



Altamira Notes
Vol. 2.5

INTRODUCTION TO SLURRY REACTORS

Many industrial processes involve multi-phase systems, and perhaps the most complex is the gas-liquid-solid or slurry reactor. The complexity of this system arises from the simultaneous presence of mass and heat transport involving all three phases in addition to reaction. Although the transport phenomena can often be theoretically evaluated, by assuming limiting cases, the addition of the reactor operating characteristics and slurry physical properties introduces further complexities. Empirical correlation based on a particular reactor at actual operating conditions must then be utilized.

This Altamira Note is an introduction to some of the initial considerations in slurry system designs, specifically mass transfer and kinetics.

Gas-Liquid-Solid Mass Transfer and Kinetics

Mass transfer in a slurry system with reaction can be summarized as follows;

1. Gas phase diffusion of reactants to the gas-liquid interface
2. Reactant diffusion from the gas-liquid interface to the bulk liquid
3. Reactant diffusion through the bulk liquid
4. Reactant diffusion from the bulk liquid to the catalyst external surface
5. Reactant diffusion within the catalyst pores
6. Reactant adsorption at the catalyst active surface sites
7. Reaction at the catalyst surface
8. Product desorption from the catalyst surface
9. Product diffusion from the catalyst pores
10. Product diffusion from the catalyst external surface to the bulk liquid
11. Product diffusion through the bulk liquid
12. Gaseous product (if any) diffusion from the bulk liquid to the gas-liquid interface
13. Gaseous product diffusion from the gas-liquid interface to the gas.

Mechanical agitation in a CSTR and hydrodynamic agitation in a bubble column slurry reactor are often sufficient to provide a well mixed slurry. The bulk liquid concentrations are uniform, and Steps 3 and 11 can often be neglected.

Likewise, the catalyst particles are typically small, less than 50-100 μ , and the intra-particle resistances are often negligible. The following discussion assumes an effectiveness factor close to one, and the overall reaction can be based on the external surface area of the catalyst particle. However, if the effectiveness factor for the catalyst is small, then internal resistance must be taken into account.

If one assumes an irreversible first-order reaction at the catalyst surface, and equilibrium at the gas-liquid interface, the steady-state reaction rate at the catalyst surface can be written as:

$$-r_A = k_r a_c C_{As} \quad \text{Eq. 1}$$

where: k_r is the first-order reaction rate constant (L/t)
 a_c is the catalyst external surface area per unit volume of bubble-free slurry (L^{-1})
 C_{As} is the concentration of reactant A at the catalyst surface (mole/L³)
 $-r_A$ is the rate of disappearance of reactant A per unit volume of bubble-free slurry (mole/L³t).

Since the rates for each step are equal at steady-state, an overall balance can be written based on concentrations. And since the reaction is assumed irreversible, the reverse transport processes for product can be neglected. Thus, the rates for mass transfer with chemical reaction (Steps 1-4, neglecting Step 3) can be expressed in terms of concentrations and mass transfer coefficients as:

Step 1:	$-r_A = k_g a_g (C_{Ag} - C_{Ai g})$	Eq. 2
Step 2:	$-r_A = k_L a_g (C_{Ai L} - C_{AL})$	Eq. 3
Step 4:	$-r_A = k_c a_c (C_{AL} - C_{As})$	Eq. 4

where: k_g is the gas-side mass transfer coefficient at the gas-liquid interface (L/t)
 k_L is the liquid-side mass transfer coefficient at the gas-liquid interface (L/t)
 k_c is the mass transfer coefficient at the catalyst external surface (L/t)
 C_{Ag} is the concentration of reactant A per unit volume of bubble-free slurry (mole/L³)
 C_{Aig} is the concentration of reactant A per unit volume of bubble-free slurry at the gas-liquid interface (mole/L³)
 C_{Ail} is the concentration of reactant A per unit volume of bubble-free slurry at the gas-liquid interface (mole/L³)
 C_{AL} is the concentration of reactant A per unit volume of bubble-free slurry (mole/L³)
 a_g is the gas-liquid interfacial area per unit volume of bubble-free slurry (L⁻¹)

Since equilibrium is assumed at the gas-liquid interface, the interfacial concentrations can be expressed in terms of Henry's law at low concentrations as:

$$C_{Aig} = H_c C_{Ail} \quad \text{Eq. 5}$$

where: H_c is the Henry's law constant (mole gas/mole liquid)

Combining Equations 1-5 and eliminating concentrations, the rate can be expressed in terms of reactant gas concentration as:

$$-r_A = k_o a_c C_{Ag} \quad \text{Eq. 6}$$

where: k_o is the overall rate constant (L/t) expressed as:

$$\frac{1}{k_o} = \frac{a_c}{a_g} \frac{1}{k_g} + \frac{a_c}{a_g} \frac{H_c}{k_L} + H_c \left[\frac{1}{k_c} + \frac{1}{k_r} \right] \quad \text{Eq. 7}$$

Note that the reciprocals in equation 7 are resistances attributed to each of the diffusions in Steps 1, 2 and 4, the reaction at the catalyst surface, and the intrinsic rate constant. The magnitude of each resistance establishes its importance in the determination of the overall reaction rate.

This discussion has been based on a single position within the reactor. However, under actual operating conditions, gas, liquid and solid dispersions may exist along the reactor height, and the global reaction rate will change with height.

The interfacial surface area per unit volume of bubble-free slurry, a_g , for spherical bubbles is:

$$a_g = 6C_g/d_s \quad \text{Eq. 8}$$

where: C_g is the gas holdup
 d_s is the mean Sauter bubble diameter (L)

defined as:

$$d_s = \frac{\sum n_i d_{bi}^3}{\sum n_i d_{bi}^2} \quad \text{Eq. 9}$$

where: d_{bi} is the equivalent bubble diameter (L)
 n_i is the number of bubbles of a particular diameter.

The external catalyst surface area per unit volume of bubble-free slurry, a_c , for spherical particles is:

$$a_c = a_m m_s \quad \text{Eq. 10}$$

and

$$a_m = \frac{6}{D_p \rho_p} \quad \text{Eq. 11}$$

where: a_m is the catalyst external surface area per unit mass
(L²/M)
 m_s is the catalyst mass per unit volume of slurry (M/L³)
 ρ_p is the density of the catalyst particle (M/L³)
 D_p is the diameter of the catalyst particle (L).

It should be noted that the gas-liquid interfacial area for mass transfer is typically less than the catalyst surface area. Thus, the gas-liquid interfacial area per unit volume of slurry often contributes a substantial resistance to the overall mass transfer and hence the overall reaction rate.

Many studies and correlations have been done involving cold flow systems with "similar" slurry physical properties and reactor configurations. However, it has been found that the correlations from these systems often cannot be applied to systems under actual operating conditions. The interfacial area in Equation 8 is based on a bubble size distribution determined in Equation 9.

Therefore, the hydrodynamics of a slurry system are important for the determination of the overall reaction rate. In fact, it is the lack of understanding of the hydrodynamics that has led to many incongruities in the importance of mass transfer resistance versus kinetic resistance in slurry studies of the overall reaction rate.

Slurry physical properties of viscosity and surface tension are important for the determination of the gas-liquid interfacial area, a_g . It has been found that impurities present in the liquid often migrate to the interfacial area and alter the "pseudo" viscosity and surface tension at the interface. The effect of temperature and the presence of solids also alter the slurry viscosity. Subsequently, the bubble size distribution, gas holdup, and hence interfacial area may be substantially different. In addition, the type of reactor and its physical characteristics: diameter, height, and gas distributor, affect the hydrodynamics of the system. Thus, reaction characterization and scale-up have proven difficult for the study of slurry systems.

Additional Information

1. Fan, L.S., Gas-Liquid-Solid Fluidization Engineering., Butterworth, Boston (1989).
2. Rase, H.F., Chemical Reactor Design for Process Plants. Vol 1. John Wiley & Sons, New York (1977) .
3. Saxena, S.C. et al., "Mathematical Modeling of Fischer-Tropsch Slurry Bubble Column Reactors," Chem. Eng. Commun., (40) 1986, 97-151.
4. Shah, Y.T., Gas-Liquid-Solid Reactor Design. McGraw-Hill, New York (1979).
5. Shah, Y.T. et al., "Design Parameters Estimations for Bubble Column Reactors," AIChE J. (28,3) May, 1982, 353-379.

