# Relative Importance of Mass Transfer and Chemical Reaction in Fixed-bed Converters

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One of the important considerations in the study or operation of a fixed-bed catalytic converter is the relative contribution of mass transfer and chemical reaction at the particle surface to the determination of the over-all reaction rate. It is obvious that, if mass transfer controls, the investigation is not a reaction study but is, in essence, a diffusion study. In industry, under such conditions, an increase in productivity can be obtained through an increase in flow rate. Conversely, if the process is controlled by the reaction occurring at or on the particle surface, then flow rate through the bed is not a significant parameter except insofar as it determines the contact time. Thus it is important in any research study utilizing a fixed-bed catalytic reactor to determine whether the rate of mass transfer between fluid phase and particle surface is approximately the same as the rate of reaction at or on the particle surface.

The word *control* as used in the previous paragraph designates a situation wherein one step is exceedingly slow in comparison with another and, hence, the over-all observed result depends upon the rate of that controlling step.

At the present time there are generally two methods used by those engaged in fixed-bed catalytic-reaction studies to determine the importance of mass transfer to the process under investigation. The first technique is to calculate the partial pressure drop through the "film" by use of the method of Wilke and Hougen (*1*) and/or that of Yang and Hougen (*2*) and to compare this with the partial pressure of the significant or limiting reactant in the gas phase. Others have varied the flow rate to observe its effect on conversion.

It is apparent that at constant contact time the rate–Reynolds-number relationship would appear as shown schematically in the figure. However, if one operates at a fixed-bed length and varies the Reynolds number and if, simultaneously, one finds oneself in the range designated by *A* in Figure 1, wherein the rate is varying almost linearly with Reynolds number, it is obvious that the effect of Reynolds number on mass transfer is confounded with the effect of contact time on reaction rate. Doubling the Reynolds number would increase the rate of mass transfer but would decrease the contact time—possibly in about the same proportion. Thus only quite sensitive analytical techniques would be expected to pick up the effect of a change

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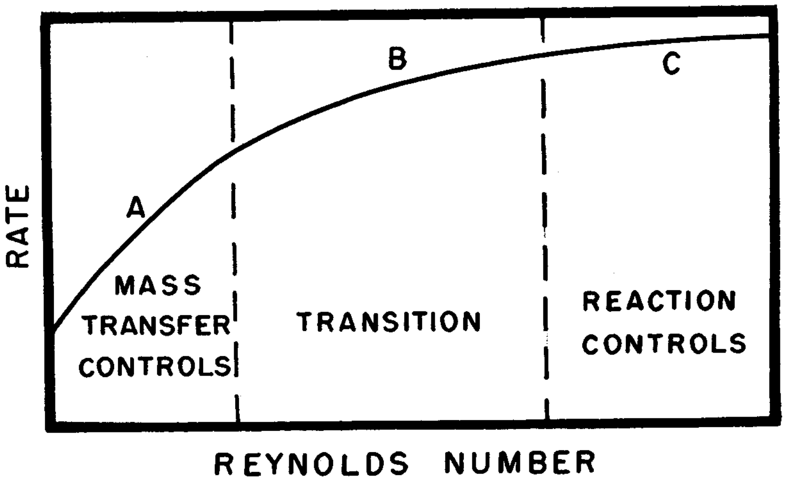

Fig. 1.

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# Dispersed-phase Holdup

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In the paper "Dispersed-phase Holdup in Packed, Countercurrent Liquid-liquid Extraction Columns," by C. E. Wicks and R. B. Beckmann, which appeared in the December, 1955, issue of the *Journal* (page 426), reference is made to a paper on the same subject by Gayler and myself. Thus, on page 427 the following statement is made:

"Gayler and Pratt also present the following equation for normal holdup at flooding:

$$X_{flood} = 0.62\,\frac{V_D{}^2 a_v}{gF^3}$$

which must be in error, for a substitution of the proper values for the variables into the equation resulted in values of $X_{flood}$ greater than one, which is an impossibility."

The above expression is quoted incorrectly and should read* as follows:

$$X_{flood} = 0.62\left[\frac{V_D{}^2 a_v}{gF^3}\,\frac{\rho_d}{\Delta\rho}\right]^{0.11}$$

Further, substitution of data from the authors' paper, as well as our original data (*2*), indicates that neither of the above expressions gives values for $X_{flood}$ greater than unity; the incorrect expression in fact gives impossibly *low* values of $X_{flood}$, owing to omission of the exponent.

The second of the above expressions represented an early attempt of ours to correlate holdup at the flood point for packed columns, and the authors may perhaps be interested in our later work. Thus, Thornton (*7*) has shown that for mechanically agitated columns, where the droplet size is determined entirely by the power input, the following expression for the holdup, derived originally by Gayler, Roberts, and Pratt (*3*) for packed columns, is applicable up to the flood point:

$$V_D + \frac{X}{1 - X}\,V_c = F\bar{v}_0 X(1 - X)$$

where $\bar{v}_0$ is the "characteristic droplet velocity."

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*The symbols of Wicks and Beckmann are used here.

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in Reynolds number on reaction rate if the process is operating in region $A$.

Calculation of the partial pressure drop of one component through the film by use of the previously mentioned methods is another standard way to ascertain whether or not mass transfer is of importance in the process; however, this technique is subject to some question and it may not yield answers which can lead to valid conclusions.

The equations developed by Wilke and Hougen (*1*) and summarized nicely by Yang and Hougen (*2*) may be shown to lead to the following:

$$\ln (P + \delta_A \mathcal{P}_A) - \ln [P + \delta_A(\mathcal{P}_A - \Delta\mathcal{P})] = \frac{r_A N^n M_m \delta_A}{m\left(\frac{\mu}{\rho D}\right)^{-2/3} G S_t} \qquad (1)$$

where

$P$ = total pressure, atm.
$p_A$ = partial pressure of component $A$, the component of interest to the problem, atm.
$\Delta\mathcal{P}$ = partial pressure drop of component $A$ through the gas film surrounding the catalyst particle, atm.
$r_A$ = reaction rate, moles reacted /(sec.)(g.) of catalyst.
$N_B$ = modified Reynolds number = $D_P G/\mu$
$D_p$ = particle diameter
$n$ = a constant, usually taken equal to 0.51
$m$ = a constant, usually taken equal to 1.82
$M_m$ = mean molecular weight of gases in the reacting system
$\mu/\rho D$ = Schmidt number
$G$ = mass velocity based on the empty cross-sectional area, g./(sq. cm.)(sec.)
$S_t$ = active surface area per unit of catalyst mass, sq. cm./g.

For a large number of reacting systems reported in the literature (the list of those referred to is presented as Appendix A) the following order-of-magnitude values apply:

$$30 < M_m < 100$$
$$0.1 \text{ cm.} < D_p < 0.2 \text{ cm.}$$
$$1 < (\mu/\rho D)^{-2/3} < 10$$
$$\mu \sim 10^{-4} \text{ g./(cm.)(sec.)}$$
$$r_A \sim 10^{-6} \text{ moles/(sec.)(g. of catalyst)}$$

The constant $\delta_A$ in Equation (1) is given by

$$\delta_A = \frac{c + d - a - b}{a}$$

where $a$, $b$, $c$, and $d$ are the stoichiometric coefficients in the reaction under study, viz:

$$aA + bB \rightarrow cC + dD$$

Thus, by means of indicated approximate values and a total pressure of 1 atm.

$$\ln \frac{1 + \delta_A \mathcal{P}_A}{1 + \delta_A \mathcal{P}_A - \delta_A \Delta\mathcal{P}} \sim \frac{10^{-3}\delta_A}{S_t\sqrt{N_B}} \qquad (2)$$

wherein the group on the left is indicated to be of the order of magnitude of the group on the right. For a specific case, $\delta_A = -1$,

$$\ln \left[1 + \frac{\Delta\mathcal{P}}{1 - \mathcal{P}_A}\right] \sim \frac{10^{-3}}{S_t\sqrt{N_B}} \qquad (3)$$

Values of $S_t$ obtained from adsorption measurements are usually quite high, often as high as $10^4$ sq. cm./g. Even with values much less than this it is apparent that for any reasonable value of $N_B$, $\Delta\mathcal{P} \rightarrow 0$. Thus it is apparent that with the order-of-magnitude values stated, Equation (1) predicts that mass transfer can be of no importance regardless of the Reynolds number used. Again, this conclusion remains valid if the measured rate were different (for example as a result as temperature changes) by as much as three orders of magnitude.

It is obviously important in studies of the chemical-reaction rate in fixed-bed catalytic reactors to know where (on the figure) the process under study is operating. The conclusion to be drawn from the foregoing is that there is only one satisfactory technique for determining the relative importance of mass transfer and chemical reaction in such studies at the present time. The effect of Reynolds number on conversion or on the over-all reaction rate must be determined *at constant contact time*. When this is done, it will become evident as to whether or not flow rate is influencing the over-all reaction rate, and it is possible to determine therefrom the relative orders of magnitude of these two rates in the process.

## LITERATURE CITED

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## APPENDIX A

### List of References Providing Data Leading to Equation (3)

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