Mass Transfer and Contactor Efficiency in a Stirred Liquid-Liquid Reactor

A. J. ENGEL and O. A. HOUGEN
University of Wisconsin, Madison, Wisconsin

This investigation was initiated to establish the chemical and physical reaction models in a two-phase liquid system catalyzed by a finely divided solid in suspension. This situation represents a missing gap in systematizing the principles of reaction rates in heterogeneous systems. The particular system chosen for study was the hydrolysis of liquid isoamyl acetate highly dispersed in a large volume of excess water where the reaction was catalyzed by an acidic ion exchange resin kept in suspension by rapid stirring in a batch reactor.

A hydrolytic reaction was selected because of its simplicity and isoamyl acetate because of its insolubility in water and the ease of titrating the acid formed by hydrolysis. Furthermore rate data on the uncatalyzed hydrolysis of isoamyl acetate were already available in the literature for comparison with the catalyzed rate. A sulfonated polystyrene cation exchanger, Amberlite IR 120, was chosen as the catalyst because of its high exchange capacity, its high degree of dissociation, and its constant catalytic activity. The combined system permitted a reaction which could be conducted at atmospheric pressures and at a low temperature ranging from 80° to 120°F.

The problem resolved itself into a study of mass transfer in a liquid-liquid-solid system from which a general procedure may be evolved for establishing contactor efficiencies in stirred reactors containing suspended solids. It was demonstrated that an ion-exchange resin provided an excellent tool for investigating mass transfer rates in stirred reactors because of its high chemical and physical stability and the accuracy in measurement of the external surface of the solid particles. In the field of hydrolysis ion exchange catalysts have certain economic advantages over other catalysts.

PREVIOUS WORK

Mixing of liquids in stirred vessels is one of the oldest unit operations. Many investigations have been attempted to establish good general correlations for scale-up purposes. These efforts have generally not been successful because of their specificity to a particular system or to a particular stirrer. The lack of a good general correlation applies particularly to solids suspended in liquids by agitation. Systems ranging from the dissolution of suspended particles (*10, 16, 18*) to complex reactions between solids and solvents (*3, 11*) have been studied, but no generalized correlations have resulted.

In other studies (*9, 12, 17*) the power input to stirred systems has been correlated with reasonable success, but again the correlations were not useful in establishing a reliable scale-up method for different stirred systems, particularly those with suspended solids.

Harriott (*6*) points out that one of the most serious errors in previous correlations involving stirred reactions is the use of the stirrer diameter as the characteristic length term in the dynamic terms expressed by Sherwood and Reynolds numbers. Harriott has shown conclusively that the solid-particle diameter greatly affects the mass transfer characteristics of such systems. Mass transfer to and from suspended solids depends principally on slip velocity, that is the relative velocities of the particles with respect to the liquid, with the terminal velocity yielding the minimum value of the mass transfer coefficient. In most studies this effect has been ignored, since experiments were conducted with particles too large to demonstrate the effect of particle size.

THEORY

The following theoretical discussion pertains to the specific reaction system used in this study, namely the hydrolysis of insoluble liquid isoamyl acetate dispersed in a large volume of excess water in a stirred batch reactor and catalyzed by suspended solid particles of an acidic ion exchange resin. All transfer rates are based on unit external surface area of the suspended catalyst.

The overall reaction rate is controlled by the following series resistances:

1. Transfer of ester from the ester droplets into the aqueous phase.
2. Transfer of ester through the aqueous phase.
3. Transfer of ester through the liquid surrounding the catalyst particles.
4. Ester diffusion into the resin particle and simultaneous reaction.

The reverse steps for the reaction products might also be considered, but these were found to offer negligible resistance. Also, under the particular experimental conditions of this study, the first two resistances were negligible, since the aqueous phase remained saturated with ester.

The mass transfer rate of ester through the liquid surrounding the catalyst particles may be expressed as

$$r = k_s\,(c_l - c_s) \tag{1}$$

where the mass transfer coefficient k_s depends on stirring speed, temperature, and catalyst particle size.

The problem of diffusion and simultaneous reaction in resin particles has been treated by Smith and Amundson (*14*). In order to apply a similar approach to the current study, it was assumed that the particles were spherical, their porosity was constant, they underwent no significant

---

A. J. Engel is at The Pennsylvania State University, University Park, Pennsylvania.

volume change during the reaction, the resin diffusivity remained constant at a fixed temperature, and the catalyzed reaction was first order with respect to the ester concentration and irreversible. When these assumptions are applied to a material balance over a spherical shell in a resin particle, the following rate expression results:

$$r = \frac{2\mathfrak{D}_r\, c_r^*}{D_c}\,[F^{1/2}\operatorname{ctnh} F^{1/2} - 1] \qquad (2)$$

where F is defined by

$$F = \frac{k_c D_c^2}{4\mathfrak{D}_r} \qquad (3)$$

and c_r^* is the ester concentration at the inner surface of the catalyst particle in equilibrium with c_s at the outer surface.

Diffusion through the catalyst skin is usually considered to be a rapid process, and thus the Donnan membrane equilibrium may be applied:

$$c_r^* = K_s c_s \qquad (4)$$

Since under steady state conditions the individual rates are equal, Equations (1), (2), and (4) can be combined to give

$$r = \frac{c_l}{\dfrac{1}{k_s} + \dfrac{D_c}{2\,K_s\mathfrak{D}_r\,[F^{1/2}\operatorname{ctnh} F^{1/2} - 1]}} \qquad (5)$$

If one now defines an overall rate coefficient by

$$k_o = \frac{r}{c_l} \qquad (6)$$

the following relationship results:

$$\frac{1}{k_o} = \frac{1}{k_s} + \frac{D_c}{2\,K_s\,\mathfrak{D}_r\,[F^{1/2}\operatorname{ctnh} F^{1/2} - 1]} \qquad (7)$$

Since resistances are reciprocal coefficients, (7) can be rewritten as

$$R_o' = R_s' + R_r' \qquad (8)$$

Resistance of Liquid Surrounding the Solid

The resistance to mass transfer of the liquid surrounding the catalyst particles depends primarily on the slip velocity of the particles and the physical properties—density, viscosity, and diffusivity—of the solution. In turn the slip velocity is strongly influenced by the degree of agitation and the particle diameter. These combined effects can be expressed in terms of the Reynolds and Schmidt numbers:

$$R_s' = A'\left(\frac{D_c^2 N\rho}{\mu}\right)^{\alpha}\left(\frac{\mu}{\rho\mathfrak{D}_l}\right)^{\beta} \qquad (9)$$

where constant A' is a function of particle size. Since the resistance is based on unit surface areas of the catalyst, the amount of catalyst present, as long as it is relatively small and in complete suspension, should have no effect. This was borne out experimentally.

Resistance of Solid

The resistance of the solid is caused by the combined effects of ester diffusion into the resin and simultaneous chemical reaction, as expressed by the second right-hand term of Equation (7). However since it proved to be experimentally unfeasible to evaluate the coefficients K_s, $\mathfrak{D}_r$, and k_c, the more rigorous mathematical model of Equation (7) had to be discarded in favor of a simpler empirical expression which fitted the data over the range of variables studied.

For a given catalyst, diffusion in the solid depends on the particle diameter and specific diffusivity, the latter varying primarily with temperature. The chemical reaction rate for constant composition depends only on temperature. Combining these effects one obtains

$$R_r' = B'\left(\frac{D_i}{D_c}\right)^{\gamma} f(T) \qquad (10)$$

The impeller diameter D_i was not varied in this study but was introduced merely for the purpose of making the catalyst particle diameter dimensionless.

Since the total resistance to the overall reaction is the sum of the individual resistances, Equations (9) and (10) can be combined to give

$$R_o' = A'\left(\frac{D_c^2 N\rho}{\mu}\right)^{\alpha}\left(\frac{\mu}{\rho\mathfrak{D}_l}\right)^{\beta} + B'\left(\frac{D_i}{D_c}\right)^{\gamma} f(T) \qquad (11)$$

But the overall resistance R_o' is inversely proportional to the overall mass transfer coefficient k_o. In order to obtain a completely dimensionless equation, k_o is introduced in the Sherwood number $k_oD_c/\mathfrak{D}_l$ with the appropriate changes to the constants A' and B', so that the final form of Equation (12) becomes

$$\frac{\mathfrak{D}_l}{k_o D_c} = A\left(\frac{D_c^2 N\rho}{\mu}\right)^{\alpha}\left(\frac{\mu}{\rho\mathfrak{D}_l}\right)^{\beta} + B\left(\frac{D_i}{D_c}\right)^{\gamma} f(T) \qquad (12)$$

or

$$\frac{1}{N_{Sh}} = A\, N_{Re}^{\alpha}\, N_{Sc}^{\beta} + B\left(\frac{D_i}{D_c}\right)^{\gamma} f(T) \qquad (12a)$$

or

$$R_o = R_s + R_r \qquad (12b)$$

EXPERIMENTAL PROCEDURE

Three forms of acidic cation exchange-resin catalyst were used: Amberlite IR 120, the commercial grade resin, CG 120, the chromatographic grade resin, and XE 69, an experimental finely ground material.

The particle size and surface area of each type of resin was determined by taking photomicrographs of the resins immersed in water. About 250 particle-diameter measurements were made on each sample by the Martin's Diameter method, according to which the diameter is determined by measuring "the distance between opposite sides of a particle crosswise of the field and on a line bisecting the projected areas of the particle" (*1*). From these measurements the average particle diameter with respect to surface area was calculated by the equation

$$D_c = \frac{\Sigma n d^3}{\Sigma n d^2} \qquad (13)$$

The photomicrographs showed the IR 120 resin to be essentially spherical particles, while the two finer types of catalysts were irregularly shaped particles. The measured particle sizes were as follows:

	Maximum diameter, mm.	Minimum diameter, mm.	D_c, mm.	Surface area, sq. cm./g.
IR 120	0.80	0.05	0.4146	159
CG 120	0.25	0.02	0.1153	431
XE 69	0.08	0.01	0.02561	1810

The surface area was calculated by assuming each catalyst sample to consist of perfect spheres of diameter D_c (*1*).

The measured exchange capacity of all three catalysts was 4.3 milliequivalents of H^+ per gram of dry resin.

A schematic diagram of the experimental apparatus is shown in Figure 1.

The reaction vessel consisted of a 6-in. diameter Pyrex cylinder, 12 in. long and fitted with a flat stainless-steel flange

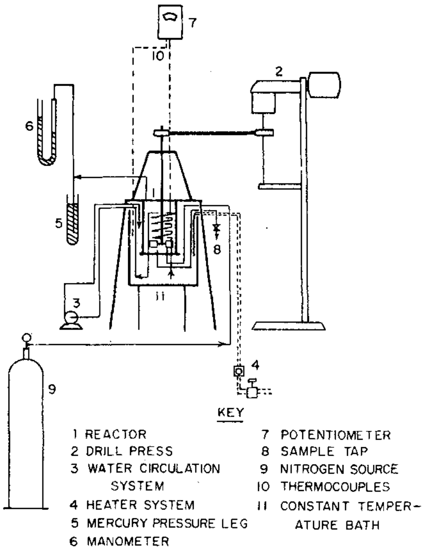

Fig. 1. Schematic diagram of the reactor system.

at the lower end and the flange from a closed-tank mixer at the top. Teflon gaskets were used.

The bottom flange was fitted to the entrance and exit leads of a 4-in. diameter internal cooling (heating) coil made of ¼-in. stainless-steel tubing, a drain plug, a ¼-in. nitrogen inlet tube, and a movable ¼-in. sampling tube. Stainless-steel compression fittings were used to give a tight seal. The top flange was fitted with a ¼-in. stainless-steel pipe nipple which served as both the outlet for the nitrogen and the loading port for the reactor. Also entering through a compression fitting in the top flange was a ¼-in. stainless-steel-tubing thermowell.

The entire reactor assembly was mounted on a tripod steel stand from which it was suspended by means of a triangular angle-iron frame.

The agitator was driven by a drill press by means of pulleys and a flexible V-belt. A ½-hp. single-phase motor normally ran at 1,725 rev./min. By using different pulley combinations, extremely constant stirring speeds ranging from 50 to 3,000 rev./min. could be achieved. Stirring speeds were measured periodically by means of a revolution counter.

The agitator was a six-bladed, 3-in. diameter, 316-stainless-steel turbine impeller mounted on a ⅞-in. shaft of the same material and suspended 3 in. above the bottom of the reactor. Four equally spaced ½-in. stainless-steel baffles were placed in the reactor to improve agitation. The stuffing box in the top flange was filled with Teflon rings.

The reactor was immersed in a square Plexiglas tank filled with water. Three 200-w. bayonet heaters wired in parallel were suspended in the tank, and the water was both agitated and circulated through the coil inside the reactor by a centrifugal pump. Water and reactor temperature was maintained constant by immersing a mercury-contact temperature controller in the tank.

The reactor was operated under a nitrogen atmosphere to minimize the explosion hazard of isoamyl acetate and to prevent oxidation of the reactants and products. A slight positive pressure facilitated liquid sampling.

The nitrogen entered the reactor through a ¼-in. tube extending through the bottom flange and into the space above the liquid. It left the reactor through the top flange, with the exit tube immersed in a glass tube filled with mercury. The hydrostatic head of the mercury served to maintain a constant gauge pressure of about 200 mm. Hg in the reactor. A very slow flow of nitrogen was passed through the mercury reservoir. The pressure was independently measured with a mercury manometer. The mercury reservoir not only aided in maintaining constant pressure in the reactor, but also served as a safety valve, since any sudden pressure surges would have been relieved through the bubble tube.

Table 1. Sample of Experimental Data

Reactor charge: 2500 cc. water, 100 cc. isoamyl acetate, 100 g. XE 69 catalyst
Temperature = 100°F.
ρ_s = 0.9931 g./cc.
μ_s = 0.6843 centipoises
$\mathcal{D}_l$ = 0.9817×10^{-5} sq. cm./sec.

Run no.	108	114	109
Agitator/Speed, rev./min.	195	345	580
Length of run, min.	105	60	45
Concentration of NaOH titer, N	1.79×10^{-3}	2.14×10^{-3}	1.79×10^{-3}
Amount of NaOH titer/1 cc. aliquot of reaction mixture, cc.	11.61	4.50	10.31
r, moles/(sq. cm.)(hr.)	1.64×10^{-7}	1.71×10^{-7}	2.52×10^{-7}
c_l, moles/cc.	1.06×10^{-5}	1.06×10^{-5}	1.06×10^{-5}
k_o, cm./hr.	1.58×10^{-2}	1.62×10^{-2}	2.38×10^{-2}
R_o	618	602	410
R_r (by extrapolation of Figure 2)	173	173	173
$R_s = R_o - R_r$	445	429	237

The analytical procedure consisted entirely of titrating with about 0.002 normal sodium hydroxide the acetic acid formed during the reaction and the catalyst to check its activity. To give highly accurate analytical determinations an automatic potentiometric titrimeter was used. This analytical procedure was accurate to 0.2 cc., giving an average error of less than 10%.

In an experimental run the reactor was half filled with 2.5 liters of water and 100 mliters of isoamyl acetate and all the reaction parameters adjusted to the desired values. The catalyst was added through the top port and the agitator started. Twenty-five milliliter samples were removed at 15-min. intervals and centrifuged at once to separate the catalyst. The aqueous phase was then filtered and titrated. On the average an experimental run lasted 1 hr.

After each run the catalyst was titrated to check the constancy of its activity.

The variables were investigated over the following ranges:

Amount of catalyst	12.5 — 100 g.
Agitator speed	100 — 3,000 rev./min.
Temperature	80 — 160°F.

Table 1 shows some typical results obtained.

EXPERIMENTAL RESULTS

Many preliminary runs were made to define the effects of operating variables and to establish an appropriate experimental technique.* The following observations were made:

1. Varying the amount of catalyst or ester had no effect on the reaction rate based on unit catalyst surface area.
2. No appreciable reaction took place in the absence of catalyst.
3. When the catalyst was removed from the reaction mixture, the reaction ceased; that is there was no noticeable hydrolysis in the aqueous phase.
4. The degree of hydrolysis did not affect the reaction rate, indicating that no autocatalysis took place and that the reverse reaction was negligible.
5. The catalyst activity remained constant during each run.
6. The large IR 120 catalyst suffered some attrition during the runs, but the two finer catalysts did not.
7. An agitation speed of 175 rev./min. or more gave complete suspension of the catalyst.

---

* For tabular data see reference 1.

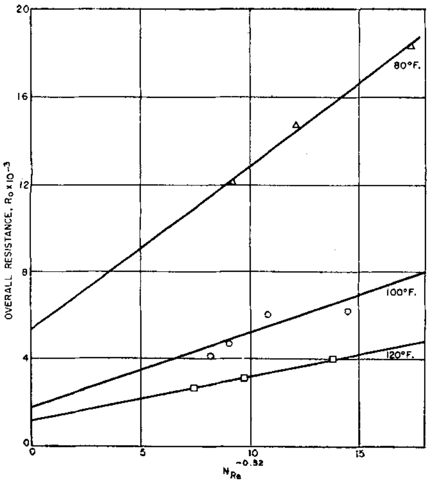

Fig. 2. Effect of Reynolds number on overall resistance for XE 69 catalyst.

8. The overall resistance to hydrolysis was strongly influenced by catalyst particle size, all other conditions being equal, but only for the catalyst particles below 100 μ in diameter was the resistance affected by the degree of agitation.

9. It was observed that at agitator speeds exceeding 600 rev./min. the overall resistance increased. After a careful study of high-speed photographs it appeared that this increase was caused by cavitation and splashing of the liquid in the half-filled reactor. The photographs clearly showed that serious cavitation commenced at stirring speeds of 600 rev./min., so that at speeds of 2,000 rev./min the reactor became completely filled with splashing and frothing liquid. This means that much of the input energy was dissipated and not used in generating high slip velocities of the catalyst particles. For this reason all runs made at speeds exceeding 600 rev./min. were discarded for correlating purposes.

Correlation of the Data

A total of fifty-two runs was made with the three catalyst samples. All runs employing the IR 120 resin (having the largest particle size) were carried out at 100°F. Those with the intermediate size CG 120 resin were made at 100°, 120°, 140°, and 160°F., and those with the fine XE 69 resin at 80°, 100°, and 120°F.

Since neither of the two catalysts having the larger particle size showed any significant variation of reaction rate with degree of agitation, the ester concentration in the aqueous phase was assumed to be constant. Also mass transfer through the liquid surrounding the particles was assumed to have negligible resistance, and all the resistance was ascribed to the solid side. This was not the case however for the fine catalyst, XE 69, for which both resistances were significant.

To obtain values for the solid-side resistance of the XE 69 catalyst use was made of a previous correlation (2) which indicated that R_s was proportional to $N_{Re}^{-0.5}$. A plot of R_s vs. $N_{Re}^{-0.5}$ was extrapolated by a least-squares fit to infinite Reynolds number (where the liquid-side resistance vanishes) and the resistance at this point assumed to be the solid-side resistance.

An attempt was then made to correlate the values of R_s with the Schmidt number, as suggested by Equation (12). However since a temperature range of only 40°F. was covered in the experimental work, this proved to be a fruitless approach. Instead the temperature variation of R_s was correlated by the equation

$$R_s = A\,N_{Re}^{-0.5}\,e^{E/RT} \tag{14}$$

Next the solid-side resistances for all three catalysts were correlated with particle size and temperature, so that the resulting correlation was of the form

$$R_r = B\left(\frac{D_i}{D_c}\right)^{\gamma} e^{E'/RT} \tag{15}$$

Finally the overall resistance R_o was calculated by Equation (12*b*). Now, the original assumption of the exponent on the Reynolds number was checked by recognizing that

$$R_s = A\,N_{Re}^{\alpha}\,e^{E/RT} = R_o - R_r \tag{16}$$

If the originally assumed value of α, -0.5, had been correct, a plot of log $(R_o - R_r)/(e^{E/RT})$ vs. log N_{Re} should have given a straight line with slope of -0.5. A least-squares analysis yielded a slightly different slope. Therefore the new slope was substituted for α and the whole correlation repeated. On the third trial the assumed and calculated values checked, and the final correlation was

$$R_o = \frac{1}{N_{Sh}} = A\,N_{Re}^{-0.52}\,e^{11{,}300/RT} + 2.7 \times 10^{-13}\left(\frac{D_i}{D_c}\right)^{1.45} e^{16{,}400/RT} \tag{17}$$

where A was negligible for the two larger-size catalysts and equal to 4.6×10^{-7} for the XE 69 catalyst. Figures 2, 3, and 4 show the graphical correlations for the last trial.

Figure 5 indicates the precision of the correlation, the average being 15.2% deviation from observed values and the algebraic average being -4.6%. It should be recognized that these values are almost within the experimental accuracy of the titration procedure.

The Contactor Efficiency

Since one of the major purposes of this study was to use the three-phase hydrolysis reaction as a measure of agitation effectiveness, the contactor efficiency concept as proposed by Hougen and Watson (8) proved to be convenient to use.

Rearranging Equation (5) and defining a solid-side coefficient by $1/k_r = D_c/2K_s\mathfrak{D}_r[F^{1/2}\,\mathrm{ctnh}\,F^{1/2} - 1]$, one obtains

$$r = \frac{k_s k_r}{k_r + k_s}\,c_l \tag{18}$$

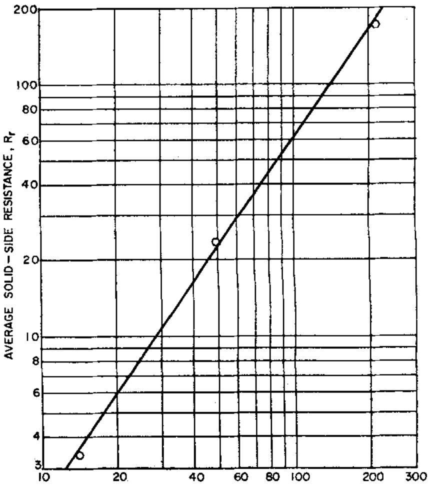

Fig. 3. Effect of catalyst particle diameter on solid-side resistance.

Since the only term on the right side of this equation that depends on agitation is k_s, one can now define the contactor efficiency E_c by

$$E_c = \frac{k_s}{k_r + k_s} \tag{19}$$

so that Equation (18) then becomes

$$r = E_c k_r c_l \tag{20}$$

It can be seen from these equations that as k_s becomes very large because of effective stirring, the contactor efficiency approaches unity. Conversely as the solid-side coefficient k_r becomes large (which is true at high temperatures at which both k_c and $\mathcal{D}_r$ increase), E_c will tend to decrease. In general it may be stated that as E_c approaches unity, internal diffusion and reaction becomes the rate controlling step.

The external resistance to mass transfer around the catalyst particles for the two larger types of catalysts (IR 120 and CG 120) was negligibly small, which is another way of saying that the external mass transfer coefficient k_s is very large. From the definition of the contactor efficiency it follows then that it will take on a value of approximately unity for these two catalysts. This does not mean however that the stirring efficiency in these cases is perfect, but rather that stirring has no effect on the overall rate, as has already been established. Therefore the evaluation of contactor efficiency for the large catalysts is meaningless, and this discussion must be confined to the fine catalyst XE 69.

Table 2 shows the values of contactor efficiency obtained for the XE 69 resin. The table indicates that there appears to be little variation of E_c with temperature; rather that it depends chiefly on the speed of stirring, as might be expected.

Although the contactor efficiency increases decidedly with stirring speed, nearly doubling in value as agitation is increased from 175 to 580 rev./min., all the values are relatively low; that is agitation is far from ideal. This may be explained by the fact that the effectiveness of stirring is a function of the slip velocity between liquid and solid. Stokes' law for particles in laminar-flow liquid indicates that the terminal velocity of the particles is proportional to the square of particle diameter. Hence for these very small particles the terminal velocity is low and can only be raised by greatly increasing the force acting on them. In the case of stirred reactors this goal can only be achieved by making the stirring speed very high. However, as indicated earlier, with the system used in the present investigation this was impossible because of excessive splashing. But it would be possible to increase the slip velocity of the particles (and thereby improve the contactor efficiency) by operating the reactor at a totally full condition. For a half-full reactor a contactor efficiency of 0.43 appears to be the maximum obtainable for the fine catalyst.

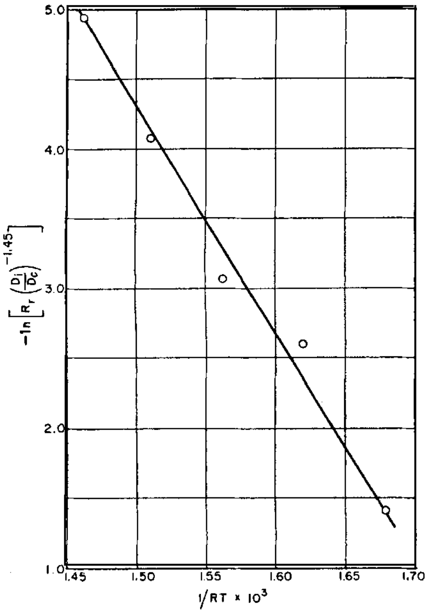

Fig. 4. Effect of temperature on solid-side resistance.

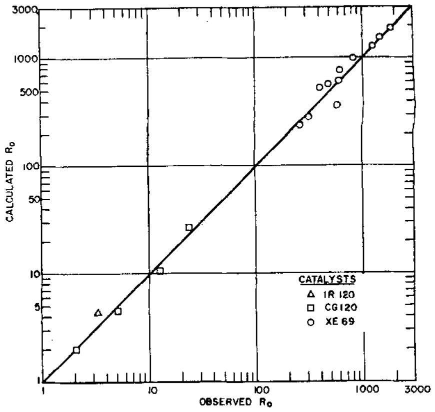

Fig. 5. Precision of correlation.

This discussion brings out the important corollary that E_c depends not alone on the physical characteristics of the agitation system (agitator, baffles, vessel shape, etc.) but also to a very great extent on the liquid-liquid system.

DISCUSSION OF RESULTS

The results of this study agree with those of Harriott (*6*) who points out that in the range of solid particle sizes from 100 to 1,000 μ the liquid-side transfer coefficient is nearly constant, which concurs with the observed behavior of the IR 120 and CG 120 catalysts. This author further states that for very small particles the mass transfer coefficient increases with decreasing particle size, which appears to be true in this study. Finally the exponent of -0.52 on the Reynolds number agrees with Harriott's value of -0.5, as well as those obtained by several other authors (*5, 7, 11*).

The effect of particle diameter on the internal solid-side resistance is in line with the theory as well as with observations made by other authors. If the expression for R_r' as given in Equation (7) is expanded in a Taylor's series, and if it is recalled that R_r' is equal to $R_r D_c/\mathcal{D}_l$, it can be shown that for large values of D_c, R_r is proportional to D_c^{-1} and for small values of D_c, R_r is proportional to D_c^{-2}. The experimental exponent of D_c, -1.45, falls between those values. In view of the fact that the theoretical expression of Equation (7) was based on spherical particles with constant porosity, while both the CG 120 and XE 69 catalysts consisted of crushed, irregularly shaped particles in which doubtless some of the pores had been destroyed, the agreement is good.

TABLE 2. CONTACTOR EFFICIENCY

Stirring speed, rev./min.		Temperature,	
	80°F.	100°F.	120°F
175	0.293	0.275	0.195
345	0.365	0.363	0.367
580	0.442	0.416	0.431

While the internal resistance per unit surface area increases with decreasing particle size, it can readily be shown that the resistance per unit mass of catalyst varies as the particle size to the 0.55 power. This implies that the availability of the catalyst diminishes with increasing diameter, a result also noted by Saletan and White (*13*), Thomas and Davies (*15*), Smith and Amundsen (*14*), and others (*19*).

The effect of temperature on both liquid-side and solid-side resistances is as expected, but values of activation energy apply only to the particular system and reaction conditions of this study.

Finally the ease and simplicity of the reaction system used might make it suitable for experimental determinations of contactor efficiencies in liquid-solid stirred reactors in which various agitators, baffle arrangements, and stirring speeds are to be tested. The reaction mixture of water, isoamyl acetate, and XE 69 resin (or a similar material) can be charged to the reactor, reacted at relatively isothermal conditions, and the product titrated. It is not even necessary to compute numerical values of contactor efficiency; the reaction rate itself may be taken as a direct relative measure of the efficiency. A further simplification might be the use of an immersed conductometric cell in the reaction mixture to yield a direct-reading measure of reaction rate.

SUMMARY OF RESULTS

1. A correlation of a liquid-liquid-solid hydrolysis reaction in a stirred tank has been developed.
2. The overall resistance to the reaction may be represented as the sum of the resistance of the liquid surrounding the catalyst particles and that of the catalyst itself.
3. The liquid-side mass transfer coefficient varies as the modified Reynolds number to the 0.52 power for very fine (less than 100-μ) particles.
4. The solid-side mass transfer coefficient per unit mass of catalyst varies inversely as the particle diameter to the 0.55 power.
5. The contactor efficiency was calculated to have a maximum value of 0.43. This could be considerably improved by operating the reactor full of liquid at a high rate of stirring.
6. The reaction system seems suitable for determining the relative efficiency of a stirred reactor and the effects of varying the structural features of such reactors.

ACKNOWLEDGMENT

E. I. duPont deNemours and Company and The University of Wisconsin Engineering Experiment Station gave financial support through fellowships and grants. The catalyst samples were graciously supplied by the Rohm and Haas Company, and thanks are due to N. W. Frisch of that company for his suggestions in the preparation of this manuscript. Much technical assistance was given by Professor W. K. Neill. All this aid is gratefully acknowledged.

NOTATION

A,A' = constants
B,B' = constants
c = concentration, moles/cc.
d = individual catalyst particle diameter, cm.
D_c = average catalyst particle diameter, cm.
D_i = impeller diameter, cm.
$\mathfrak{D}$ = diffusivity, sq. cm./hr.
E,E' = constants, cal./mole
E_c = contactor efficiency
F = catalyst kinetic modulus [defined in Equation (3)]
k_c = catalytic rate coefficient, 1/hr.
k_o = overall transfer coefficient, cm./hr.
k_r = resin-phase transfer coefficient, cm./hr.
k_s = liquid-phase transfer coefficient, cm./hr.
K_s = Donnan membrane equilibrium constant
n = number of catalyst particles
N = agitator speed, rev./hr.
r = transfer rate, moles/(sq. cm.)(hr.)
R,R' = transfer resistances
R = gas constant
T = absolute temperature, °K.

Greek Letters

α = exponent of Reynolds number
β = exponent of Schmidt number
γ = exponent of diameter ratio
ρ = density, g./cc.
μ = viscosity, g./(cm.)(hr.)

Subscripts

c = chemical reaction
l = liquid solution phase
o = overall
r = resin phase
s = liquid side

Dimensionless Numbers

$$N_{Re} = \frac{D_c^2 N \rho}{\mu} = \text{Reynolds number}$$

$$N_{Sc} = \frac{\mu}{\rho \mathfrak{D}_l} = \text{Schmidt number}$$

$$N_{Sh} = \frac{k_o D_c}{\mathfrak{D}_l} = \text{Sherwood number}$$

LITERATURE CITED

1. Chamot, E. M., and C. W. Mason, "Handbook of Chemical Microscopy," 3 ed., Wiley, New York (1958).
2. Engel, A. J., Ph.D. thesis, Univ. Wisc., Madison, Wisconsin (1961).
3. Friend, J. A., and J. H. Bennett, *J. Chem. Soc.*, **121**, 41 (1922).
4. Frisch, N. W., "Fundamental Engineering Aspects of Ion Exchange," Rohm and Haas Company (March 7, 1958).
5. Froessling, N., *Beitraege zur Geophysik von Gerland*, **52**, 170 (1938).
6. Harriott, Peter, *A.I.Ch.E. Journal*, **8**, 93 (1962).
7. Hixson, A. W., and S. J. Baum, *Ind. Eng. Chem.*, **33**, 478, 1433 (1941).
8. Hougen, O. A., and K. M. Watson, "Chemical Process Principles," Part III, Wiley, New York (1948).
9. Mack, D. E., and R. A. Marriner, *Chem. Eng. Progr.*, **45**, 345 (1949).
10. Noyes, A. A., and W. R. Whitney, *J. Am. Chem. Soc.*, **19**, 930 (1897).
11. Polejes, J. D., Ph.D. thesis, Univ. Wisc., Madison, Wisconsin (1959).
12. Rushton, J. H., *Chem. Eng. Progr.*, **47**, 485 (1951).
13. Saletan, D. I., and R. R. White, *Chem Eng. Progr. Symposium Ser. No. 4*, **48**, 59 (1952).
14. Smith, N. L., and N. R. Amundson, *Ind. Eng. Chem.*, **43**, 2156 (1951).
15. Thomas, G. C., and C. W. Davies, *Nature*, **159**, 372 (1947).
16. van Name, R. G., and G. Edgar, *Z. physik. Chem.*, **73**, 97 (1910).
17. White, A. M., et al., *Trans. Am. Inst. Chem. Engrs.*, **30**, 570 (1934).
18. Wood, J. C., E. R. Whittemore, and W. L. Badger, *ibid.*, **14**, 435 (1922).
19. Anonymous, *Chem. Ztg.*, **79**, 733, 768, 804 (1955).

Manuscript received November 26, 1962; revision received May 22, 1963; paper accepted June 7, 1963. Paper presented at A.I.Ch.E. Chicago meeting.