Tubular reactor at low flow rates

Increase efficiency of continuous tubular reactors by use of strategically-spaced baffles.

The design of chemical reactors is a matter of paramount importance to many chemical engineers, and much has been written about methods that may be employed for carrying out such designs (2, 5, 7, 10, 15). With the advent of precision automation, the trend in reactor design has been, where possible, toward the use of continuous reactors. The design of these reactors has been complicated by the inherent presence within them, in most cases, of a condition of axial mixing—or "backmixing"—which causes a decrease in the efficiency of the reactors.

It has been shown (2, 7, 10) that a flow reactor is most efficient; that is, it permits the greatest degree of conversion for a given reactor volume, when no backmixing is permitted to occur within it as the reactant stream passes through. This "zero backmixing" condition is approximated when the reactants flow through a tubular (longitudinal) reactor under conditions of turbulent (plug) flow. However, a disadvantage encountered in the use of tubular reactors at high flow rates arises from the fact that these high flow rates are apt to force the use of an extremely long reactor to assure that sufficient retention time is provided for in the reactor.

This article presents the results of a study of reaction kinetics in a tubular reactor at low flow rates which should be of interest as such rates allow a greater reaction time for a given reactor, or allow the design of a shorter reactor to perform a desired conversion. It might be expected, however, that these low (essentially laminar) rates would lead to considerable backmixing or its equivalent. To overcome this tendency, baffles were placed in the tubular reactor to produce turbulence and, hopefully, lessen backmixing.

In this investigation, a tubular flow reactor was operated at low Reynolds Numbers to determine the percentage conversion of reactants. Next, baffles—at various baffle spacings—were inserted in the reactor and their effect upon the conversion was observed. The system employed in the study was the second-order saponification reaction of ethyl acetate, in aqueous solution, with sodium hydroxide at 29.8°C.

Background study

For the sake of kinetic analysis chemical reactors may be classified into the following four main categories:

1. Batch
2. Tubular, or longitudinal, flow
3. Tank flow
4. Semi-batch (non-steady state)

Literature discussing the obtaining of kinetic data and their interpretation, as applied in the design of these reactor types, have appeared recently (2, 4, 5, 9, 10). Only a brief review will be presented here of the basic kinetic equations that have been developed for the first three reactor types listed. This survey will serve as background for the analysis of the kinetics of a second-order reaction taking place in a tubular reactor at low flow rates.

Consider a bimolecular reaction of the type:

\[ A + B \rightarrow C + D \]  \hspace{1cm} (1)

If this reaction is second-order, the rate equation obtained in a batch reactor is:

\[ \text{rate} = \frac{dx}{dt} = k_2(a - x)(b - x) \]  \hspace{1cm} (2)

where:
- \( a \) = amount of product formed at time, \( t \)
- \( a = \) initial concentration of reactant \( A \)
- \( b = \) initial concentration of reactant \( B \)
- \( k_2 = \) second-order reaction rate constant

When \( a \) and \( b \) are equal, that is, for equimolar initial concentrations of reactants, Equation 2 can be solved to yield:

\[ (a - x) = \frac{x}{a k_2 t} \]  \hspace{1cm} (3)

A tubular flow reactor operating at high Reynolds Number may be considered as a batch reactor through which the reactants pass in plug flow; that is, with no axial mixing along the reactor. Thus the retention time \( t \) is directly related to the length, or volume, of tubular reactor through which a particular plug of reactants has flowed. For this longitudinal flow reactor, operated at high flow rates, Equation 3 becomes:

\[ (a - x) = \frac{x}{a k_2 V/F} \]  \hspace{1cm} (4)

where: \( V = \) reactor volume
\( F = \) volumetric flow rate
\( V/F = \) retention time in the reactor, corresponding to \( t \) in Equation 3.

Another type of flow reactor, discussed by Corrigan and Young (2), Lessells (7), Sherwood (9), and Smith (10) is the "complete backmix" reactor (or stirred, tank-flow reactor).
REACTOR DESIGN

In this type, feed is added and product removed continuously at equal mass rates. Once flow equilibrium is established in the system, the reactor operates at steady state and concentrations of materials in the reactor are constant.

Corrigan derives the design equation for the equimolar second-order reaction in the backmix reactor from a mass balance over the reactor. This equation, quite different in form from Equation 4, is:

\[
(a - x) = \left(\frac{(F/2V_k^2)}{a}\right)^{1/2} - \frac{1}{2(F/2V_k^2)} \quad (5)
\]

For any value of \( t \) or \( V/F \), a value of \( x \) is obtained from Equation 5 that is always smaller than that obtained from Equation 4. Thus, a backmix reactor operated under the above conditions produces a lower conversion in a given reactor volume or in a given time than does a longitudinal flow reactor.

When dealing with reaction kinetics in laminar flow reactors, as in part of this investigation, the method developed by Denbigh (8) is useful. This development rests upon a statistical distribution of residence times in the reactor from a knowledge of the parabolic laminar flow profile. Basically, Equation 3 is combined with:

\[
t = 2t_0 \quad (6)
\]

to give:

\[
\frac{x}{a} = 2a(ak^2t_0) \left[1 + \frac{(ak^2t_0)}{(1 + ak^2t_0)}\right] \quad (7)
\]

where: 
\( t = V/F \) = average retention time in reactor
\( t_0 = \) time of passage down center of tube (minimum time)
\( x \) = average concentration of products at reactor outlet.

Equation 7 is a particular solution for the kinetics of a homogeneous second-order reaction in a tubular reactor operating with a parabolic flow profile and negligible diffusion.

Actually, molecular diffusion, either longitudinal or axial, should be considered. Bosworth (1) has studied this problem and has shown that in laminar flow diffusion may be neglected if:

\[ d > 36 \sqrt{D/l} \quad \text{and} \quad l > 10d \]

where:
\( d \) = reactor I.D.
\( l \) = reactor length
\( D \) = diffusivity of reactants.

These two conditions are satisfied in this investigation.

It was thought that the insertion of baffles in the tubular reactor might have one or both of two possible effects:
1. increase eddy turbulence and thus, backmixing in the reactor
2. break up the laminar flow profile and thus increase the plug flow character of the flow.

It developed in this work that the latter effect was more important. The determination of the actual magnitude of the effect of placing baffles in the system was a primary objective of this investigation.

The reaction. The saponification reaction of ethyl acetate with sodium hydroxide in aqueous solution was chosen for this investigation for two reasons:

a. reaction rate constants for the reaction were well established, and
b. a simple, continuous analytical method (13) was available for the system. This reaction has been shown by many (11-14) to be bimolecular and second-order according to the following stoichiometric and rate equations:

\[
\text{NaOH} + \text{EtOAc} \rightarrow \text{NaOAc} + \text{EtOH} \quad (8)
\]

\[
(a - x) = \frac{x}{ak^2t} \quad (3)
\]

The stoichiometric equation, Equation 8, indicates an irreversible reaction. The investigators mentioned above have shown that in this reaction the equilibrium lies nearly to the point of complete reaction. Thus the reverse rate term is very small, and the assumption of essentially complete reaction, as written, is valid.

The solution of Equation 3 requires
a knowledge of the value of the rate constant $k_r$ for this reaction. Therefore, values of $k_r$ were determined in a small batch reactor at several temperatures, and a plot of these values is shown in Figure 1.

**The apparatus**

A schematic diagram of the entire apparatus is shown in Figure 2. The constituent parts of the assembly are briefly described below.

**Reactor.** The flow reactor was constructed from a 6-ft. length of 14-in. I.D. polyethylene tubing. To prevent sagging, this tubing was supported along its entire length by Pyrex glass tubing, into which the plastic tubing was fitted. The tube assembly was clamped in place at a 5° angle with the horizontal. This slight upward slope, from the inlet to the outlet, allowed any air in the system to flow out of the reactor.

The 3-ft. long baffle assembly was mounted from the center of the 6-ft. length to the outlet end, from which end the baffles were inserted and removed.

Reactants were introduced into the reactor through a plastic "tee", which also served as a mixer for the reactants. Injection of the reactants into the reactor tube in this manner caused considerable turbulence in the vicinity of the reactor inlet. For this reason, 33-in. of calming section was provided between the reactor inlet and the baffles.

A second reactor, similar to the first but only half as long, was also constructed and mounted parallel to the first reactor and directly below it. This smaller reactor was used to determine the extent of the reaction in the first three feet (calming section) of the main reactor.

**Auxiliary equipment.** Reactants were charged to the system and stored in covered 30-qt. plastic tanks, Figure 2. From these tanks, reactants were pumped to the constant-head tanks located above the reactor.

These tanks, also of polyethylene and covered, had a capacity of 10-qt. ea. and were fitted with reactant outlets at the bottom, and overflow lines near the top which led back to the storage tanks. Inserted through the covers on the constant head tanks, and not shown in Figure 2, were the constant temperature control devices and the agitators. Knife heaters were used for heating the solutions in the constant head tanks, and temperature control was maintained by standard thermometer-relay systems. Flow control was provided by flowmeters connected through needle valves to the outlets of the constant head tanks.

**Electrode assembly.** Analysis of the extent of reaction in the system was accomplished by conductance measurement techniques. These conductance measurements required an assembly which would hold two electrodes rigidly in place. It was also necessary that the assembly provide a source of turbulent mixing in the region immediately ahead of the electrodes to insure uniformity of solution composition at the time of electrical measurement.

The electrode was constructed with a rubber stopper, large enough to fit into the 14-in. tubular reactor, as a base. Six holes were drilled in the stopper, and platinum electrodes were inserted through two of these. Another hole in the stopper held a 29 to 31°C range thermometer, and a fourth hole served as an effluent port for the reacting solution. The remaining two holes were used to support brass rods that extended several inches beyond the electrodes into the reactor. A brass ring was soldered to these rods at the ends extending into the reactor. This ring served to support a 3-in. thick layer of glass wool which, in turn, provided turbulence and mixing in the reacting solution just prior to the conductivity measurement.

The electrical resistance of the solution was measured using a simple Wheatstone bridge circuit. Such circuits for measuring solutions are described by several references (6, 8). Electrical power was provided by a 1000 cycle oscillator, and a cathode ray oscilloscope was used as null indicator. Electrodes were platinumized platinum.

**Baffle assembly.** A sketch of the baffle assembly is shown in Figure 3. The assembly was approximately 3-ft. long, and a total of 13 quarter-cut brass baffles, 14-in. diameter and 8-in. thick, were made. The baffles were mounted on two 3-ft. long X 8-in. brass rods. Construction of the baffle unit for each baffle spacing required that the baffles be mounted on the rods a measured distance apart, lined up parallel with one another, and then soldered in place to provide a rigid structure.

**The methods involved**

For the saponification reaction, 0.1000 N (±0.0005) solutions of NaOH and EtOAc were prepared by standard techniques. The solutions were standardized once during each run.

**Extent of reaction.** The reaction between EtOAc and NaOH was chosen for use in this work because it offered a convenient, simple, and continuous method of analysis (13).

At the beginning of the reaction, when percent conversion is zero, the reactant solution consists of NaOH and EtOAc dissolved in water. The measured conductance indicates the extent of ionization. At the start of this process, the only ions present are those provided by the ionization of NaOH. Upon completion of the reaction, assuming equimolar quantities of reactants, ions are present in the solution because of the ionization of NaOAc. At any intermediate time, when a fraction $\chi$ of the OH- ions have been replaced by acetate ions, the conductance is defined:

$$L' = L'_Na^+ + \chi L'_{OAc} + (1 - \chi) L'_{OH^-}$$

(9)

where:

$$L'_{Na^+}, L'_{OAc}, L'_{OH^-}$$ are electrical conductances in the solution due to the presence of these ions.

Solving Equation 9 for $\chi$:

$$\chi = \frac{(L'_0 - L')}{(L'_0 - L'_1)}$$

(10)

where $L'_0$ is the conductance of the original solution: $L'_Na^+ + L'_OH^-$

$L'_1$ is the conductance of the final solution: $L'_Na^+ + L'_{OAc}$

Thus, determination of $\chi$ depends upon conductance measurements at the beginning of reaction, at the completion of reaction, and at some desired intermediate time.

The technique has been used by Walker (13) to determine the reaction rate constant for the saponification of both methyl and ethyl acetate.

Results agree with those obtained by other techniques (11, 12, 14). This procedure reduces the errors caused when samples must be removed from the reacting system and chemically or thermally treated to "freeze" the reaction.

Prior to the start of an experimental run, reactant solutions were prepared and placed in the feed storage tanks. The solutions were pumped continuously from the storage tanks to the
constant-head tanks, where the temperature controllers and heaters were in operation, and back again until the temperature of each solution levelled off at the control temperature, 30°C. This process took thirty minutes to one hour. At this time a sample of NaOH solution was analyzed and a sample of EtOAc was removed for later analysis.

At the start of the run, the electrode assembly with its glass wool turbulence section, was inserted into the outlet of the reactor, and the flowrators were adjusted to provide constant and equal volumetric flow of reactants. Equilibrium was considered to be attained when the conductivity of the reactor effluent remained constant for more than two minutes. The time required for the attainment of equilibrium normally varied from about 4 min. at the higher flow rates to 10 min. at the lower rates.

Record data for each run included the “known” resistance box reading, the slide wire position, flowrator readings, and the temperature. After these data had been recorded, the flow rates were adjusted to new values and, at equilibrium, the experimental data were once again recorded.

The end results

Backmixing has been defined (5) as the effect when “particles of feed intermix immediately with all other particles in a reactor, thus losing their identity”. This is what happens in a tank-flow reactor in which the reactants are added continuously, products removed continuously, and the reactor contents are perfectly mixed.

It was mentioned earlier that the study of reactions occurring in continuous tubular reactors at low Reynolds Numbers is important because these flow rates permit the reactants to remain in a given reactor for a longer time than would be possible at the high rates required for plug flow. In addition, the use of low flow rates makes it possible to design shorter reactors than would be possible at higher flow rates (and correspondingly shorter retention times). These conclusions do not, however, take into consideration the differences in conversion per given reactor volume resulting from differences in flow pattern, and these effects may be considerable. It has been established that the greatest degree of reaction in a flow reactor occurs when the reactants are flowing at high velocities in true plug flow. Under conditions of laminar flow, a partial backmixing effect can be noticed at any cross-section in the reactor due to the differences in velocity of reactants at various positions within the cross-section.

The partial backmixing in such reactors at low Reynolds Numbers, due to the partially or fully developed laminar flow profile, may be quite serious. To overcome some of this effect, baffles may be inserted to break up the laminar profile and thus reduce the backmixing. The results of this investigation show the relative effects of the partially developed laminar profile and of the baffles—such as baffles spacing—on the conversion obtained in a laminar reactor.

Figure 4 shows the variation of conversion in a chemical reactor as a function of the reaction time. Three curves for the saponification reaction at 29.8°C are shown: the batch (identical to the longitudinal flow case), backmix, and partial backmix curves.

Curve A, is calculated for the batch reactor on the basis of Equation 3, 4.2 is typical of any second-order homogeneous reaction with a one-to-one molar ratio of reactants.

Curve C, the backmix case, is also a calculated curve; based on Equation 5, another form of which is:

\[ \frac{dC}{dt} = x^2 / (1 - x)^2 \]

This curve represents a reaction process in which reactants and products are being added and removed from the reactor constantly, while holding the overall concentration of material in the reactor constant. Such backmixing decreases the rate of reaction and, therefore, the conversion per unit time by decreasing the concentration of reactants. This shows clearly in comparing curves A and C.

Curve B shows the conversion vs. time relationship in the open (un-baffled) tubular reactor operating at low Reynolds Numbers (440 to 1630, corresponding to flow rates of 560 to 2072 cm. cm./min.). This curve is experimentally determined and illustrates the basic point that the conversion in such a reactor follows neither the batch curve nor the complete backmix curve.

The experimental results for curve B can be compared to the predicted data of Denbigh (3). To do this, it is necessary to assume that flow in the experimental reactor has a fully developed laminar flow profile. The results of this comparison can be seen in Table 1, and it is apparent that the experimental and calculated (Denbigh's laminar flow model) conversions approximate each other.
The point in this investigation, however, was not to prove Denbigh either correct or incorrect in his analysis but, rather, to show whether or not conversion in this type reactor followed a different relationship than do the batch or backmix cases.

Figure 5 illustrates the effect of baffles on a system operating on the partial backmix (laminar flow) curve. These curves show the change in composition, $\Delta x$, across the 37% in. reactor section as a function of the flow rate for the following cases:

1. Batch (longitudinal flow) reactor—calculated
2. 6-in. baffle spacing
3. 9-in. baffle spacing
4. 12-in. baffle spacing
5. Open tube—no baffles

In each case the reactant stream entering the reactor section of the experimental tube possessed a well developed laminar flow profile. Upon striking the baffles, this profile was destroyed, with beneficial results. It is interesting to note the large difference between the curve for no baffles and that for the widest baffle spacing used. This difference points out that even an occasional baffle provides much more efficient reaction conditions than no baffle at all. It is also interesting to note that as the flow rate increases, the curves for the baffled reactors come closer together and approach the batch curve. This indicates that, as expected, the conditions in the baffled reactor approach those expected in a longitudinal flow reactor as the flow rate increases.

The beneficial effect of the baffles may really be a combination of two effects: break up of the laminar profile and subsequent formation of a turbulent profile typical of Reynolds Numbers greater than 10,000; or, effective division of the tubular section into a series of stirred tanks.

The formation of a turbulent profile of flow will allow the use of the longitudinal equations for reactor design. This can be accomplished either by using high flow rates or by using enough baffles in the reactor to assure approximately plug-type flow conditions, as illustrated in Figure 5.

Young (15) has shown that for a series of more than five continuously stirred reactors, the over-all effect is for the series to approach operation as a longitudinal reactor. In this investigation, the baffles divided the complete reactor into 3-, 4-, and 6-sections for the 12-, 9-, and 6-in. spacings respectively. These units were not, however, perfectly stirred and Young's methods of handling the system did not apply exactly. Nevertheless, the pattern described by Young was followed since, as the number of sections increased, the over-all conversion approached the longitudinal reactor limit.

This work has shown that the conversion in a continuous reactor is not a simple process capable of being expressed by the equations for the batch or backmix cases. The use of baffles may be one technique that can be employed for increasing the conversion in a continuous tubular reactor at low flow rates.

Conclusion

The objectives of this work were to determine whether either theoretical batch or backmix equations applied to reactions occurring in an open tubular reactor at low flow rates; and to determine the effect upon the reaction of placing baffles, at various baffle spacings, in the reactor. The conclusions reached apply specifically to second-order homogeneous reactions with a molar ratio of reactants equal to one and with initial reactant concentrations of 0.0500N. However, it seems reasonable to suspect that these same tendencies, at least, would be observed in reacting systems not completely fulfilling these conditions.

The conclusions are as follows:

1. Reaction kinetics in an open tubular reactor operating at low Reynolds Numbers (laminar flow) may not be predicted accurately from either the theoretical batch or backmix equations. In the absence of contrary data, the application of Denbigh's model might be the best available approximation.

2. Insertion of baffles into the open tubular reactor, operating at low Reynolds Numbers, decreases the efficiency of the reactor, as shown by the increased conversion in the reactor.

3. Baffle spacings as wide as 12 in. ($l/d = 9.6$) provide a marked increase in reactor conversion.

4. Baffle spacings of less than 12 in. are progressively better, as the spacing decreases, in increasing conversion in the reactor. However, the decreased baffle separation and the additional number of baffles required does not offer as much improvement over the 12-in. spacing as the latter does over the open reactor. This is especially true as the flow rate increases.

5. The trend in conversion as a function of baffle spacing indicates that as the spacing is decreased, the conversion approaches as a limit that which would be obtained in a longitudinal reactor.

LITERATURE CITED