12.8 Multiphase Reactors

Multiphase reactors are reactors in which two or more phases are necessary to carry out the reaction. The majority of multiphase reactors involve gas and liquid phases which contact a solid. In the case of the slurry and trickle bed reactors, the reaction between the gas and the liquid takes place on a solid catalyst surface (see Table 12-2). However, in some reactors 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 multiphase reactors discussed in this edition of the book are the slurry reactor, fluidized bed, and the trickle bed reactor. The trickle bed reactor which has reaction and transport steps similar to the slurry reactor is discussed in the first edition of the book and on the CD-ROM along with the bubbling fluidized bed. In slurry reactors, the catalyst is suspended in the liquid and gas is bubbled through the liquid. A slurry reactor may be operated in either a semibatch or continuous mode.

TABLE 12-2. 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 Pd-$CaCO_3$ catalyst
    3. of glucose over a Raney nickel catalyst
  B. Oxidation
    1. of C_2H_4 in an inert liquid over a $PdCl_2$-carbon catalyst
    2. of 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 $CaCl_2$-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 Cu-Ni catalyst
    3. of benzene, α-CH_3 styrene, and crotonaldehyde
    4. of aromatics in napthenic lube oil distilate
  C. Hydrodenitrogenation
    1. of lube oil distillate
    2. of cracked light furnace oil
  D. Oxidation
    1. of cumene over activated carbon
    2. of 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, *AIChE J.*, *26*, 177 (1980).

12.8.1 Slurry Reactors

Uses of a slurry reactor

In recent years there has been an increased emphasis on the study of slurry reactors in chemical reactor engineering. A slurry reactor is a multiphase flow reactor in which 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, a product as in the case of the production of hydrocarbon wax, or an inert, as in the Fischer–Tropsch synthesis of methane. 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.

Example 12–4 Industrial Slurry Reactor

Describe the operation an industrial slurry reactor used to convert synthesis gas (CO and H_2) to a hydrocarbon wax by the Fischer–Tropsch synthesis.

Solution

The Fischer–Tropsch reactions were discussed in Example 1-4. A schematic of the Sasol slurry reactor, used to make wax, is shown in Figure E12-4.1. In the slurry reactor, a typical reaction stoichiometry might be

$$25CO + 51H_2 \longrightarrow C_{25}H_{52} + 25H_2O$$

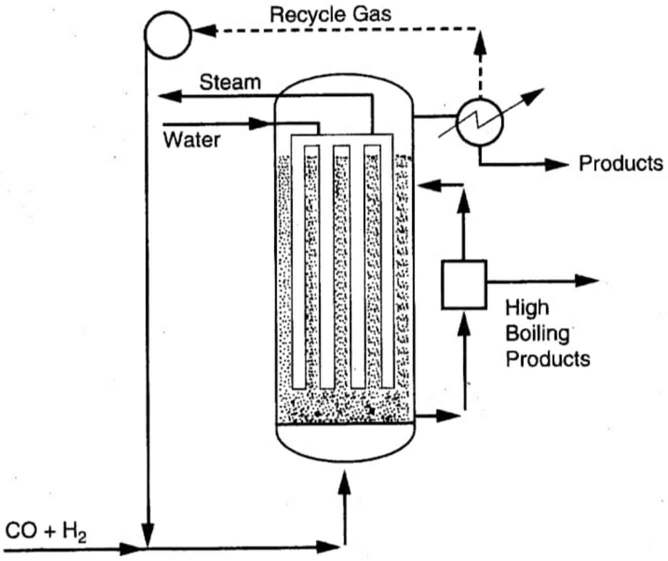

Figure E12-4.1 Sasol slurry reactor.

The reactor is 5 m in diameter and 22 m high and is operated at a temperature of 240°C and pressure of 20 atm. The synthesis gas is bubbled through a heavy oil which is usually a product of the Fischer–Tropsch reaction itself. The catalyst loading (i.e., density in the solution) is the order of 100 kg/m^3 with a typical operating range of 1 to 20 wt % solids. The reactor is cooled by an internal heat exchanger through which the coolant stream enters as water exits as steam to maintain the reactor at 240°C.

Synthesis gas is fed at a rate of 150,000 m^3/h (STP) and has a composition of 12% CH_4, 1% CO_2, 29% CO, and 58% H_2. The fresh gas is mixed with the recycled gas and the mixture enters the reactor at 120°C. The liquid wax product stream exits at flow rate of 4.5 m^3/h and has a mixture of hydrocarbons with the general formula of C_nH_{2n}, with n varying between 20 and 50. The exit tail gas stream contains methane (38%), hydrogen (37%), CO_2 (14%) with CO, water, and light hydrocarbons C_2 to C_5 making up the remaining 11%. The Sasol reactor is actually modeled as three or four slurry reactors in series. The liquid-phase of each slurry reactor in series is modeled as being well mixed, while the gas phase is modeled as being in plug flow as it moves up the column.

A more detailed schematic diagram of a slurry reactor is shown in Figure 12-11. 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:

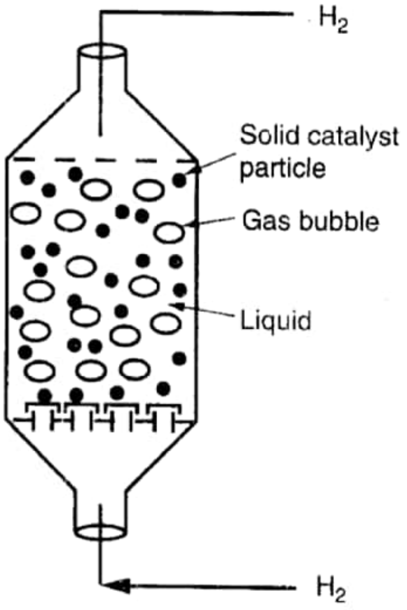

Figure 12-11 Slurry reactor for the hydrogenation of methyl linoleate.

steps in a
rry reactor

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

The reaction products participate in the steps above but in reverse ((5 through 1). Each step may be thought of as a resistance to the overall of reaction R_A. These resistances are shown schematically in Figure 1 The concentration in the liquid phase is related to the gas-phase concentr through Henry's law:

rium at the
d interface

$$C_i = P_i H' \qquad \text{(12}$$

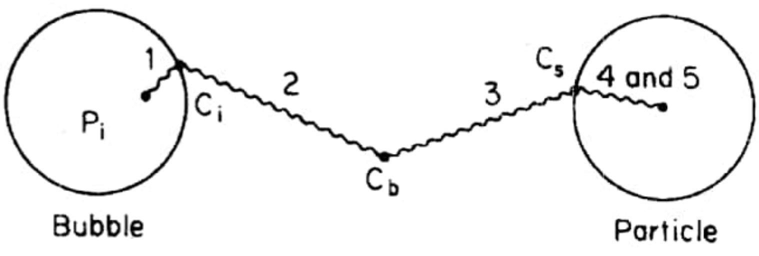

Figure 12-12 Steps in a slurry reactor.

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

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

$$\text{methyl linoleate}(l) + \text{hydrogen}(g) \longrightarrow \text{methyl oleate}(l)$$

$$\text{L} + \text{H}_2 \longrightarrow \text{O}$$

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 with methyl linoleate, L, to form methyl oleate, O. Methyl oleate then diffuses out of the pellet into the bulk liquid.

Rate of Gas Absorption The rate of absorption of H_2 per unit volume of linoleate oil is

$$\boxed{R_A = k_b a_b (C_i - C_b)} \tag{12-76}$$

where k_b = mass transfer coefficient for gas absorption,[8] dm/s
a_b = bubble surface area, $\text{dm}^2/(\text{dm}^3$ of solution)
C_i = H_2 concentration in the oil at the oil–H_2 bubble interface, mol/dm^3
C_b = bulk concentration of H_2 in solution, mol/dm^3

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

Equation (12-76) gives the rate of H_2 transport from the gas–liquid interface to the bulk liquid.

Transport to the Catalyst Pellet The rate of mass transfer of H_2 from the bulk solution to the external surface of catalyst particles is

$$\boxed{R_A = k_c a_p m (C_b - C_s)} \tag{12-77}$$

where k_c = mass transfer coefficient for particles, dm/s
a_p = external surface area of particles, dm^2/g of catalyst
m = mass concentration of catalyst (g of catalyst/dm^3 of solution); the parameter m is also referred to as the *catalyst loading*
C_s = concentration of H_2 at external surface of catalyst pellet, mol/dm^3

alyst loading

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

Diffusion and Reaction in the Catalyst Pellet In Section 12.2 we showed that the internal effectiveness factor was the ratio of the actual rate of reaction, $-r'_A$, to the rate r'_{As} that would exist if the entire interior of the pellet were exposed to the reactant concentration at the external surface, C_{As}. Consequently, the actual rate of reaction per unit mass of catalyst can be written

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[8] Correlations for $k_b a_b$ for a wide variety of situations can be found in the review article "Design parameter estimations for bubble column reactors," by Y. T. Shah et al., *AIChE J.*, *28*, 353 (1982).

$$\boxed{-r'_A = \eta(-r'_{As})} \tag{12-38}$$

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

$$R_A = m\eta(-r'_{As})$$

$$R_A\,[=]\,\frac{\text{g of catalyst}}{\text{dm}^3\text{ of solution}}\left(\frac{1}{1}\right)\frac{\text{mol}}{\text{g cat.}\cdot\text{s}} = \frac{\text{mol}}{(\text{dm}^3\text{ of solution})\cdot\text{s}} \tag{12-78}$$

The Rate Law The rate law is first-order in hydrogen and first-order in methyl linoleate. However, because the liquid phase is essentially all linoleate, it is in excess and its concentration, C_L, remains virtually constant at its initial concentration, C_{L0}, for small to moderate reaction times.

$$-r'_A = k'C_{L0}C = kC \tag{12-79}$$

The rate of reaction evaluated at the external pellet surface is

$$-r'_{As} = kC_s \tag{12-80}$$

where C_s = concentration of hydrogen at the external pellet surface, mol/dm^3
k = specific reaction rate, dm^3/g cat.·s

Determining the Limiting Step Because 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. Consequently, for a reactor that is perfectly mixed, *or* one in which the catalyst, fluid, and bubbles all flow upward together in plug flow, we find that

$$R_A = k_b a_b(C_i - C_b) = k_c m a_p(C_b - C_s) = m\eta(-r'_{As})$$

Equations (12-76) through (12-80) can be arranged in the form

$$\frac{R_A}{k_b a_b} = C_i - C_b$$

$$\frac{R_A}{k_c a_p m} = C_b - C_s$$

$$\frac{R_A}{mk\eta} = C_s$$

Adding the equations above yields

$$R_A\left(\frac{1}{k_b a_b} + \frac{1}{k_c a_p m} + \frac{1}{k\eta m}\right) = C_i \tag{12-81}$$

Rearranging, we have

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y reactor

$$\boxed{\frac{C_i}{R_A} = \frac{1}{k_b a_b} + \frac{1}{m}\left(\frac{1}{k_c a_p} + \frac{1}{k\eta}\right)} \tag{12-82}$$

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

$$\frac{C_i}{R_A} = r_b + \frac{1}{m}(r_c + r_r) \tag{12-83}$$

or

$$\frac{C_i}{R_A} = r_b + \frac{1}{m} r_{cr} \tag{12-84}$$

where

$r_b = \dfrac{1}{k_b a_b}$ = resistance to gas absorption, s (12-85)

$r_c = \dfrac{1}{k_c a_p}$ = specific resistance to transport to surface of catalyst pellet, gcat · s/dm^3 (12-86)

$r_r = \dfrac{1}{\eta k}$ = specific esistance to diffusion and reaction within the catalyst pellets, gcat · s/dm^3 (12-87)

$r_{cr} = r_r + r_c$ = specific combined resistance to internal diffusion, reaction, and external diffusion, gcat · s/dm^3 (12-88)

For reactions other than first-order,

$$r_r = \frac{C_s}{\eta(-r'_{As})} \tag{12-89}$$

We see from Equation (12-84) that a plot of C_i/R_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 specific combined resistance r_{cr} and the intercept will be equal to the gas absorption resistance r_b. Consequently, to learn the magnitude of the resistances, we would vary the concentration of catalyst (i.e., the catalyst loading, m) and measure the corresponding overall rate of reaction (Figure 12-13). The ratio of gas absorption resistance to diffusional resistance to and within the pellet at a particular catalyst loading m is

$$\frac{\text{absorption resistance}}{\text{diffusion resistance}} = \frac{r_b}{r_{cr}(1/m)} = \frac{\text{intercept} \times m}{\text{slope}}$$

g the limiting resistance

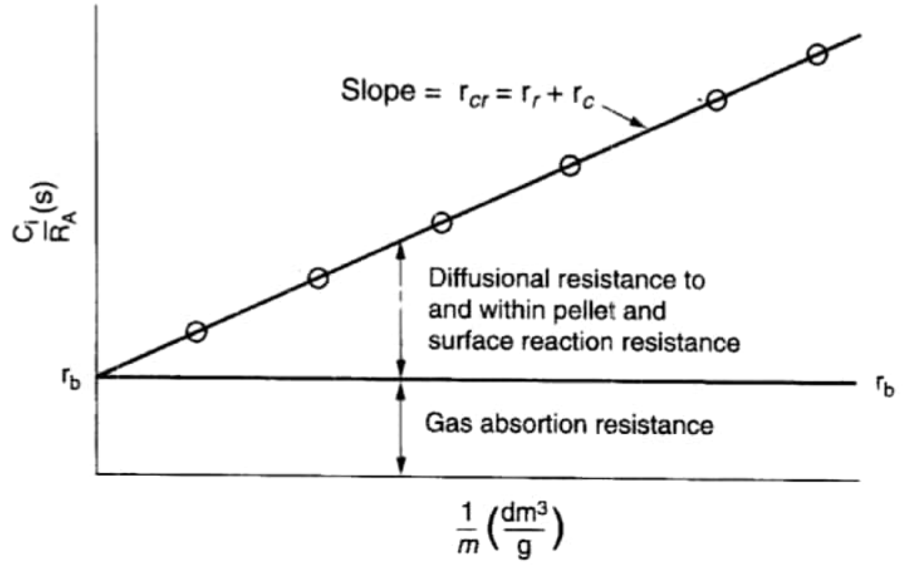
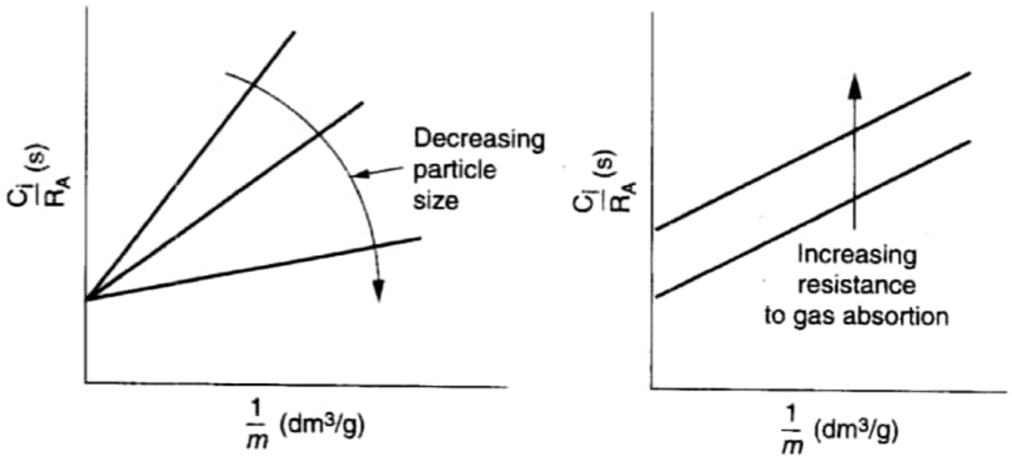


Figure 12-13 Plot to delineate controlling resistances.

Suppose it is desired to change the catalyst pellet size (to make them smaller, for example). Because 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_{cr}. As the particle size is decreased, both the effectiveness factor and mass transfer coefficient increase. As a result, the combined resistance, r_{cr}, decreases, as shown by the decreasing slope in Figure 12-14a. In Figure 12-14b we see that as the resistance to gas absorption increases, the intercept increases but the slope does not change. The two extremes of these controlling resistances are shown in Figure 12-15. Figure 12-15a shows a large intercept (r_b) and a small slope ($r_c + r_r$), while Figure 12-15b shows a large slope ($r_c + r_r$) and a small intercept. To decrease the gas absorption resistance, we might consider changing the sparger to produce more gas bubbles of smaller diameters.

Now that we have shown how we learn whether gas absorption r_b or diffusion-reaction ($r_c + r_r$) is limiting by varying the catalyst loading, we will

If diffusion trols, decrease ticle size, use more catalyst



(a) (b)

Figure 12-14 (a) Effect of particle size; (b) effect of gas absorption.