can diffuse out of the B-rich zone relative to the rate at which it reacts with B.

PRIOR WORK

Most of the research on reactions of this sort is for the case where reactants are premixed prior to being fed to a continuous reactor. There has been both theoretical and experimental study of the influence of mixing where reactants are introduced separately into a continuous reactor (*4* to *6*, *16*, *19*). Consideration of mixing in semibatch reactors for second-order competitive-consecutive reactions seems to be confined to the qualitative discussion of Levenspiel (*10*), and the case where the added reactant is a gas (*18*). There appears to be no prior study corresponding to the present case, where the reactants are miscible liquids.

EXPERIMENTAL PROCEDURE

The reaction used in this study was the iodination of L-tyrosine to form 3-iodo-L-tyrosine and 3,5-diiodo-L-tyrosine:



The kinetics of a very similar reaction, the iodination of *N*-acetyl-L-tyrosine, were studied by Mayberry et al. (*12*). The reaction was found to be second order, and this result is assumed to be applicable to the present reaction, making it consecutive in L-tyrosine and competitive in iodine. It is therefore an example of the multiple reaction scheme of Equations (1) and (2).

A standard operating procedure was developed in which a solution of iodine in aqueous potassium iodide was added to a solution of L-tyrosine in aqueous base. Phosphate buffers were added to minimize the change in pH resulting from the formation of hydrogen iodide. The procedure, based on 1 mole of L-tyrosine, is as follows:

1. The initial charge of L-tyrosine is dissolved in water by the addition of two equivalents of sodium hydroxide. This is the minimum quantity of base required to dissolve the L-tyrosine, which has an extremely small water solubility unless converted to the sodium salt.

2. Di- and tri-sodium phosphate buffers are added and dissolved. The resulting pH is 11.7.

3. One mole of iodine is dissolved in aqueous potassium iodide solution. This is enough iodine to convert all of the L-tyrosine charged to 3-iodo-L-tyrosine if no diiodo product were formed.

4. The iodine solution is added to the L-tyrosine solution over a fixed time period while the temperature is maintained constant. The reaction is very slightly exothermic with an estimated adiabatic temperature rise of approximately 0.5°C. The final pH is 10.5.

The rate constants k_1 and k_2 were determined by running the reaction in a cell inside a Cary spectrophotometer. The disappearance of iodine was measured as a function of time, and the constants evaluated from integrated, second-order rate equations. In the case of reaction (2), the starting material was pure R, and S was the only product. In the case of reaction (1), both reactions occurred but only the rate equation for the first was considered. This was assumed adequate to provide a reasonably good approximation of k_1 since reaction (1) is seven to ten times faster than the second.

The rate constants were determined at three temperatures, and each yield an excellently straight Arrhenius plot. Expected yields, calculated through Equation (3), depend upon temperature since k_1/k_2 is temperature dependent. The data are summarized, for an equimolar charge of A and B, in Table 1. Details are available elsewhere (*13*).

The analytical procedure used throughout follows the standard for analyzing mixtures by ultraviolet absorption (*3*). The ultraviolet absorption of the final product solution was determined in a Cary-15 spectrophotometer, using 1-cm. quartz cuvettes. Readings were taken at three wavelengths at which the absorption of the three pure organic components is known. The three readings were used in the solution of three simultaneous equations whose unknowns are the concentrations of components A, R, and S. Thus the amount of R and the yield was obtained directly. Mixtures of known compositions were analyzed to determine the accuracy of the technique: the assay differed from the charge composition by between 1.0 and 1.3% for all three components. This assay technique also gives the total organic and iodine material balances. They were consistent (±1%), as was the ratio of A to S (theoretically 1.0) (*13*).

The basic reaction vessel was a 5.85-in. I.D., flat-bottomed, glass cylinder with a capacity of 5 liters. The impellers were each six-bladed, flat-blade turbines, diameter/blade length/blade width = 2/0.5/0.4, driven by a ¼-h.p. motor with a Vickers variable-speed drive. The vessel contained four, equally spaced, vertical baffles, each of width equal to 10% of the vessel diameter [fully baffled (*11*)], but several runs were made in the absence of baffles, with a Plexiglas plate arranged to cover the liquid to eliminate vortexing from an air-liquid interface. Scale-up was tested in a geometrically similar vessel, 11.3 in. diameter, capacity 36 liters. The vessel operating variables are summarized in Table 2. The combination of turbine speed and diameter used in all runs was sufficient to give impeller Reynolds number in the turbulent regime (>10,000).

The other major vessel variable was the position of the feed line opening in the vessel. Two positions, shown schematically in Figure 1, were used for the majority of the work with a ⅛-in. diameter tube. A third position, not shown, 0.5 in. directly below the center line of the impeller, was used for a limited number of runs. The effect of feed distribution was studied by introducing the feed through a nine-hole distributor placed 6 in. above the turbine in the smaller vessel. The distributor was circular, of 1.5-in. radius, and the hole diameters were 0.04 in.

TABLE 1. REACTION RATE CONSTANTS AND EXPECTED YIELDS

Temperature, °C.	11	25	43
k_1, liters/(g.-mole)(sec.)	8.5	35	163
k_2, liters/(g.-mole)(sec.)	0.58	3.8	25
Conversion of A, %	90.5	88	85
Expected yield of R, %	81	75.5	70

TABLE 2. OPERATING VARIABLES

Mixing		
Vessel capacity, liters	5	36
Vessel diameter, in.	5.85	11.3
Depth of liquid,* in.	10.0	19.6
Turbine diameter, in.	2,3	4,6
Turbine speed, r.p.m.	200 to 1600	95 to 788
Baffles	0,4	4
Feed location, number of positions	3	2
Feed distribution, number of holes	1,9	1
Reaction	Normal	Also studied
Temperature, °C.	25	11, 43
Initial A concentration, g.-mole/liter	0.2	0.1, 0.4
Feed B concentration, g.-moles/liter	2.0	—
Solution kinematic viscosity, centistokes	1.08	0.765 to 6.35
Addition time for B, sec.	1080	15, 60

*Depth of liquid increases as feed solution is added. The depths given are averages of initial and final values.

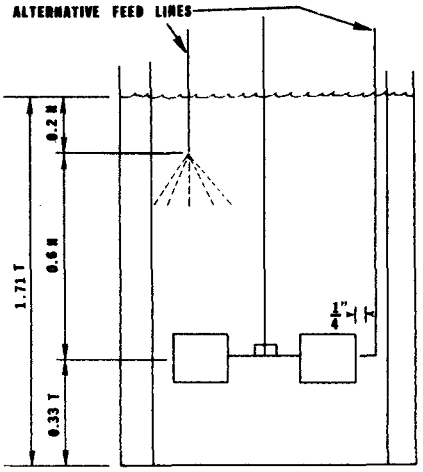


Fig. 1. Feed inlet locations.

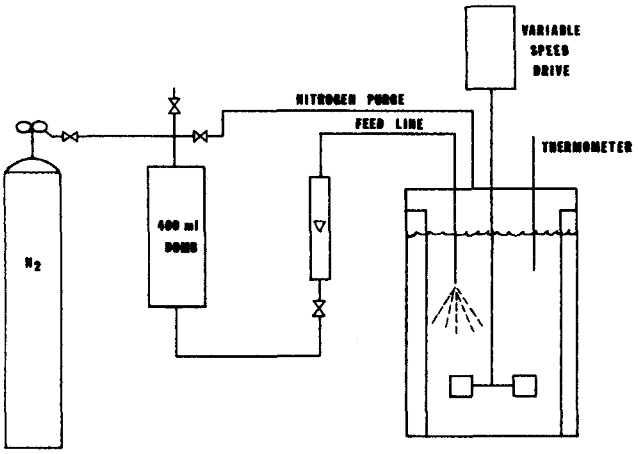


Fig. 2. Apparatus arrangement.

The 5-liter vessel contained a coil of 0.25 in. stainless steel tubing for heating and cooling. No coil was used in the 36-liter vessel, where the solution temperature was preset to 25°C. and allowed to rise to 25.5 to 26.0°C.

Feed was transferred to the reaction vessel from a 400-ml. stainless steel cylinder under nitrogen pressure. The rate of flow was measured with a rotameter. Figure 2 shows the arrangement.

Operating Variables

The reaction was run under various conditions of temperatures, concentrations, etc., to determine their effects on product distribution. The bulk liquid viscosity was increased by adding suitable amounts of a flocculating agent, Primafloc A-10, an anionic polymeric emulsion exhibiting carboxylic acid functionality obtained from Rohm and Haas. This material did not interfere with the reaction or assay. Table 2 summarizes the range of the operating variables.

EXPERIMENTAL RESULTS

For each run a final yield of *R* is obtained after sufficient time has elapsed to ensure complete reaction of the *B* charged. As shown in Figure 3 for the 5-liter vessel, the yield is very responsive not only to turbine speed, but also to turbine diameter and feed-line position. Directing the feed into the impeller discharge produces the highest yield for a given turbine speed, and achieves the highest yield at a relatively low speed. This position is superior to that commonly used, directly below the turbine center line. Feed location in the upper portion of the vessel produces sharply reduced yields. It might be anticipated that feed from a line above the liquid surface would give even poorer results. An increase in turbine diameter produces increased yield for both feed positions, a result which is expected since the power input is greatly increased. The horsepower input increase

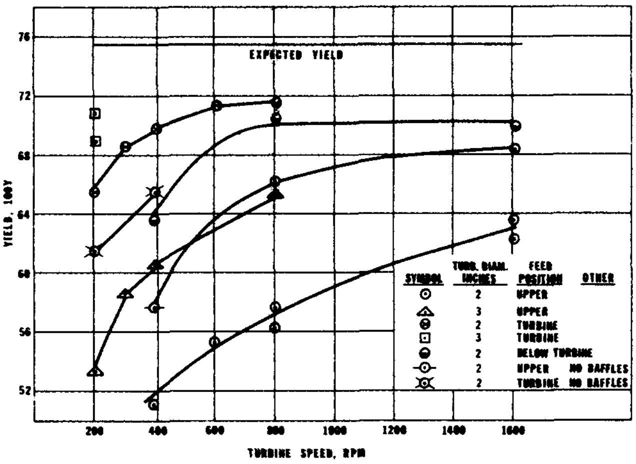


Fig. 3. Yield of *R* in the 5-liter vessel, 25°C. Eightfold difference in horsepower input between 2- and 3-in. turbines.

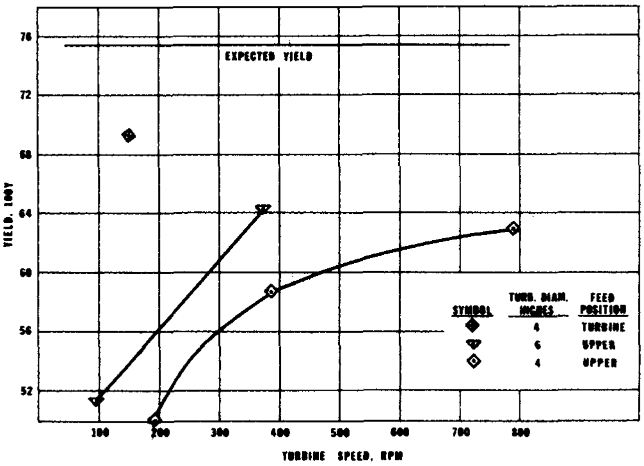


Fig. 4. Yield of *R* in the 36-liter vessel, 25°C. Eightfold difference in horsepower input between 4- and 6-in. turbines.

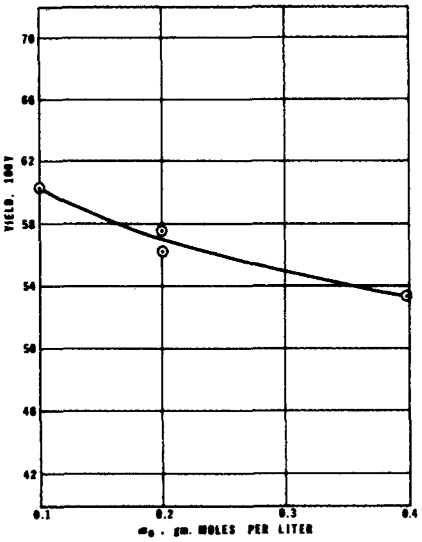


Fig. 5. Effect of initial *A* concentration on yield of *R*, 5-liter vessel, 25°C., 2-in. impeller, 800 r.p.m., upper feed position.

from the small to large turbine is approximately eight-fold. The yield is also improved by the removal of baffles for the upper feed position, but reduced for the turbine-discharge position.

Figure 4 summarizes the data from the 36-liter vessel, which produced basically similar results. Again, the horsepower drawn by the larger turbine is approximately eight times that of the smaller turbine. Figure 5 shows the effect of initial A concentration.

CORRELATION OF EXPERIMENTAL RESULTS

Our objective was to develop a method of correlating the experimental data in terms of mixing parameters. The first variables considered were turbine speed, turbine and vessel diameter, and feed position. The large yield differences experienced at the different feed locations indicate that local conditions in the vicinity of the feed point must be considered rather than average conditions for the vessel as a whole. This precludes overall factors such as impeller power.

Examples of variables that can vary from point to point in a stirred vessel are the bulk liquid velocity U, the fluctuating velocity u', the intensity of segregation, and the local rate of energy dissipation ε. The intensity of segregation depends on local concentration fluctuations. The extent of conversion of A and B prior to complete mixing of B to a molecular level can thus be seen to be a function of local intensity of segregation. Since all A converted prior to complete mixing is exposed to increased overreaction to S, this degree of completion could be the governing factor in the course of the reaction. No attempt was made to measure the intensity of segregation, although some investigators have done this but under different conditions (*1*, *9*, *14*). However, applicable measurements of the local intensity of turbulence, more particularly the local fluctuating velocity, are available, and a correlation based on this variable will be discussed.

Schwartzberg (*15*) measured local velocities at various levels above the turbine in a fully baffled vessel, and also turbulence intensities. An average value for the fluctuating velocity in the upper portion of the vessel is given by

$$u' = 0.581 \frac{ND^2}{(T^2H)^{1/3}} \tag{4}$$

which can be used to calculate u' for the upper feed position for all of the vessel variables except in the absence of baffles.

For the feed position at the turbine discharge, values of u' may be estimated from the work of Cutter (*2*), who measured turbulence intensity u'/U as a function of the radial position on the horizontal plane of the turbine. Our feed line was as close as practicable (ca. 0.25 in.) from the turbine tip, where the velocity may be taken as the impeller tip speed. With an intensity of 0.45 estimated from Figure 7 of Cutter's paper, then

$$u' = 0.45\,\pi DN \tag{5}$$

The values of u' chosen are composite averages of the three components of the fluctuating velocity, since further refinement seemed unwarranted. The third feed position, directly below the impeller center line, is not considered further since no estimate of u' is available. Similarly, the case of the unbaffled vessel cannot be included, although it will be considered later.

Figure 6 is a plot of yield against fluctuating velocity at the feed line position, where the mixing variables included are turbine speed, turbine diameter, vessel diameter, and feed location. The correlation based on u' is seen to approximate the yield response to mixing suggesting the importance of this turbulence parameter.

The correlation can be extended further to examine the importance of microscale eddies in determining the course of the reaction. One measure of the characteristic length of a microscale eddy is given by Kolmogoroff's universal equilibrium theory (*7*).

$$\eta = \left\{\frac{\nu^3}{\varepsilon}\right\}^{1/4} \tag{6}$$

Combining this with the fluctuating velocity provides a parameter τ, with dimensions of time, which can be visualized as the time required for an eddy of characteristic length η to move one eddy length at a velocity u':

$$\tau = \frac{\eta}{u'} = \frac{\nu^{3/4}}{\varepsilon^{1/4} u'} \tag{7}$$

The local rate of energy dissipation ε has been empirically related to u' (*17*):

$$\varepsilon = 1.65 \frac{u'^3}{L_f} \tag{8}$$

where L_f is a length scale associated with the vessel dimensions. Substitution of Equation (8) into Equation (7) then provides

$$\tau = \frac{\eta}{u'} = 0.882 \frac{\nu^{3/4} L_f^{1/4}}{u'^{7/4}} \tag{9}$$

The quantity τ can be considered as a microtime scale characteristic of the length of time available for reaction between the eddies of B feed and the bulk liquid.

Equation (9) contains the kinematic viscosity, and predicts an increase in τ with increasing ν, which should result in a decrease in yield. This prediction was tested by running the reaction with the viscosity of the bulk liquid increased sixfold by addition of a suitable nonreactive agent (Primafloc A-10). A decrease in yield resulted, but the viscosity could not be varied over a large enough range to determine whether the $\frac{3}{4}$ power for ν predicted by Equation (9) is ultimately correct. The limitation on increased viscosity was imposed by the resulting reduction in impeller Reynolds number to values no longer in the turbulent range.

Figure 7 shows the correlation of yield with τ, with impeller speed and diameter, vessel size, feed location, and solution viscosity as the variables. Values of L_f were taken as the vessel radius for the upper feed location and the turbine diameter for the turbine feed location. The figure also includes the results for increased feed addition rates. These fall on the correlation without further correction because this variable did not produce significant differences over the range tested. The same is true for the effect of a feed distributor, in agreement with the correlation based on u', because this variable would not be affected by either addition time or feed distribution. All of

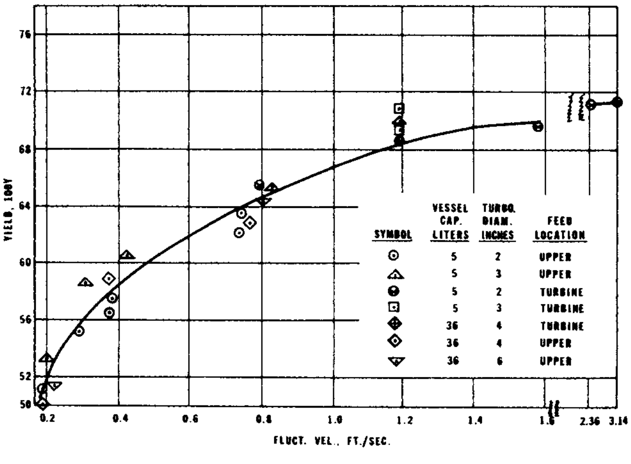


Fig. 6. Yield of *R* correlated with fluctuating velocity, 25°C.

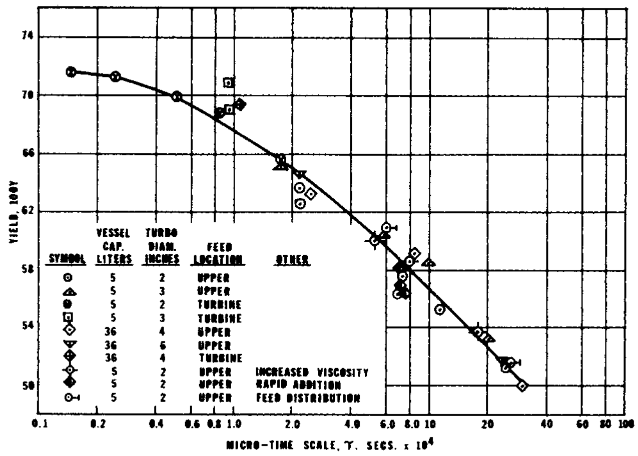


Fig. 7. Yield of R correlated with τ, 25°C.

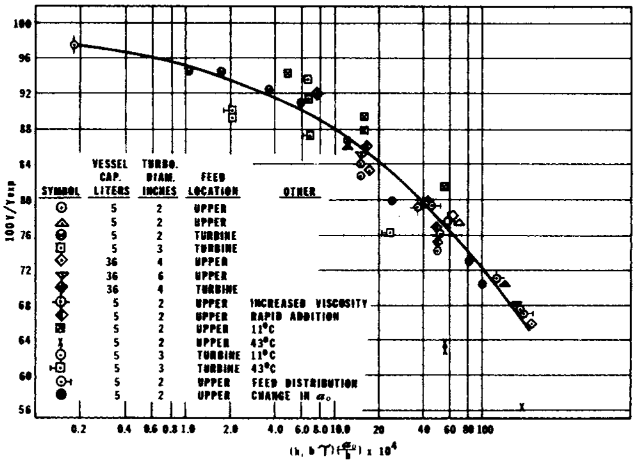


Fig. 8. Yield of R correlated with $(k_1 b\tau)(a_0/b)$.

these data are in Figure 7. The correlation seems to represent well the variables associated with mixing within the vessel.

REACTION RATE

It was considered important to investigate how the change in the speed of a reaction affects the overall results. This was done by varying the reaction temperature, thereby altering the k's. Increased reaction rates can be expected to decrease the yield because the amount of A and B that can react prior to complete mixing will be increased, subjecting the A thus reacted to increased overreaction to S. A correlation based on the amount of reaction occurring under partially mixed conditions would include k_1 to represent the reaction rate; the high B concentration in the B-rich eddies makes it possible to treat the reaction as pseudofirst order in this zone. Thus, neglecting the second reaction

$$\frac{da}{d\tau} = -k_1 ab$$

where b can be considered constant. Integration for a first-order reaction gives

$$\frac{a}{a_0} = e^{-k_1 b\tau} \tag{11}$$

If time τ is taken as the microtime scale previously discussed, the group $k_1 b\tau$ is a measure of the extent of conversion of A and B under conditions of partial segregation. The group is similar to the dimensionless reaction time when the time is the total elapsed time.

The effect of mixing on yield for different reaction rate constants must be separated from the effect caused by a change of the ratio, k_1/k_2. This can be accounted for through the ratio (Y/Y_{exp}) 100, which reflects the percentage decrease in yield attributable to mixing and is used in comparisons of data taken at different temperatures.

The dimensionless group $k_1 b\tau$ also predicts an influence of B feed concentration on yield. This was examined, but the simultaneous effect of potassium iodide concentration on rate could not be separated from that due to iodine concentration, and the data are unsuitable for correlation. The effect of initial A concentration was also studied. An increase in this concentration decreased the yield, and this can be included in the overall correlation by the combination $(k_1 b\tau)(a_0/b)$. The results for all the data are shown in Figure 8, which includes the full range of all the variables listed in Table 2. The two points at 45°C. for the upper addition point are not well correlated by this technique. No satisfactory reason could be assigned, although these runs did result in some iodine loss as indicated by the iodine balance. Nevertheless, all the yield trends for the nine variables are reasonably well handled. The runs made without baffles are not included in any of the correlations because no method of evaluating the local fluctuating velocities is available.

POWER/VOLUME

A scale-up method based on equal fluctuating velocities can be compared with a commonly used method based on equal power per unit volume for geometrically similar vessels. Power input for the 25°C. runs was computed from the standard correlations (*8*, *17*), and its effect on yield is shown in Figure 9. Power per unit volume is obviously incapable of correlating the widely different local conditions within a stirred vessel. In a fixed feed position the agreement is improved. However, for scale-up from 5 to 36 liters, the power per unit volume required for equal yields on the larger scale is approximately one-half that for the smaller scale with the smaller turbines. The larger turbines produce better agreement. Within the 5-liter vessel the two turbine sizes are not well correlated, with the larger turbine requiring roughly one-half the power for an equivalent yield with the smaller turbine. The reduction in power required for the unbaffled case is evident, making this an interesting area for further work.

Another frequently used scale-up technique is that of maintaining equal impeller tip speed. That is in agreement with the results of this work for the case of feed addition at the turbine discharge, since the fluctuating velocity at

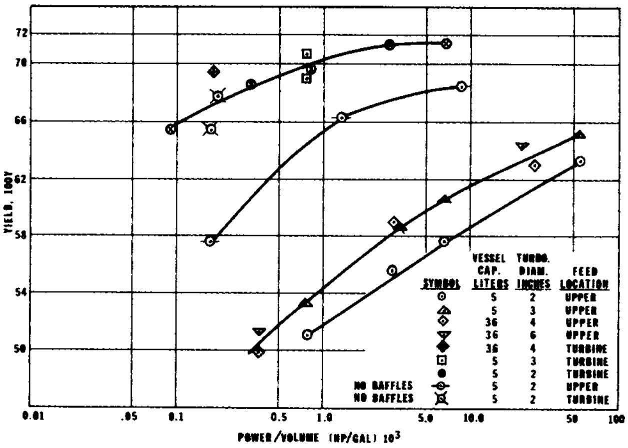


Fig. 9. Influence of impeller power/volume, 25°C.

that location is directly dependent on turbine-tip speed, Equation (5). The tip speed will not correlate the data for the upper feed position, however, as indicated by Equation (4).

DISCUSSION

The first objective of this study was to establish whether a measurable effect of mixing could be demonstrated for a homogeneous, multiple-reaction system. This was accomplished in the case of the reactions studied, where yields ranging from 50 to 72% were obtained, depending on mixing conditions within the turbulent regime of impeller Reynolds numbers.

The second objective was to establish a method of predicting under what conditions a multiple-reaction system would be subject to mixing effects. At any given mixing condition the magnitude of the rate constant k_1 will determine whether the maximum yield will result as determined by k_2/k_1, or a reduced yield because of the finite time associated with the mixing process. Values of k_1 can range over several orders of magnitude. For slow reactions, turbulent mixing will play no part because homogeneity on a molecular scale will be achieved in a very short time relative to the reaction time. Faster reactions will result in increasing amounts of starting material being converted under partially segregated conditions until this amount significantly affects the yield.

The primary value of this work is believed to be in suggesting for what order of magnitude of k_1 mixing effects become important. The dimensionless microtime scale for partially segregated reactions, as given by the group $(k_1 b \tau)(a_0/b)$, can be estimated for any reaction system, provided k_1 and an estimate of the fluctuating velocity are at hand. If necessary, an estimate of τ of the order of magnitude used in this work will be suitable. As suggested by Figure 8, if the value of the group is less than 10^{-5}, the reaction is possibly not subject to significant mixing effects. Furthermore, the rate constant k_1 can be expressed as a pseudofirst-order constant k_1' for constant b by combining k_1 and b. With values of a_0 and τ used in this work, a pseudofirst-order rate constant k_1' of approximately 0.5 sec.$^{-1}$ can be shown to be an estimate of the lower limit for which mixing will be important. As the rate increases, a decrease in yield can be anticipated for constant mixing conditions. For values of $(k_1 b \tau)(a_0/b)$ greater than 10^{-5} or of k_1' greater than 0.5 sec.$^{-1}$, special mixing design is indicated. If no additional mixing equipment is to be used, the feed position at the turbine discharge is superior to the two other positions studied. Feed injection near the turbine is common practice, but for sufficiently high reaction rates even this position does not give perfect mixing in a short enough time to prevent significant yield loss. Such rapid reactions require auxiliary equipment such as line mixers to maximize the yield.

The third objective was to define what mixing parameters best describe the mixing regime critical to chemical reaction. The fluctuating velocity at the point of feed introduction was found to be very effective in determining yield response, and is therefore suggested as a critical mixing parameter. Thus, when the reaction was scaled up from 5 to 36 liters, the turbine speeds for the larger scale were calculated by maintaining u' constant on both scales, and the yields were identical within expected experimental error. This suggests a scale-up method based on constant u' at the point of feed introduction to maintain constant yield. Experimental work on still a larger scale would be of great value, but was too expensive for the present study.

It should be noted that these considerations can apply to reactions in which a definite consecutive or competing reaction cannot be defined. On a small scale the secondary reaction may produce only a nondetectable amount of impurity. However, if mixing conditions on scale-up are not properly designed, the extent of such side reactions could increase and cause process difficulties, particularly in recycle processes where trace impurity concentrations could build to unexpectedly high levels.

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NOTATION

a = concentration of A, g.-moles/liter
A = moles of reactant A
b = concentration of B, g.-moles/liter
B = moles of reactant B
D = impeller diameter, ft.
H = average liquid depth, ft.
k_1 = second-order rate constant for first reaction, liters/(g.-mole)(sec.)
k_2 = second-order rate constant for second reaction, liters/(g.-mole)(sec.)
L_f = characteristic length scale for vessel, ft.
N = impeller rotational speed, rev./sec.
R = moles of product R
T = vessel diameter, ft.
u' = fluctuating velocity, ft./sec.
U = average velocity, ft./sec.
Y = reaction yield, R/A_0
Y_{exp} = Y for instantaneous, perfect mixing
ε = local rate of energy dissipation/mass, sq. ft./sec.^{3}
η = characteristic length of microscale eddy, ft.
ν = kinematic viscosity, sq. ft./sec.

Subscript

$_0$ = initial value

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