When a man blames others for his failures, it's a good idea to credit others with his successes.

Howard W. Newton
The multiphase reactors to be discussed in this chapter are those in which gas and liquid phases are contacted with a solid catalyst. The reaction generally takes place between the gas and the liquid on the catalyst surface. However, in some reactions the liquid phase is an inert medium for the gas to contact the solid catalyst. The latter situation arises when a large heat sink is required for highly exothermic reactions. In many cases the catalyst life is extended by these milder operating conditions.

The two types of three-phase reactors to be discussed are the slurry reactor and the trickle bed reactor. In the slurry reactor the catalyst is suspended in the liquid and the gas is bubbled through the liquid. The slurry reactor may be operated in either the semibatch or continuous mode. The trickle bed reactor is essentially a vertical packed (fixed)-bed reactor in which the liquid and gas flow cocurrently down the reactor. Trickle beds saw their first use in the removal of organic material from wastewater streams. Here, aerobic bacteria would attach themselves to stones or other supports over which the wastewater was "trickled" and contacted with air. Since this first application the trickle bed reactor has been used for a wide variety of reactions (see Table 12-1).

The range of operating flow rates in commerical trickle bed reactors are 0.8 to $25 \mathrm{~kg} / \mathrm{m}^{2}$. s for liquids and 0.013 to $1.97 \mathrm{~kg} / \mathrm{m}^{2}$. s for gases. For pilot-plant operation the corresponding flow rates range from 0.08 to $2.5 \mathrm{~kg} / \mathrm{m}^{2}$. s for liquids and 0.0013 to $0.197 \mathrm{~kg} / \mathrm{m}^{2} \cdot \mathrm{~s}$ for gases.

Table 12-1. Applications of Three-Phase Reactors
I. Slurry Reactor
A. Hydrogenation

1. of fatty acids over a supported nickel catalyst.
2. of 2-butyne-1,4-diol over a $\mathrm{Pd}-\mathrm{CaCO}_{3}$ catalyst.
3. of glucose over a Raney nickel catalyst
B. Oxidation
4. of $\mathrm{C}_{2} \mathrm{H}_{4}$ in an inert liquid over a $\mathrm{PdCl}_{2}$-carbon catalyst
5. of $\mathrm{SO}_{2}$ in inert water over an activated carbon catalyst
C. Hydroformation
of CO with high-molecular-weight olefins on either a cobalt or ruthenium complex bound to polymers
D. Ethynylation

Reaction of acetylene with formaldehyde over a $\mathrm{CaCl}_{2}$-supported catalyst
II. Trickle Bed Reactors
A. Hydrodesulfurization

Removal of sulfur compounds from crude oil by reaction with hydrogen on Co-Mo on alumina
B. Hydrogenation

1. of aniline over a Ni-clay catalyst
2. of 2-butyne-1,4-diol over a supported $\mathrm{Cu}-\mathrm{Ni}$ catalyst
3. of benzene, $\alpha-\mathrm{CH}_{3}$ styrene, and crotonaldehyde
4. of aromatics in napthenic lube oil distillate
C. Hydrodenitrogenation
5. of lube oil distillate
6. of cracked light furnace oil
D. Oxidation
7. of cumene over activated carbon
8. of $\mathrm{SO}_{2}$ over carbon

Source: C. N. Satterfield, AIChE J., 21, 209 (1975); P. A. Ramachandran and R. V. Chaudhari, Chem. Eng., 87(24), 74 (1980); R. V. Chaudhari and P. A. Ramachandran, AIChEJ., 26, 177 (1980).

## R12.1 Slurry Reactors

In recent years there has been an increased emphasis on the study of slurry reactors in chemical reactor engineering. ${ }^{\dagger}$ A slurry reactor is a multiphase flow reactor in which the reactant gas is bubbled through a solution containing solid catalyst particles. The solution may be either a reactant, as in the case of the hydrogenation of methyl linoleate, or an inert, as in the Fischer-Tropsch synthesis of methane.

Uses of a slurry reactor Slurry reactors may be operated in a batch or continuous mode. One of the main advantages of slurry reactors is that temperature control and heat recovery are easily achieved. In addition, constant overall catalytic activity can be maintained by the addition of small amounts of catalyst with each reuse during batch operation or with constant feeding during continuous operation.
${ }^{\dagger}$ See the journal review "Three phase slurry reactors," by R. V. Chaudhari and P. A. Ramachandran, AIChE J., 26, 177 (1980).

Reaction steps in a slurry reactor

Equilibrium at the gas-liquid interface

A schematic diagram of a slurry reactor is shown in Figure 12-1. In modeling the slurry reactor we assume that the liquid phase is well mixed, the catalyst particles are uniformly distributed, and the gas phase is in plug flow. The reactants in the gas phase participate in five reaction steps:

1. Absorption from the gas phase into the liquid phase at the bubble surface
2. Diffusion in the liquid phase from the bubble surface to the bulk liquid
3. Diffusion from the bulk liquid to the external surface of the solid catalyst
4. Internal diffusion of the reactant in the porous catalyst
5. Reaction within the porous catalyst


Figure 12-1 Slurry reactor for the hydrogenation of methyl linoleate.
The reaction products participate in the steps above but in reverse order (5 through 1). Each step may be thought of as a resistance to the overall rate of reaction $R$. These resistances are shown schematically in Figure 12-2. The concentration in the liquid phase is related to the gas-phase concentration through Henry's law:

$$
\begin{equation*}
C_{i}=P_{i} H^{\prime} \tag{12-1}
\end{equation*}
$$

One of the things we want to achieve in our analysis of slurry reactors is to learn how to detect which resistance is the largest (i.e., slowest step) and how we might operate the reactor to decrease the resistance of this step and thereby increase the efficiency of the reactor.

To illustrate the principles of slurry reactor operation, we shall consider the hydrogenation of methyl linoleate, L, to form methyl oleate, O.

$$
\begin{array}{cccc}
\text { methyl linoleate }(\mathrm{l}) & + \text { hydrogen }(\mathrm{g}) & \longrightarrow & \text { methyl oleate }(\mathrm{l}) \\
\mathrm{L} & +\mathrm{H}_{2} & \longrightarrow & \mathrm{O}
\end{array}
$$

Hydrogen is absorbed in liquid methyl linoleate, diffuses to the external surface of the catalyst pellet, and then diffuses into the catalyst pellet, where it reacts


Figure 12-2 Steps in a slurry reactor.
with methyl linoleate, L, to form methyl oleate, O. Methyl oleate then diffuses out of the pellet into the bulk liquid.

### 12.1.1 Rate of gas absorption

The rate of absorption of $\mathrm{H}_{2}$ per unit volume of linoleate oil is

$$
\begin{equation*}
R_{\mathrm{A}}=k_{b} a_{b}\left(C_{i}-C_{b}\right) \tag{12-2}
\end{equation*}
$$

where $\quad k_{b}=$ mass-transfer coefficient for gas absorption, ${ }^{\dagger} \mathrm{dm} / \mathrm{s}$
$a_{b}=$ bubble surface area, $\mathrm{dm}^{2} /\left(\mathrm{dm}^{3}\right.$ of solution $)$
$C_{i}=\mathrm{H}_{2}$ concentration at oil- $\mathrm{H}_{2}$ bubble interface, $\mathrm{mol} /(\mathrm{dm})^{3}$
$C_{b}=$ bulk concentration of $\mathrm{H}_{2}$ in solution, $\mathrm{mol} /(\mathrm{dm})^{3}$

$$
R_{\mathrm{A}}[=] \frac{\mathrm{dm}}{\mathrm{~s}}\left(\frac{\mathrm{dm}^{2}}{\mathrm{dm}^{3} \text { of solution }}\right) \frac{\mathrm{mol}}{\mathrm{dm}^{3}}=\frac{\mathrm{mol}}{\left(\mathrm{dm}^{3} \text { of solution }\right) \cdot \mathrm{s}}
$$

Equation (12-2) gives the rate of $\mathrm{H}_{2}$ transport from the gas-liquid interface to the bulk liquid.

## R12.1B Transport to catalyst

The rate of mass transfer of $\mathrm{H}_{2}$ from the bulk solution to the external surface of catalyst particles is

$$
\begin{equation*}
R_{\mathrm{A}}=k_{c} a_{c} m\left(C_{b}-C_{s}\right) \tag{12-3}
\end{equation*}
$$

where $\quad k_{c}=$ mass-transfer coefficient for particles, $\mathrm{dm} / \mathrm{s}$
$a_{c}=$ external surface area of particles, $\mathrm{dm}^{2} / \mathrm{g}$
$m=$ mass concentration of catalyst (g of catalyst/dm $\mathrm{dm}^{3}$ of solution); the parameter $m$ is also referred to as the catalyst loading
$C_{s}=$ concentration of $\mathrm{H}_{2}$ at external surface of catalyst pellet, $\mathrm{mol} /(\mathrm{dm})^{3}$

$$
R_{\mathrm{A}}[=]\left(\frac{\mathrm{dm}}{\mathrm{~s}}\right) \frac{\mathrm{dm}^{2}}{\mathrm{~g}}\left(\frac{\mathrm{~g}}{\mathrm{dm}^{3} \text { of solution }}\right) \frac{\mathrm{mol}}{\mathrm{dm}^{3}}=\frac{\mathrm{mol}}{\left(\mathrm{dm}^{3} \text { of solution }\right) \cdot \mathrm{s}}
$$

${ }^{\dagger}$ Correlations for $k_{b} a_{b}$ for a wide variety of situations can be found in the review article "Design parameters estimations for bubble column reactors," by Y. T. Shah et al., AIChE J., 28, 353 (1982).

### 12.1.3 Diffusion and reaction in the catalyst pellet

In Chapter 11 we showed that the internal effectiveness factor was the ratio of the actual rate of reaction, $-r_{\mathrm{A}}^{\prime}$, to the rate $-r_{\mathrm{A} s}^{\prime}$ that would exist if the entire interior of the pellet were exposed to the reactant concentration at the external surface, $C_{\mathrm{A} s}$. Consequently, the actual rate of reaction per unit mass of catalyst can be written

$$
\begin{equation*}
-r_{\mathrm{A}}^{\prime}=\eta\left(-r_{\mathrm{A} s}^{\prime}\right) \tag{11-38}
\end{equation*}
$$

Multiplying by the mass of catalyst per unit volume of solution, we obtain the rate of reaction per volume of solution:

$$
\begin{align*}
& R_{\mathrm{A}}=m \eta\left(-r_{\mathrm{A} s}^{\prime}\right)  \tag{12-4}\\
& R_{\mathrm{A}}[=] \frac{\mathrm{g} \text { of catalyst }}{\mathrm{dm}^{3} \text { of solution }}\left(\frac{1}{1}\right) \frac{\mathrm{mol}}{(\mathrm{~g} \text { of cat }) \cdot \mathrm{s}}=\frac{\mathrm{mol}}{\left(\mathrm{dm}^{3} \text { of solution }\right) \cdot \mathrm{s}}
\end{align*}
$$

### 12.1.4 The rate law

The rate law is first order in hydrogen and first order in methyl linoleate. However, since the liquid phase is essentially all linoleate, it is in excess and its concentration, $C_{L}$, remains virtually constant at its initial concentration, $C_{L 0}$, for small to moderate reaction times:

$$
\begin{equation*}
-r_{\mathrm{A}}^{\prime}=k^{\prime} C_{L 0} C=k C \tag{12-5}
\end{equation*}
$$

The rate of reaction evaluated at the external pellet surface is

$$
\begin{equation*}
-r_{\mathrm{A} s}^{\prime}=k C_{s} \tag{12-6}
\end{equation*}
$$

where $C_{s}=$ concentration of hydrogen at the external pellet surface, $\mathrm{mol} / \mathrm{dm}^{3}$
$k=$ specific reaction rate, $\mathrm{dm}^{3} / \mathrm{g}$ cat•s

### 12.1.5 Determining the limiting step

Since, at any point in the column, the overall rate of transport is at steady state, the rate of transport from the bubble is equal to the rate of transport to the catalyst surface, which in turn is equal to the rate of reaction in the catalyst pellet. Then

$$
R_{\mathrm{A}}=k_{b} a_{b}\left(C_{i}-C_{b}\right)=k_{c} m a_{c}\left(C_{b}-C_{s}\right)=m \eta\left(-r_{\mathrm{A} s}^{\prime}\right)
$$

Equations (12-2) through (12-6) can be rearranged in the form

$$
\begin{aligned}
\frac{R_{\mathrm{A}}}{k_{b} a_{b}} & =C_{i}-C_{b} \\
\frac{R_{\mathrm{A}}}{k_{c} a_{c} m} & =C_{b}-C_{s} \\
\frac{R_{\mathrm{A}}}{m k \eta} & =C_{s}
\end{aligned}
$$

Adding the equations above yields

$$
\begin{equation*}
R_{\mathrm{A}}\left(\frac{1}{k_{b} a_{b}}+\frac{1}{k_{c} a_{c} m}+\frac{1}{k \eta m}\right)=C_{i} \tag{12-7}
\end{equation*}
$$

Rearranging, we have

$$
\begin{equation*}
\frac{C_{i}}{R_{\mathrm{A}}}=\frac{1}{k_{b} a_{b}}+\frac{1}{m}\left(\frac{1}{k_{c} a_{c}}+\frac{1}{k \eta}\right) \tag{12-8}
\end{equation*}
$$

Each of the terms on the right-hand side can be thought of as a resistance to the overall rate of reaction such that

$$
\begin{equation*}
\frac{C_{i}}{R_{\mathrm{A}}}=r_{b}+\frac{1}{m}\left(r_{c}+r_{r}\right) \tag{12-9}
\end{equation*}
$$

or

$$
\begin{equation*}
\frac{C_{i}}{R_{\mathrm{A}}}=r_{b}+\frac{1}{m} r_{c r} \tag{12-10}
\end{equation*}
$$

where

$$
\begin{align*}
& r_{b}=\frac{1}{k_{b} a_{b}}=\text { resistance to gas absorption, } \mathrm{s}  \tag{12-11}\\
& r_{c}=\frac{1}{k_{c} a_{c}}=\begin{array}{r}
\text { resistance to transport to surface of catalyst pellet, } \\
\mathrm{g} \cdot \mathrm{~s} / \mathrm{dm}^{3}
\end{array}  \tag{12-12}\\
& r_{r}=\frac{1}{\eta k}=\begin{array}{l}
\text { resistance to diffusion and reaction within the catalyst } \\
\text { pellets, } \mathrm{g} \cdot \mathrm{~s} / \mathrm{dm}^{3}
\end{array}  \tag{12-13}\\
& r_{c r}=r_{r}+r_{c} \begin{array}{l}
\text { (combined resistance to internal diffusion, } \\
\text { reaction, and external diffusion), } \mathrm{g} \cdot \mathrm{~s} / \mathrm{dm}^{3}
\end{array}
\end{align*}
$$

For reactions other than first order,

$$
\begin{equation*}
r_{r}=\frac{C_{s}}{\eta\left(-r_{\mathrm{A} s}^{\prime}\right)} \tag{12-15}
\end{equation*}
$$

We see from equation (12-10) that a plot of $C_{i} / R_{\mathrm{A}}$ as a function of the reciprocal of the catalyst loading, $(1 / m)$ should be a straight line. The slope will be equal to the combined resistance $r_{c r}$ and intercept equal to the gas absorption resistance $r_{b}$. Consequently, to learn the magnitude of the resistances, one varies the concentration of catalyst, $m$, and measures the corresponding overall rate of reaction (see Figure 12-3). The ratio of gas absorption resistance to

Finding the limiting resistance


Figure 12-3 Plot to delineate controlling resistances.
diffusional resistance to and within the pellet at a particular catalyst loading $m$ is

$$
\frac{\text { absorption resistance }}{\text { diffusion resistance }}=\frac{r_{b}}{r_{c r}(1 / m)}=\frac{\text { intercept } \times m}{\text { slope }}
$$

Suppose it is desired to change the catalyst pellet size (to make them smaller, for example). Since gas absorption is independent of catalyst particle size, the intercept will remain unchanged. Consequently, only one experiment is necessary to determine the combined diffusional and reaction resistances $r_{c r}$. As the particle size is decreased, both the effectiveness factor and the mass-transfer coefficient increase. As a result, the combined resistance, $r_{c r}$, decreases, as shown by the decreasing slope in Figure 12-4a. In Figure 12-4b we see that as the resistance to gas absorption increases the intercept increases. The two extremes of these controlling resistances are shown in Figure 12-5. Figure 12-5a shows a large intercept $\left(r_{b}\right)$ and a small slope $\left(r_{c}+r_{r}\right)$, while Figure 12-5b shows a large slope $\left(r_{c}+r_{r}\right)$ and a small intercept. To decrease the gas absorption resistance, one might consider changing the sparger to produce more gas bubbles of smaller diameter.

Now that we have shown how we learn whether gas absorption $r_{b}$ or diffu-sion-reaction $\left(r_{c}+r_{r}\right)$ is limiting by varying the catalyst loading, we will focus on the case when diffusion and reaction combined are limiting. The next step is to learn how we can separate $r_{c}$ and $r_{r}$ to learn whether

1. External diffusion is controlling,
2. Internal diffusion is controlling, or
3. Surface reaction is controlling.

To learn which of these steps controls, one must vary the particle size. After deter-


Figure 12-4 (a) Effect of particle size; (b) effect of gas absorption.

If gas absorption controls, might want to change the sparger to get smaller bubbles

Combined external and internal resistances

Surface reaction rate is independent of particle size


Figure 12-5 (a) Gas absorption controls; (b) diffusion and reaction control.
mining $r_{c r}$ from the slope of $C_{i} / R$ versus $1 / m$ at each particle size, one can construct a plot of $r_{c r}$ versus particle size, $d_{p}$.

$$
\begin{equation*}
r_{c r}=\frac{1}{k_{c} a_{c}}+\frac{1}{\eta k} \tag{12-16}
\end{equation*}
$$

a. Very small particles: It has been shown in Chapter 11 (see Figure 11-5) that as the particle diameter becomes small, the surface reaction controls and the effectiveness factor approaches 1.0. For small values of $k$ (reaction control)

$$
r_{c r} \simeq \frac{1}{k}
$$

Consequently, $r_{c r}$ and $r_{r}$ are independent of particle size and a plot of $\ln r_{c r}$ as a function of $\ln d_{p}$ should yield a zero slope for this condition of surface reaction limitations.
b. Small to moderate-size particles: For large values of the Thiele modulus
we have shown [equation (11-33)] that

$$
\eta=\frac{3}{\phi}=\frac{6}{d_{p}}\left(\frac{D_{e}}{k \rho_{p} S_{a}}\right)^{1 / 2}
$$

If internal diffusion controls, resistance will vary linearly with particle size

$$
\begin{equation*}
r_{r}=\frac{1}{\eta k}=\alpha_{1} d_{p} \tag{12-17}
\end{equation*}
$$

We see that internal diffusion limits the reaction if a plot of $r_{c r}$ versus $d_{p}$ is linear. Under these conditions the overall rate of reaction can be increased by decreasing the particle size. However, the overall rate will be unaffected by the mixing conditions in the bulk liquid that would change the mass-transfer boundary layer thickness next to the pellet surface.
c. Moderate to large particles: External resistance to diffusion was given by the equation

$$
\begin{equation*}
r_{c}=\frac{1}{k_{c} a_{c}} \tag{12-12}
\end{equation*}
$$

The external surface area per mass of catalyst is

$$
\begin{equation*}
a_{c}=\frac{\text { area }}{\operatorname{mass}}=\frac{\pi d_{p}^{2}}{(\pi / 6) d_{p}^{3} \rho_{p}}=\frac{6}{d_{p} \rho_{p}} \tag{12-18}
\end{equation*}
$$

Next we need to learn the variation of the mass-transfer coefficient with particle size.

Case 1: No Shear Stress between Particles and Fluid. If the particles are sufficiently small, they move with the fluid motion such that there is no shear between the particle and the fluid. This situation is equivalent to diffusion to a particle in a stagnant fluid. Under these conditions the Sherwood number is 2, i.e.,

$$
\begin{equation*}
\mathrm{Sh}=\frac{k_{c} d_{p}}{D_{\mathrm{AB}}}=2 \tag{12-19}
\end{equation*}
$$

Then

$$
k_{c}=2 \frac{D_{\mathrm{AB}}}{d_{p}}
$$

and

$$
\begin{equation*}
r_{c}=\frac{\rho d_{p}^{2}}{12 D_{\mathrm{AB}}}=\alpha_{2} d_{p}^{2} \tag{12-20}
\end{equation*}
$$

Consequently, if external diffusion is controlling and there is no shear between the particle and fluid, the slope of a plot of $\ln r_{c r}$ versus $\ln d_{p}$ should be 2 . Since the particle moves with the fluid, increasing the stirring would have no effect in increasing the overall rate of reaction.

For external diffusion control resistance varies with square of particle size for small particles and $\frac{3}{2}$ power of particle size for large particles

Algorithm to determine reactionlimiting step

Case 2: Shear between Particles and the Fluid. If the particles are sheared by the fluid motion, one can neglect the 2 in the Frössling correlation between the Sherwood number and Reynolds number, and
becomes

$$
\begin{equation*}
\mathrm{Sh}=2+0.6 \mathrm{Re}^{1 / 2} \mathrm{Sc}^{1 / 3} \tag{10-40}
\end{equation*}
$$

$$
S h \propto \operatorname{Re}^{1 / 2}
$$

Then

$$
\frac{k_{c} d_{p}}{D_{\mathrm{AB}}} \propto\left(\frac{d_{p} U}{v}\right)^{1 / 2}
$$

or

$$
k_{c} \propto \frac{U^{1 / 2}}{d_{p}^{1 / 2}}
$$

and

$$
k_{c} a_{c} \propto \frac{U^{1 / 2}}{d_{p}^{1.5}}
$$

$$
\begin{equation*}
r_{c}=\alpha_{3} d_{p}^{1.5} \tag{12-21}
\end{equation*}
$$

Another correlation for mass transfer to spheres in a liquid moving at a low velocity ${ }^{\dagger}$ gives

$$
\begin{equation*}
\mathrm{Sh}^{2}=4.0+1.21(\mathrm{ReSc})^{2 / 3} \tag{12-22}
\end{equation*}
$$

From which one obtains, upon neglecting the first term on the right-hand side,

$$
r_{c}=\alpha_{4} d_{p}^{1.7}
$$

If it is found that if the combined resistance varies with $d_{p}$ from the 1.5 to 1.7 power, then external resistance is controlling and the mixing (stirring speed) is important. Figure 12-6 shows a plot of the combined resistance $r_{c r}$ as a function of particle diameter $d_{p}$ on $\log$-log paper for the various rate-limiting steps.

Given a set of reaction rate data, we can carry out the following procedure to determine which reaction step is limiting:

1. Construct a series of plots of $C_{i} / R$ as a function of $1 / m$.
2. Determine the combined resistance from the slopes of these plots for each corresponding particle diameter.
3. Plot $r_{c r}$ as a function of $d_{p}$ on log-log paper. From the slope of this plot determine which step is controlling. The slope should be $0,1,1.5,1.7$, or 2 .
4. If the slope is in between any of these values, say 0.5 , this suggests that more than one resistance is limiting.

[^0]

Figure 12-6 Effect of particle size on controlling resistance.
The variables that influence reactor operation under each of the limiting conditions just discussed are shown in Table 12-2.

## Example 12-1 Determining the Controlling Resistance

The catalytic hydrogenation of methyl linoleate ${ }^{\dagger}$ was carried out in a laboratoryscale slurry reactor in which hydrogen gas is bubbled up through the liquid and catalyst. Unfortunately, the pilot-plant reactor did not live up to the laboratory reactor expectations. The catalyst particle size normally used is between 10 and $100 \mu \mathrm{~m}$. In an effort to deduce the problem, the experiments listed in Table E12-1.1 were carried out on the pilot-plant slurry reactor at $121^{\circ} \mathrm{C}$.

Table E12-1.1

|  | Partial <br> Pressure <br> of | $\mathrm{H}_{2}$ <br> $\left(\mathrm{Solubility} \mathrm{a}^{2}\right.$ <br> of $\mathrm{H}_{2}$ | Size of <br> Catalyst <br> Particles <br> $\left(\mathrm{kmol} / \mathrm{m}^{3}\right)$ | Catalyst <br> Charge <br> $\left(\mathrm{kg} / \mathrm{m}^{3}\right)$ | $\mathrm{H}_{2}$ Rate of <br> Run <br> $\left(\mathrm{kmol} / \mathrm{m}^{3} \cdot r_{\mathrm{H}_{2}}\right.$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 3 | 0.007 | 40.0 | 5.0 | 0.0625 |
| 2 | 6 | 0.014 | 40.0 | 0.2 | 0.0178 |
| 3 | 6 | 0.014 | 80.0 | 0.16 | 0.0073 |

${ }^{\text {a }}$ Henry's law: $H^{\prime} P_{\mathrm{H}_{2}}=C_{\mathrm{H}_{2}}$ with $H^{\prime}=0.00233 \mathrm{~mol} \mathrm{H} / \mathrm{atm} \cdot \mathrm{dm}^{3}$.
a. What seems to be the problem (i.e., major resistance) with the pilotplant reactor and what steps should be taken to correct the problem? Support any recommendations with calculations.

[^1]Table 12-2. Variables Affecting Observed Reaction Rate

| Controlling Step | Variables with: |  |  |
| :---: | :---: | :---: | :---: |
|  | Major Influence | Minor Influence | Insignificant Influence |
| Gas-liquid mass transport | Stirring rate | Temperature | Concentration of liquidphase reactant |
|  | Reactor design (impeller, gas distributor, baffling, etc.) |  | Amount of catalyst Catalyst particle size |
|  | Concentration of reactant in gas phase |  | Concentration of active component(s) on catalyst |
| Liquid-solid mass transport (gaseous reactant) | Amount of catalyst | Temperature | Concentration of liquid- |
|  | Catalyst particle size | Stirring rate | phase reactant |
|  | Concentration of reactant in gas phase | Reactor design <br> Viscosity | Concentration of active component(s) on catalyst |
|  |  | Relative densities |  |
| Liquid-solid mass transport (liquid reactant) | Amount of catalyst | Temperature | Concentration of gas-phase |
|  | Catalyst particle size | Stirring rate | reactant |
|  | Concentration of reactant in liquid phase | Reactor design | Concentration of active |
|  |  | Viscosity | component(s) on catalyst |
|  |  |  |  |
| Chemical reaction (insignificant pore diffusion resistance) | Temperature |  | Stirring rate |
|  | Amount of catalyst |  | Reactor design |
|  | Reactant concentrations |  | Catalyst particle size |
|  | Concentration of active component(s) on catalyst |  |  |
| Chemical reaction (significant pore diffusion resistance) | Amount of catalyst | Pore structure | Stirring rate |
|  | Reactant concentrations |  | Reactor design |
|  | Temperature ${ }^{\text {a }}$ |  |  |
|  | Catalyst particle size |  |  |
|  | Concentration of active component(s) on catalyst ${ }^{\text {a }}$ |  |  |

${ }^{\mathrm{a}}$ These variables do not exert as strong an influence as when pore diffusion resistance is negligible.
Source: G. Roberts, Catalysis in Organic Synthesis, ed. P. N. Rylander and H. Greenfield (New York: Academic Press, 1976). Reprinted with permission of Academic Press and Engelhard Industries, Edison, N.J.
b. For the $80-\mu \mathrm{m}$ particle size, what are the various percentage resistances to absorption, diffusion, and so on, when the catalyst charge is $0.40 \mathrm{~kg} / \mathrm{m}^{3}$ ?

## Solution

To determine the major resistance we need to plot $\left(C_{i} /-r_{\mathrm{H}_{2}}\right)$ as a function of $1 / m$. First, compare the slope and intercept of the $40.0-\mu \mathrm{m}$ particle size experiment to learn if gas absorption is the major resistance. From the data in Table E12-1.1, we develop Table E12-1.2. These data are plotted in Figure E12-1.1. For catalyst charges below $2.0 \mathrm{~kg} / \mathrm{m}^{3}$, diffusion is the major resistance to the overall reaction for the $80-\mu \mathrm{m}$ particle.


Figure E12-1.1
Table E12-1.2

| Run | $C_{i} / R_{i}(\mathrm{~min})$ | $1 / m\left(\mathrm{~m}^{3} / \mathrm{kg}\right)$ |
| :--- | :---: | :---: |
| 1 | 0.112 | 0.20 |
| 2 | 0.787 | 5.00 |
| 3 | 1.92 | 6.25 |

From the slope of the line corresponding to the $40-\mu \mathrm{m}$ particle size, the combined external and internal diffusion and reaction resistance is

$$
\begin{equation*}
r_{c r(40.0 \mu \mathrm{~m})}=\frac{0.787-0.112}{5.00-0.2}=0.140 \frac{\mathrm{~min} \cdot \mathrm{~kg}}{\mathrm{~m}^{3}} \tag{E12-1.1}
\end{equation*}
$$

For the $80.0-\mu \mathrm{m}$ particle size, we obtain

$$
\begin{equation*}
r_{c r(80.0 \mu \mathrm{~m})}=\frac{1.92-1.00}{6.25-3.00}=0.283 \frac{\mathrm{~min} \cdot \mathrm{~kg}}{\mathrm{~m}^{3}} \tag{E12-1.2}
\end{equation*}
$$

Comparing equations (E12-1.2) and (E12-1.1) gives us

$$
\frac{r_{c r(80)}}{r_{c r(40)}}=\frac{0.283}{0.140}=2.02
$$

We see that when the particle size is doubled, the resistance is also doubled.

$$
r_{c r} \propto d_{p}
$$

Since the combined resistance is proportional to the particle diameter
to the first power, internal diffusion is the controlling resistance of the three resistances. To decrease this resistance a smaller catalyst particle size should be used.

For the $80.0-\mu \mathrm{m}$ particle size at a catalyst charge of $0.4 \mathrm{~kg} / \mathrm{m}^{3}$, the overall resistance at $1 / m=2.5$ is 0.84 min (see Figure E12-1.2).
percent gas absorption resistance $=\frac{0.08}{0.84} \times 100=9.5 \%$
percent internal diffusion resistance $=\frac{0.84-0.08}{0.84} \times 100=90.5 \%$


Figure E12-1.2

### 12.1.6 Slurry reactor design

In the material above we have discussed the transport and reactor steps and developed an equation for the overall resistance. A rearrangement of equation (12-7) gives

$$
\begin{equation*}
R_{\mathrm{A}}=-r_{\mathrm{A}}=\frac{C_{i}}{1 / k_{a} a_{b}+1 / m\left(1 / k_{c} a_{c}+1 / \eta k\right)} \tag{12-23}
\end{equation*}
$$

To design slurry reactors one simply couples this rate law with the appropriate mole balance ${ }^{\dagger}$ (see Chapters 1 and 2).
${ }^{\dagger}$ An interesting example of a slurry reactor modeled as a plug-flow reactor for FischerTropsch synthesis is given by D. Stern, A. T. Bell, and H. Heinemann, Chem. Eng. Sci., 38, 597 (1983).

## Example 12-2 Slurry Reactor Design

Methyl linoleate is to be converted to methyl oleate in a $2-\mathrm{m}^{3}$ slurry reactor. The molar feed rate of methyl linoleate to the reactor is $0.7 \mathrm{kmol} / \mathrm{min}$. The partial pressure of $\mathrm{H}_{2}$ is 6 atm and the reactor is considered to be well mixed. Calculate the catalyst charge necessary to achieve $30 \%$ conversion for a $60-\mu$ m particle size. The reaction conditions are the same as those described in Example 12-1.

## Solution

For a well-mixed reactor, the CSTR design equation is

$$
\begin{equation*}
V=\frac{F_{\mathrm{A} 0} X}{-r_{\mathrm{A}}} \tag{E12-2.1}
\end{equation*}
$$

Multiplying by the solubility of hydrogen and rearranging gives us

$$
\begin{equation*}
\frac{V C_{i}}{F_{\mathrm{A} 0} X}=\frac{C_{i}}{-r_{\mathrm{A}}} \tag{E12-2.2}
\end{equation*}
$$

Equating equations (E12-2.2) and (12-10), we have

$$
\begin{equation*}
\frac{V C_{i}}{F_{\mathrm{A} 0} X}=r_{b}+\frac{1}{m} r_{c r} \tag{E12-2.3}
\end{equation*}
$$

From Example 12-1,

$$
r_{b}=0.08 \mathrm{~min}
$$

and for the $80-\mu \mathrm{m}$ particle,

$$
r_{c r}=0.283 \mathrm{~min} \cdot \mathrm{~kg} / \mathrm{m}^{3}
$$

Since internal diffusion controls,

$$
\begin{aligned}
r_{c r} & =\alpha d_{p} \\
r_{c r}(60 \mu \mathrm{~m}) & =\frac{60}{80}(0.283)=0.21 \mathrm{~min} \cdot \mathrm{~kg} / \mathrm{m}^{3}
\end{aligned}
$$

Substituting the parameter values into equation (E12-2.3) gives us

$$
\frac{\left(2 \mathrm{~m}^{3}\right)\left(0.014 \mathrm{kmol} / \mathrm{m}^{3}\right)}{(0.7 \mathrm{kmol} / \mathrm{min})(0.3)}=0.08 \mathrm{~min}+\frac{1}{m}\left(0.21 \mathrm{~kg} \cdot \mathrm{~min} / \mathrm{m}^{3}\right)
$$

which solves to a catalyst charge of

$$
m=3.95 \mathrm{~kg} / \mathrm{m}^{3}
$$


[^0]:    ${ }^{\dagger}$ Satterfield, Mass Transfer in Heterogeneous Catalysis (Cambridge, Mass.: MIT Press, 1970), p. 114.

[^1]:    ${ }^{\dagger}$ W. A. Cordova and P. Harriott, Chem. Eng. Sci., 30, 1201 (1975).

