Liquid-Solid Mass Transfer in Trickle Beds

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A reactor in which a liquid phase and a gas phase flow concurrently downward through a fixed bed of catalyst particles while reaction proceeds by a combination of interphase mass transfer and intraparticle transport is known as a trickle-bed reactor. Trickle-bed reactors have considerable importance in the petroleum industry for such processing as hydrodesulfurization of heavy oil fractions, hydrocracking of high boiling point stocks, and hydrotreating and refining of lubricating oils and waxes. Their application in the chemical and pharmaceutical industries as well as in the environmental control is gaining importance.

The flow patterns in a trickle-bed reactor were clearly categorized as the gas continuous, transition, pulsing (Weekman and Myers, 1964) and dispersed bubble flow regimes (Sato et al., 1973).

In a trickle-bed reactor, Satterfield et al. (1969) pointed out that the rate controlling step can be one or a combination of the following processes:

1. The rate of mass transfer of reactant between the bulk gas phase and the gas-liquid interface.
2. The rate of mass transfer between the gas-liquid interface and the bulk liquid.
3. The rate of mass transfer between the bulk liquid and the catalyst surface.
4. The rate of diffusion and simultaneous reaction within the catalyst pores.

Thus, in three-phase reactors, interphase mass transfer from liquid to catalyst particle and also the mass transfer between gas and liquid are important in evaluating the overall yield for a reaction.

Sylvester and Pitayagulsarn (1973) have presented a trickle-bed reactor model which shows the combined as well as the individual effects of axial dispersion, external mass transport, intraparticle diffusion, and chemical reaction on conversion. Satterfield (1975) has recently presented a comprehensive review of trickle-bed reactors.

The purpose of this paper is to present a correlation for the liquid-solid mass transfer coefficient in concurrent, two-phase downflow in a packed bed. The correlation is presented as the J_D factor as a function of liquid Reynolds number and is applicable in the range of gas and liquid flow rates from 0 to 2 m/s and 0.0005 to 1 m/s, respectively, corresponding to the gas continuous, transition, pulsing, and dispersed bubble flow regimes. Although some dependence on particle size and shape was apparent, it could not be correlated. The correlation presented should be useful in trickle-bed reactor design.

LITERATURE REVIEW

The study of liquid-solid mass transfer in concurrent two-phase downflow in packed beds is important to the design of trickle-bed reactors. The first study was that of Van Krevelen and Krekels (1948). However, very little further work was done until the last few years. A recent work by Hirose et al. (1976) covers a wide range of process variables and flow patterns.

Van Krevelen and Krekels studied the dissolution rate of benzoic acid and sulfur particles (d_p = 0.29 to 1.45 cm) for filmlike flow, considered to be similar to trickle flow at zero gas rate. The liquid velocity was varied from 0.0001 to 0.0035 m/s. The experimental results, in terms of a Sherwood number, were correlated as a function of the Reynolds and Schmidt numbers. The data were found quite useful by other workers, although there is some question as to how the filmlike flow was maintained without bed flooding.

Sato et al. (1972) determined k_{ls} by measuring the dissolution rate of benzoic acid spheres (d_p = 0.55 and 1.22 cm). The bed (6.58 cm in diameter) was packed to a height of 0.05 m for small spheres and 0.2 m for large spheres. Air flows ranged from 0.01 to 0.2 m/s. For a constant liquid rate, k_{ls} increased by as much as a factor of 5 with increasing gas rate. This increase of k_{ls} was believed due to an acceleration effect of the accompanying gas flow. At low gas rates, the results agreed with an extrapolation of Van Krevelen and Krekels' data. The experimental results were not correlated.

Lemay et al. (1975) measured the liquid-solid mass transfer coefficient for a bed of spheres for concurrent air-water flow in the pulsing flow regime. Benzoic acid spheres ($d_p = 0.6$ cm) were packed in a bed of glass spheres of the same size. The packed bed height was 76 cm, and its diameter was 7.6 cm. Air flows ranged from 0.27 to 0.55 m/s, and the water rate was varied from 0.01 to 0.04 m/s. The data were correlated by an equation of the Calderbank-Moo-Young form (1961). The k_{ls} was found not especially sensitive to radial position.

Sylvester and Pitayagulsarn (1975) studied liquid-to-solid mass transfer rates for concurrent, two-phase downflow in a 6 in. I.D. column packed with ⅛ × ⅛ in. cylindrical pellets. The gas rate was varied from 0.19 to 0.76 m/s, and the liquid rate was varied from 0.004 to 0.02 m/s, covering the gas continuous, transition, and pulsing flow regimes. The results showed that k_{ls} increased with liquid and gas rates. However, for liquid flow beyond about 0.008 m/s corresponding to the transition flow regime, k_{ls} became independent of the liquid rate. On the basis of experimental results, a correlation was developed which compared favorably with results of others.

Farazimajd (1975) extended the experimental study of Sylvester and Pitayagulsarn (1975) to larger ranges of gas and liquid rates. Gas and liquid rates ranged from 0.6 to 1.28 and 0.019 to 0.029 m/s, respectively. Over the range of variables studied, the liquid-solid mass transfer coefficient increased with gas rate but was nearly independent of liquid rate.

Goto and Smith (1975) measured liquid-solid mass transfer rates by flowing distilled water down through short beds of β-naphthol particles. The particle diameters were 0.241 cm for bed depth of 2.6 cm and 0.0541 cm for bed depth of 1.98 cm. The k_{ls} was found insensitive to gas rate in the range from 0 to 0.0076 m/s. The k_{ls} values increased in the range of liquid flow from 0.0005 to 0.0053 m/s. The results did not agree when used in Van Krevelen and Krekels' correlation. This was attributed to the fact that Van Krevelen and Krekels' correlation is based on a much larger particle diameter ($d_p = 0.29$ to 1.4 cm). Thus, it was concluded that the effect of particle size on k_{ls} in trickle beds could change for particles smaller than 0.2 cm.

Goto et al. (1975) determined k_{ls} in a 2.58 cm I.D. glass tube packed with naphthalene particles (d_p = 0.0541, 0.108, and 0.241 cm) for concurrent downflow of water and air. Air flows ranged from 0 to 0.0076 m/s, and the water rate was varied from 0.27 to 0.55 m/s. Calculated mass transfer coefficients were nearly insensitive to the gas flow rate in the range from 0 to 0.0076 m/s. The results on naphthalene particles were compared with those on β-naphthol (Goto and Smith, 1975) particles. They showed no consistent difference, and there was no effect of particle size. The results were plotted on a logarithmic graph of J_D vs. $(Re)_L$. The results fell on a convex curve, and initial flattening at low Reynolds numbers was attributed to the decrease in effective surface area for mass transfer. The results deviated from Van Krevelen and Krekels' correlation.

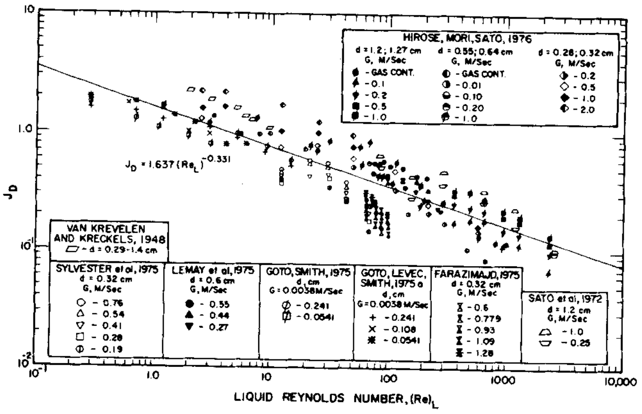

Fig. 1. Correlation of k_{ls}: J_D vs. $(Re)_L$ for concurrent two-phase downflow.

Hirose et al. (1976) measured liquid-to-solid mass transfer coefficients for two systems. In the first system, dissolution of benzoic acid spherical particles (d_p = 0.28 to 1.2 cm) in concurrent air-water flow was studied. In the second system, a diffusion limited redox reaction between metallic copper and dichromate ion in sulfuric acid solution was investigated. Commercial brass spheres ($d_p = 0.32$ to 1.27 cm) were the packing materials.

Gas and liquid superficial velocities ranged from 0.007 to 1 m/s and 0.006 to 0.245 m/s for the former system and from 0 to 2 m/s and 0.0005 to 0.02 m/s for the later system. It was found that with increase in gas flow from about 1 m/s (beyond gas continuous region) k_{ls} increased. Mass transfer rate was found to depend on gas flow in the pulsing regime, and a single correlation line for gas continuous flow branched into many corresponding to gas velocities. In the dispersed bubble flow, the effect of gas velocity was less significant. Thus, mass transfer was periodical in the pulse flow and steady in the dispersed flow.

CORRELATION AND DISCUSSION

From the k_{ls} values, the J_D factor was calculated from

$$J_D = k_{ls}\left(\frac{1}{u_L}\right)\left(\frac{\mu_L}{\rho_L D}\right)^{2/3}$$

where the effective mass transfer surface was taken to be the total external surface of the particles per unit volume of bed. The viscosity and density in the above equation were at respective experimental conditions. The molecular diffusivity in water was calculated from the Othmer and Thaker equation (Reid and Sherwood, 1966) unless otherwise reported. Figure 1 is the graph of J_D factor vs. liquid Reynolds number (Re_L) with particle size and gas velocity as parameters. The data were correlated by a least-squares technique. The resulting equation is

$$J_D = 1.637(Re_L)^{-0.331}(0.2 < Re_L < 2\,400)$$

The mean and standard deviation are 7.14 and 0.28%, respectively.

Though J_D factor increases with gas flow for a given liquid flow (thus Re_L), the increase is not appreciable. For a given gas flow, increasing liquid rate results in reduced values of J_D due to the predominance of the velocity factor in the expression for J_D. Though it seems probable that mass transfer characteristics change for particle diameters larger than 0.32 cm (as suggested by Goto and Smith, 1975), thus resulting in correlating lines for different range of particle diameters, more data are required to substantiate this trend. Also, the data seem to fall in a single band, especially at high Re_L with scatter. The lower values of mass transfer coefficients obtained by Sylvester and Pitayagulsarn (1975) in comparison with those of Hirose et al. (1976) for similar flow conditions may be due to the dissimilar shape of particles which affects the in situ flow patterns. More experimental data are needed to explain this deviation.

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NOTATION

D = molecular diffusivity in liquid, cm^2/s
d_p = particle diameter, cm
G = superficial gas velocity, cm/s
J_D = mass transfer factor
k_{ls} = liquid phase mass transfer coefficient in particle-to-liquid transport cm/s
Re_L = liquid-phase Reynolds number, $(d_p u_L \rho_L)/\mu_L$
u_L = superficial velocity of liquid, cm/s
ρ_L = density of liquid, g/cm^3
μ_L = viscosity of liquid, g/(cm)(s)

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Process Synthesis Using Structural Parameters: A Problem with Inequality Constraints

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In this note, we shall expose a problem with the structural parameter method for process synthesis. The problem is almost obvious once stated, but until now, to the authors' knowledge, it has not been mentioned in the literature. It can seriously affect the expected results. The problem to be exposed does not mean that the method is valueless, as it clearly is not; it simply means that care must be taken to insure the method is really useful for a given problem.

A system of interconnected process subsystems can be modeled by the use of structural parameters which are defined by

$$x_i = \sum_{j=1}^{N} \alpha_{ij} y_j \quad i = 1, 2, 3, \ldots . N$$

$$0 \leq \alpha_{ij} \leq 1, \quad \sum_{i=1}^{N} \alpha_{ij} = 1$$

where x_i and y_i are, respectively, the input and output variables of the i^{th} subsystem, N is the total number of subsystems in the entire system, and the parameters α_{ij} are the structural parameters; that is, each is the fraction of the output stream of the j^{th} subsystem which flows into the i^{th} subsystem.