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Gas-Particle Mass Transfer in Trickle Beds

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At relatively low rates in trickle-bed reactors, flowing liquid appears not to cover the entire outer surface of the catalyst particles (Satterfield, 1975; Herskowitz et al., 1979). Under these conditions mass transfer from gas-to-particle as well as from gas-to-liquid and liquid-to-particle can influence reactor performance (when there is a limiting gaseous reactant). Mass transport from liquid to particle has been studied, for example by Goto et al. (1975), and from gas to liquid by Reiss (1967), Gianetto et al. (1973), and others. However, no information seems to be available for mass transfer coefficients k_{gs} from gas to the so-called gas-covered surface, that is, the particle surface not covered by flowing liquid. For catalysts of moderate or low activity and for slightly soluble gaseous reactants, the concentrations of reactant in the gas and on the gas-covered surface are nearly in equilibrium with each other. Thus, Herskowitz et al. (1979) found no effect of gas flow rate for the hydrogenation of α -methyl styrene using a Pd/Al₂O₃ catalyst of moderate activity. Hence, equilibrium could be safely assumed at the gas to gas-covered surface. With a more active catalyst for the same reaction, Herskowitz and Mosseri (1981) observed a significant change in global rate of reaction with gas flow rate, suggesting that gas-to-particle transport retarded the rate.

It is difficult to conceive of a reliable, direct method of measuring k_{gs} . However, the rate data of Herskowitz and Mosseri, along with available correlations for liquid-to-particle mass transfer coefficients, k_{LS} , can be used for an indirect evaluation of k_{gs} . We present here values of k_{gs} for trickle beds determined in this way. The method is suitable when the global rate is observed to vary with gas velocity.

In the Herskowitz and Mosseri study a differential reactor was used and the gas and liquid feed streams were in equilibrium with respect to hydrogen concentration. Hence, gas-to-liquid-to-particle mass transfer could be expressed in terms of a mass-transfer coefficient k_{LS} from liquid to particle. For these conditions, and assuming the weighting factor model, Tan and Smith (1980) devel-

oped a relationship between the overall effectiveness factor η_o (a measure of the global reaction rate), the fraction f of the particle surface covered by flowing liquid, and the two mass transfer coefficients k_{gs} and k_{LS} . Solved for k_{gs} this relationship is

$$Nu_{gs} = \frac{\epsilon_p k_{gs} H r}{D_e} = \frac{\phi_s \left[\frac{1}{\tanh \phi_s} - \frac{1}{\phi_s} \right]}{(1-f) \frac{3}{\phi_s} \left(\frac{1}{\tanh \phi_s} - \frac{1}{\phi_s} \right)^{-1} - \left[\eta_o - \frac{f \left(\frac{C_L^b}{C_L^*} \right) \frac{3}{\phi_s} \left(\frac{1}{\tanh \phi_s} - \frac{1}{\phi_s} \right)}{1 + \frac{\phi_s}{Nu_{LS}} \left(\frac{1}{\tanh \phi_s} - \frac{1}{\phi_s} \right)} \right]} \quad (1)$$

where

$$Nu_{LS} = \frac{\epsilon_p k_{LS} r}{D_e} \quad (2)$$

$$\phi_s = r \left(\frac{k \rho_p}{D_e} \right)^{1/2} \quad (3)$$

The concentration ratio (C_L^b/C_L^*) is equal to unity for the differential reactor conditions employed, and k and D_e are known from the experimental data of Herskowitz and Mosseri, as is η_o . The surface coverage f was also calculated by these authors from an equation like Eq. 1 but based upon negligible mass transfer resistance from gas to particle; that is, taking $Nu_{gs} = \infty$. Such f values will be correct only for a gas flow rate equal to infinity. Hence, the f results of Herskowitz and Mosseri are first extrapolated to an infinite velocity as shown in Figure 1.

The only remaining unknown in Eq. 1 is Nu_{LS} , and this can be estimated from the correlation of Goto et al. (1975). The results for k_{gs} calculated in this way are given in Figure 2 for various liquid

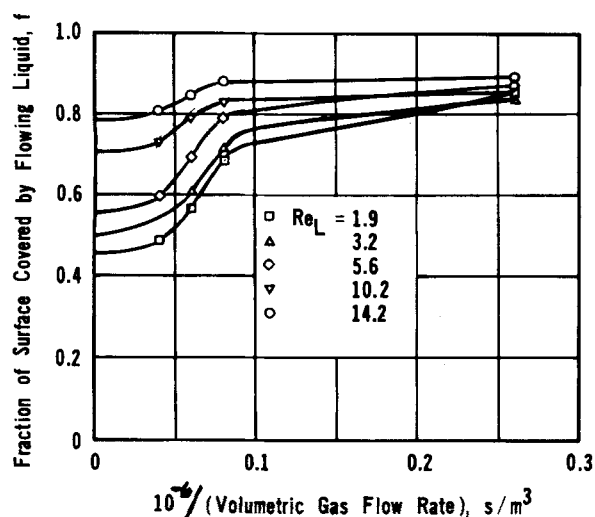


Figure 1. Effect of Gas Flow Rate on Surface Coverage, f .

and gas flow rates (represented in terms of Reynolds numbers). These coefficients apply to transport of hydrogen from the gas phase to the surface of the catalyst particle containing pores filled with liquid. Probably even the non-porous part of this surface is covered with a thin film of liquid. The distinguishing characteristic of this part of the surface is that there is no *flowing* liquid. Such a concept is a much-simplified model of what must be a complex phenomenon. Its use, dating back to the Satterfield review (1975), is an attempt to account for the effects of f . That f is not unity at low liquid rates can be observed visually and also shown indirectly from rate measurements (Herskowitz et al., 1979).

The magnitude of k_{gs} in Figure 2 is about five times the values for k_{gL} and k_{Ls} reported in the literature (Goto et al., 1975; Gianetto et al., 1973). However, when our k_{gs} is based upon a liquid-phase concentration difference, to be consistent with k_{gL} and k_{Ls} , the difference is more than one order of magnitude. Both k_{gs} and k_{gL} represent transport from gas to liquid. The difference is that k_{gs} refers to a very thin film of liquid on the surface of the particle. Only limited accuracy can be claimed for the values in Figure 2 because of the indirect method of calculation using reaction rate data. The possible error in assuming the weighting-factor model is estimated by Tan and Smith (1980) to be 7%. The uncertainty introduced by the extrapolation in Figure 1 to infinite gas rate may change k_{gs} by 30%. This was determined by calculating k_{gs} for extreme, maximum, and minimum, values of the intercepts (Figure 1) for a given liquid rate. The error caused by the method of calculation is difficult to estimate. However, the sensitivity of k_{gs} to uncertainty in f in Eq. 1 can be established. Calculations indicate that an uncertainty of 12% in f will cause k_{gs} to change by about 30%. A 12% error in f would include the maximum uncertainty as proposed by Satterfield (1975). The increase in k_{gs} with gas flow rate indicated in Figure 2 is reasonable. However, it is difficult to

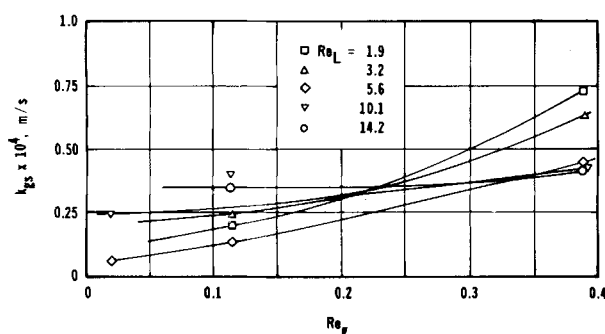


Figure 2. Gas-Particle Mass Transfer Coefficient, k_{gs} .

explain the variation with liquid Reynolds number, and this may represent the accuracy of the results.

An interesting point is that the gas-to-particle mass transfer coefficients in packed beds (only two phases, no liquid phase), as calculated from the correlation of Dwivedi and Upadhyay (1977), are three orders of magnitude greater than the k_{gs} values in Figure 2 for trickle beds. Since the latter involve a liquid phase (liquid-filled pores and a thin film of liquid on the nonporous part of the gas-covered surface), agreement with two-phase correlations is not expected.

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NOTATION

- C_L^b = concentration of reactant in the bulk liquid, kmol/m³
- C_L^e = concentration of reactant in the liquid in equilibrium with its concentration in the gas phase, kmol/m³
- C_{sat} = concentration of reactant in the liquid in equilibrium with pure gaseous reactant, kmol/m³
- D_e = effective diffusivity of the reactant in the liquid-filled pores of the catalyst, m²/s
- f = fraction of the outer surface of the catalyst particles covered by flowing liquid
- H = Henry's law constant for the reactant, [kmol/(m³ of gas)]/[kmol/(m³ of liquid)]
- k = first-order rate constant, m³/(s)(kg catalyst)
- k_{gs} = gas-to-particle mass transfer coefficient on the (1 - f)—fraction of catalyst surface (based upon gas-phase concentrations), m/s
- k_{gL} = gas-to-liquid mass transfer coefficient based upon liquid-phase concentrations, m/s
- k_{Ls} = liquid-to-particle mass transfer coefficient on the liquid-covered, f -fraction, of the catalyst surface, m/s
- Nu_{gs} = gas-particle Nusselt number, defined by Eq. 1
- Nu_{Ls} = liquid-particle Nusselt number defined by Eq. 2
- r = radius of granular catalyst particle (assumed spherical shape), m
- R = global reaction rate, kmol/(s)(kg catalyst)
- Re_g = Reynold's number for the gas, $(2r)u_g\rho_g/\mu_g$
- Re_L = Reynold's number for the liquid, $(2r)u_L\rho_L/\mu_L$
- u_g = superficial velocity of the gas, m/s
- u_L = superficial velocity of the liquid, m/s

Greek Letters

- ϵ_p = porosity of catalyst particles
- η_o = overall effectiveness factor, defined as R/kC_{sat}
- ρ_g = density of the gas phase, kg/m³
- ρ_L = density of the liquid phase, kg/m³
- ϕ_s = Thiele modulus for the catalyst particle, defined by Eq. 3
- μ_g = gas-phase viscosity, kg/(m)(s)
- μ_L = liquid-phase viscosity, kg/(m)(s)

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Turbulence and Surface Renewal at the Clean Surface of a Stirred Vessel

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INTRODUCTION

Whether the clean free surface of an agitated liquid is truly turbulent (i.e., undergoing random fluctuations) is of considerable importance (Davies, 1971); in particular, the distribution of residence times of elements of liquid at the surface has been widely discussed. Higbie (1935) proposed a single residence time, while the theory of Danckwerts (1951) was based on an exponential distribution of residence times.

Direct experimental tests of the residence time distribution have been lacking, though indirect gas absorption studies (Springer and Pigford, 1970) and experiments using radioactive tracers in a liquid stream projected towards a free surface (Davies, 1980) have suggested that the Danckwerts distribution function is indeed physically realistic.

The present work involves direct measurements of the turbulence parameters of the liquid in the plane of the surface at the surface of a stirred vessel. The distribution of the residence times of eddies is obtained from these experimental results by use of the appropriate autocorrelation functions. The latter describes the turbulence by correlations between the flows (at a given point) after various delay times Δt . For a random process, the correlation will be a maximum at $\Delta t = 0$, decreasing monotonically to zero at large times. This is the general pattern we have observed (Figure 1). We now proceed to derive the distribution of eddy residence times from these measured autocorrelations.

THEORY

The autocorrelation coefficient of velocity with respect to time, $Q(\Delta t)$, is defined as:

$$Q(\Delta t) = \overline{v'_x(t) \cdot v'_x(t + \Delta t)} \quad (1)$$

where the overbar refers to the mean value, the prime to fluctuations, and subscript x to flow in the plane of the surface. It is convenient to normalize $Q(\Delta t)$ by dividing by the mean square of the fluctuation velocity:

$$Q^*(\Delta t) = Q(\Delta t)/(\overline{v_x'^2}) \quad (2)$$

The time macroscale t_L is the mean time over which an observed fluctuation is correlated with itself, and in the mean time of persistence of the larger (energy containing) eddies, before they are replaced by another large eddy. The time t_L is defined by:

$$t_L = \int_0^\infty Q^*(\Delta t) d(\Delta t) \quad (3)$$

and is a measure of the average time for which each eddy persists in the surface region under study.

The fractional disappearance of the original eddies after time t is then given by:

fractional disappearance of original eddies =

$$(1/t_L) \int_0^t Q^*(\Delta t) d(\Delta t) \quad (4)$$

This is our model (assuming turbulence theory) for the nonpersistence of eddies in the immediate vicinity of the surface. We now compare this model with the well-known model of Danckwerts.

In the theory of Danckwerts (1951) the fraction of free surface of a turbulent liquid having ages between times t and $(t + dt)$ is designated ϕdt , where ϕ is the surface age distribution function. Assuming that the fractional rate of replacement of the "elements of liquid" in the surface, of any age group, is constant at a value s (stirring being at a steady shaft speed), Danckwerts showed that

$$\phi = se^{-st}$$

where s has the dimension of $(\text{time})^{-1}$.

Hence one derives that the fraction of surface having an age less than t is given by $\int_0^t \phi dt$, i.e.

Fraction of surface renewed by fresh eddies within time t

$$= \int_0^t se^{-st} dt = 1 - e^{-st} \quad (5)$$

In this paper we test experimentally the assumption of Danckwerts that the replacement of "elements of liquid" in the surface is independent of the time they have been there. We also try to check from turbulence measurements the value of s^{-1} , i.e., of the mean time of persistence of an eddy in the surface. We proceed

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