JOURNAL REVIEW

Trickle-Bed Reactors: A Review

Fixed-bed, catalytic reactors in which gas and liquid phases flow concurrently downward, termed trickle beds, are becoming more widely used in chemical processing, particularly in the petrochemical industry. Shah (1979) has summarized the advantages of trickle-bed reactors and mentioned some of the processes in which the reactors are used. Shah's monograph and earlier reviews (Satterfield, 1975; Goto et al., 1977; Hofmann, 1978; Gianetto et al., 1978) have discussed factors affecting reactor performance.

In the last few years additional experimental and theoretical studies that contribute to improved design and scaleup of trickle-bed reactors have been published. The scope of this paper is to review critically these improvements. Progress in understanding local rates of reaction is considered first. Then recent developments in reactor design are analyzed.

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SCOPE

The two flowing phases in trickle-beds make the reactor design problem complex. Interphase mass transfer can be important between gas and liquid and between liquid and catalyst particle. Also the rivulet-type flow of the liquid falling through the packed bed may result (particularly at low liquid flow rates) in only a part of the outer surface of the particles being covered with flowing liquid; that is, the wetting efficiency is less than 100%. This introduces a third mass transfer process from gas to the so-called "gas-covered" surface. In addition to this additional interphase mass transfer process, the conventional effectiveness factor concepts are not applicable when the wetting efficiency is not 100%. This is because the concentration of reactant is not the same on all parts of the outer surface of the particles. As a result of these and other factors, predicting the local (global) rate of reaction for a catalyst particle in a trickle-bed requires not only intrinsic kinetics but also a knowledge of the wetting efficiency and considerable mass transfer rate information.

From an intrareactor standpoint, the design of trickle-bed reactors is complicated by potential non-uniform distribution of the liquid flow across the reactor diameter and possible temperature gradients.

In the last few years the complications, both in predicting global rates and in intrareactor design, have been intensively studied. The purpose of this review is to summarize these recent developments.

CONCLUSIONS AND SIGNIFICANCE

In trickle beds the pores of the catalyst particles are normally filled with liquid. However, the outer surface of the particles may not be completely covered with flowing liquid. For reactions in which the intrinsic rate is controlled by a non-volatile reactant, such reduced wetting efficiency leads to reduced global rates. If the limiting reactant is in the gas phase, and mass transport resistances are significant, partial wetting results in increased global reaction rates. This is because the mass-transfer resistance on the non-wetted surface is less than on the surface covered with flowing liquid (the rivulets of liquid). Satterfield (1975) discussed the question of wetting efficiency f_e in general terms and presented a range of values for f_e. Since then numerous studies have provided data for wetting efficiency and a correlation has been developed (Mills and Dudukovic, 1981). With this information it is now possible to make a reasonably accurate prediction for f_e. The wetting efficiency is accounted for by expressing the global rate in terms of an overall effectiveness factor, η_o, which is a function of f_e, interphase mass transfer, intraparticle diffusion and intrinsic kinetics. Considerable progress has been made in developing approximate methods for predicting η_o. Hence, the estimation of a global reaction rate on a fundamental basis has been improved in the last few years. The new experimental data and procedures for estimating η_o are reviewed in this paper.

In designing a trickle-bed reactor, in addition to the global rate, an intrareactor model is needed. The latter aspect introduces the question of liquid distribution. Here again new information has become available for predicting: 1) the equilibrium distribution (the distribution that no longer changes with bed depth) and the length of bed necessary to achieve this distribution. Data are now available showing the effects of particle size and shape, but more information is needed on the influence of physical properties such as surface tension. Very recently the question of intrareactor heat transfer has been addressed in several studies. When reactant concentrations and heats of reaction are high, for example, in some reforming processes, interphase temperature differences and intrareactor temperature variations can be significant. Most of the progress to date has been directed toward effective radial thermal conductivities and wall heat transfer coefficients. Less information is available on predicting the performance of the complete non-isothermal reactor. An important need is for experimental data for intrareactor temperature and conversion profiles. Then reactor models such as that of Stanek et al. (1981), which includes liquid distribution and temperature variations, can be evaluated.

It is more difficult to obtain reproducible data in trickle beds than in two-phase reactors such as the gas-solid catalytic type. This seems to be due to the lack of uniformity in flow pattern of the liquid when the bed is repacked. This phenomenon makes it difficult to develop and evaluate satisfactory design methods.

LOCAL RATES OF REACTION

The rate of reaction in a single catalyst particle depends on intrinsic kinetics, intraparticle and interphase mass transfer resistances and the effective wetting of the particle. While mass transfer resistances are encountered in other three-phase reactors, the partial wetting of catalyst particles, which leads to more direct contact between the gas and the solid catalyst, is a unique feature of trickle-bed reactors.

0001-1541-83-7509-0001-$2.00.

WETTING EFFICIENCY

In trickle beds, the liquid phase flows downward in rivulets and may cover only a fraction of the external surface of the particle, especially at low superficial velocities. The fraction of the external surface of the particle that is effectively wetted is termed the external wetting efficiency.

The internal volume of the porous particles may also be only partially filled with liquid as a result of poor liquid distribution (across the reactor diameter), or vaporization of a volatile liquid in a highly exothermic reaction. The fraction of the internal volume of the particle filled with liquid is the internal wetting efficiency. With reasonable distribution of non-volatile liquid and under steady-state conditions, the internal wetting efficiency is expected to be close to unity due to capillary action.

Recent studies carried out in reacting systems have indicated that the wetting efficiency has a significant effect on the global rate of reaction.

Wetting Efficiency in Reacting Systems

The rate of reaction in partially wetted catalyst particles may be higher or lower than that obtained with completely wetted particles, depending on whether the limiting reactant is present only in the liquid or in both flowing phases. When the limiting reactant is non-volatile, as in many hydroprocessing reactions, decreasing the external and internal wetting efficiency decreases the liquid-solid mass transfer area and the active surface of the catalyst, respectively, causing the rate of reaction to drop.

Bondi (1971) reported that hydrodesulfurization rate data, obtained in a pilot-scale reactor, yielded apparent, first-order reaction rate constants at various liquid flow rates which were lower than the true rate constants. Considering interphase mass transfer resistances to be negligible, he suggested that partial external wetting lowered the rate constants. Studies of hydrotreating reactions of oil (Montagna et al. 1977) and denitrogenation of hydrotreated oil (van Klinken and van Dongen, 1980) support the findings of Bondi.

Koros (1976) carried out extensive experimental work on the decomposition of H_2O_2 in a methanol-water mixture at room temperature and pressure. He calculated the ratio of the rate constant in the trickle-bed to the rate constant obtained with the same catalyst in a stirred tank reactor. This ratio was less than unity at liquid superficial velocities less than about 0.5×10^{-2} m/s, in spite of negligible external mass transfer resistance.

In systems where the gaseous reactants are limiting, as in hydrogenation reactions, decreasing the wetting efficiency enhances the rate of reaction. This is supported by rate data reported in two recent studies. Sedriks and Kenney (1973) in experiments on the hydrogenation of crotonaldehyde on a Pd supported catalyst, at 31°C and atmospheric pressure, found that the gas-phase reaction was considerable at superficial velocities of 4.5×10^{-5} m/s for the liquid and 5.7×10^{-3} m/s for the gas. Furthermore, the rate of reaction in a preflooded bed was lower than in an initially dry bed. In case the internal wetting efficiency is less than unity, the rates of reaction in the gas-filled pores may be higher than in the liquid-filled pores due both to lower interphase and to intraparticle mass transfer resistances. Satterfield and Ozel (1973) studied the hydrogenation of benzene at 76°C, four degrees below its boiling point, where substantial gas-phase reaction was expected. The authors report that the extent of gas phase reaction decreased with increasing liquid flow rate due to higher wetting efficiencies.

However, as previously noted, the internal wetting is usually complete while the external wetting is partial. Then the gaseous reactants are transferred directly from the gas phase to the particle surface, which may be covered by a thin film of liquid. In systems where the gas-liquid and liquid-solid mass transfer resistances are significant, the gas-solid mass transfer may enhance greatly the global rate of reaction.

The significance of this effect was tested in studies recently published by Morita and Smith (1978) and Herskowitz et al. (1979). The reaction was the hydrogenation of α-methyl styrene on Pd/Al_2O_3 catalysts. Global rates were measured in a differential trickle-bed reactor operated at 40°C and atmospheric pressure. The packed bed was preflooded to ensure complete internal wetting. Morita and Smith found that the measured reaction rates were substantially higher than those calculated for completely wetted particles. It should be mentioned that the experiments were performed with pure hydrogen flowing concurrently with α-methyl styrene saturated with hydrogen. Similar experiments reported by Herskowitz et al. (1979) were performed with a more active catalyst than in the previous study, so that the liquid-solid mass transfer resistance was more significant. Rates of reaction measured as a function of the liquid flow rate yielded a minimum at a liquid superficial velocity of about 5.0×10^{-3} m/s while the rate of reaction at a velocity of 5×10^{-4} m/s was higher by 20% than the one obtained at 2×10^{-2} m/s and eight fold higher than the calculated rate of reaction assuming complete wetting. This behavior suggests that the effect of the liquid flow rate on the rate of reaction was twofold. On one hand, decreasing the liquid flow rate increases the liquid-solid mass transfer resistance causing the reaction rate to drop. On the other hand, it decreases the external wetting efficiency. Assuming that the gas-solid mass transfer resistance is negligible, lower external wetting efficiencies enhance the reaction rate.

The assumptions involved in this analysis were further tested in two sets of experiments. In one set the α-methyl styrene was almost completely free of hydrogen and the gas was pure hydrogen, and in the other, the α-methyl styrene was saturated with hydrogen and the gas was pure nitrogen. For the runs with nitrogen as the gas feed, the global rate approached zero as the liquid rate decreased. In contrast, the rate increased sharply as the liquid rate decreased for the runs with hydrogen-gas feed but a liquid feed low in hydrogen concentration. This is striking evidence that the contribution of the gas-covered surface to the global rate was greater than that of the liquid-covered surface.

A similar effect of liquid flow rate on reaction rate, including the minimum at an intermediate liquid rate, was reported recently by Mata and Smith (1981). They studied the oxidation of sulfur dioxide in liquid water catalyzed by activated carbon.

The experimental work performed in reaction systems, that included volatile and non volatile liquids and limiting reactants in both flowing phases or only in the liquid, indicates that at low liquid superficial velocities that catalyst particles are partially wetted. Furthermore, it shows that the wetting efficiency, which may have a significant effect on the global rate of reaction, depends on various operating parameters.

Effect of Operating Parameters on Wetting Efficiency

For packed-bed absorbers several correlations have been proposed for the wetting efficiency as a function of liquid and gas superficial flow rates, liquid physical properties, and particle size. Applying these results, summarized by Schwartz et al. (1976), for estimating the wetting efficiency in trickle-bed reactors is questionable, as pointed out by Satterfield (1975). Hence, data are needed for trickle beds, and several investigations have been carried out.

The first systematic studies were carried out using tracer methods. Schwartz et al (1976) developed a two-tracer method, one non-adsorbable (heptane) and one adsorbable (benzene or naphthalene), to measure indirectly the wetting efficiency. Hexane and helium were employed as liquid and gas phases respectively. The ratio of the apparent adsorption equilibrium constant, of the adsorbing tracer, determined in a trickle-bed to the equilibrium constant determined in a batch reactor was found to be 0.65, independent of liquid flow rate. The analysis published later by Mills and Dudukovic (1981) indicated that this ratio is a measure of the internal wetting efficiency.

Colombo et al (1976) determined both the internal and external wetting efficiency from the analysis of the response curves to a step decrease in the inlet concentration of a tracer (KCl and $ZnSO_4$ in aqueous solutions were used). The effective diffusivity coefficients calculated from the first moment were a function of the liquid rate

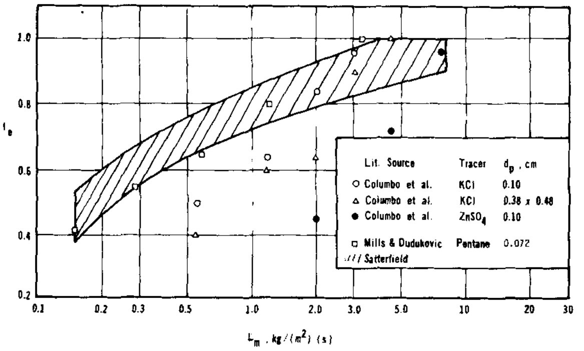

Figure 1. Effect of liquid rate on the wetting efficiency as defined by Columbo et al. (1976) and Satterfield (1975).

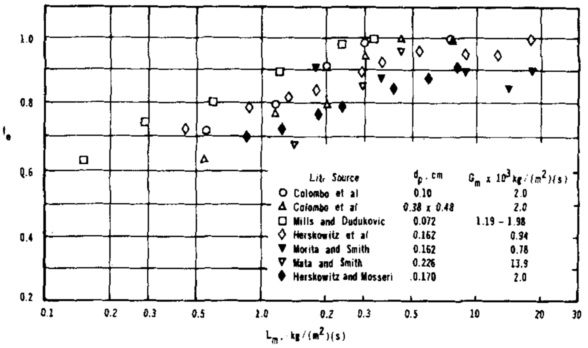

Figure 2. Effect of liquid rate on the wetting efficiency as defined by Sicardi et al. (1980) from Tracer and Reaction Studies.

in the trickle-bed reactor. Then, the external wetting efficiency was defined as the ratio of the effective diffusivity coefficients measured in the trickle-bed to those measured in a liquid-full reactor (found to be, as expected, independent of liquid rate). The values calculated for two particle sizes (1 and 3 mm) are compared in Figure 1 with the range of efficiencies proposed earlier by Satterfield (1975). Satterfield's results, for which the efficiency is defined as the ratio between the first-order rate constants obtained in a trickle-bed and a liquid-full reactor, are based upon the data of Bondi (1971). Interestingly, Colombo et al. (1976) reported that the wetting efficiency was affected by the molecular diffusivity of the tracer.

Recently Mills and Dudukovic (1981) obtained additional wetting efficiency data using the tracer method developed by Schwartz et al. (1976). Analysis of the impulse response curves yielded values of the internal and external wetting efficiencies as a function of the liquid flow rate for small particles (7.2×10^{-4}m). The internal wetting efficiency was found to be close to unity over the range of liquid rates: 0.15 to 3.5 kg/(m)²(s). They obtained a similar result from the analysis of the Colombo et al (1976) data. Mills and Dudukovic pointed out that the lower value reported by Schwartz et al. may be attributed to the different state of activation of the packing, in the batch experiments and the trickle bed experiments, which affected the adsorption equilibrium constants.

The external wetting efficiency was calculated from the ratio of the effective diffusivities in the trickle-bed and liquid-full reactor, as proposed by Colombo et al. (1976). The values of f_e increased with increasing liquid rate, in agreement with previous studies, as shown in Figure 1.

A significant effect of liquid rate on the external wetting efficiency was also reported by Koros (1976). At a liquid flow rate of less than 10 kg/m²·s, the external wetting efficiency, calculated as suggested by Satterfield, increased with increasing liquid rate. However Koros also found that the packing procedure was not reproducible. Impurities in the hydrogen peroxide may have contributed to the reproducibility problem.

A different method was employed by Specchia et al. (1978). These authors measured the dissolution of phthalic anhydride in $KHCO_3$-K_2CO_3 aqueous solution. From solubility measurements and the physico-chemical constants previously determined, the ratio of the effective area for liquid-solid mass transfer to the total external area of the particles was calculated. This ratio, termed the external wetting efficiency, increased with increasing liquid flow rate but its values were lower than those found from the tracer experiments. The authors pointed out that this "chemical method" is strongly dependent on the chosen hydrodynamic model.

Wetting efficiencies also have been evaluated in reacting systems where the gaseous reactant is rate limiting, (Morita and Smith, 1978; Herskowitz et al., 1979; Mata and Smith, 1981; Herskowitz and Mosseri, 1981). Global rates of reaction measured for one or two catalyst activities were used to calculate the wetting efficiency from one of the models of a partially-wetted particle presented in the following section. The gas-solid mass transfer resistance was assumed to be negligible, and the liquid-solid mass transfer coefficient was calculated from the Goto and Smith (1975) correlation. The results plotted in Figure 2 indicate a reasonable agreement. The discrepancy observed at low liquid flow rates may be a result of the effect of gas flow rate on the wetting efficiency. Herskowitz and Mosseri report that the wetting efficiency decreased with increasing gas flow rate, especially at low liquid rates. Specchia et al. (1978) and Sicardi et al. (1981) found an opposite trend.

Sicardi et al. (1980) suggested that the external wetting efficiency calculated from tracer data may also be defined as the square root of the ratio of the effective diffusivities. Neither of the definitions has been proven to be equal to the efficiency defined as the ratio of the wetted to total outer surface, as pointed out by Mills and Dudukovic. However, if the latter definition is used, a better agreement between the wetting efficiencies calculated from tracer and reaction data is obtained, as illustrated in Figure 2. The external wetting efficiency calculated from the Colombo et al (1976) and Mills and Dudukovic (1981) studies, together with the external wetting efficiency values reported by Herskowitz et al. (1979), were correlated by Mills and Dudukovic as a function of the Reynolds, Weber and Froude numbers:

$$f_e = \tanh\left[0.664\, Re_L{}^{0.333} Fr_L{}^{0.195} We_L{}^{-0.171}\left(\frac{a_t d_p^2}{\epsilon_B^2}\right)^{-0.0615}\right] \tag{1}$$

This correlation is based on very few data points. A comparison of the predicted values of f_e with the recently published data by Mata and Smith (1981) shows significant discrepancies at low liquid flow rates but good agreement at high rates ($f_e \rightarrow 1$). For example, at $u_L = 1.4 \times 10^{-3}$ m/s, the predicted value is 0.85 while the experiments give 0.68.

Normally, the external wetting efficiency ranges from 0.6 to 1.0. So the fractional error in estimating f_e cannot be large. However, in the case of a fast reaction limited by mass transfer resistances and a volatile reactant, a little change in f_e changes the global rate of reaction greatly. More data are needed for testing the correlation of Eq. 1.

Two principal methods for measuring f_e have been presented, a tracer method and a reaction method. The heterogeneous chemical reaction method has several advantages:

1. The external wetting efficiency is clearly defined and may be calculated from the model described in the next section.
2. The existence of dry regions in the bed may be detected. If the limiting reactant is volatile, such dry regions would decrease the global rate of reaction significantly (Herskowitz and Mosseri, 1981). The internal wetting efficiency calculated from tracer data may also indicate that dry regions are formed.
3. Since external wetting efficiencies are required for calculations of global rates of reaction, values obtained under reaction conditions may be more reliable.

Theoretical Models

The global rate of reaction r_o may be expressed as a product of an overall effectiveness factor (which includes interphase mass transfer resistances) and the rate of reaction evaluated at the bulk

TABLE 1. APPROXIMATE EXPRESSIONS FOR THE OVERALL EFFECTIVENESS FACTOR IN PARTIALLY WETTED PARTICLES

Geometry	η_o
Slab	$\dfrac{f_e C_L^*}{\dfrac{\phi^2}{\alpha_{gLS}} + \dfrac{\phi}{\tanh\phi}} + \dfrac{1-f_e}{\dfrac{\phi^2}{\alpha_{gs}} + \dfrac{\phi}{\tanh\phi}}$
Cylinder	$\dfrac{f_e C_L^*}{\dfrac{\phi^2}{\alpha_{gLS}} + \phi\dfrac{I_o(2\phi)}{I_1(2\phi)}} + \dfrac{1-f_e}{\dfrac{\phi^2}{\alpha_{gs}} + \phi\dfrac{I_o(2\phi)}{I_1(2\phi)}}$
Sphere	$\dfrac{f_e C_L^*}{\dfrac{\phi^2}{\alpha_{gLS}} + \dfrac{3\phi^2}{3\phi\coth(3\phi)-1}} + \dfrac{1-f_e}{\dfrac{\phi^2}{\alpha_{gs}} + \dfrac{3\phi^2}{3\phi\coth(3\phi)-1}}$

conditions. For an isothermal, irreversible, m-th order reaction, it is expressed as follows:

$$r_o = \eta_o k_v C_L^m = k_v \frac{\int_{v_p} C_i^m dV}{V_p} \tag{2}$$

C_L is the bulk liquid concentration in nonvolatile limiting reactant systems, or the reactant concentration in the liquid in equilibrium with its concentration in the bulk gas in volatile, limiting-reactant systems. From the equality in Eq. 1 the overall effectiveness factor η_o is given by:

$$\eta_o = \frac{1}{V_p}\int_{V_p} C^m dV \tag{2a}$$

where

$$C = C_i/C_L$$

The dimensionless intraparticle concentration C is the solution of the governing differential equation which results from a differential mass balance for the reactant inside the liquid-filled, porous particle:

$$\nabla^2 C - \phi^2 C^m = 0$$

where

$$\phi = \frac{V_p}{S_x}\sqrt{\frac{\rho_p k_v C_L^{m-1}}{D_e}} \tag{3}$$

The external surface of the particle is assumed to be divided into a wetted surface S_w and a so-called "dry" surface S_D which actually may be covered by a very thin film of liquid. Furthermore, it is assumed that the rates of gas-liquid and liquid-solid mass transfer are equal. Accordingly, appropriate boundary conditions may be written:

$$\frac{\partial C}{\partial n} = \alpha_{gLs}(C_L^* - C) \quad \text{on } S_w \tag{4a}$$

$$\frac{\partial C}{\partial n} = \alpha_{gs}(1 - C) \quad \text{on } S_D \tag{4b}$$

where

$$C_L^* = \frac{C_{L,b}}{C_L} \tag{4c}$$

$$\frac{1}{\alpha_{gLS}} = \frac{S_x}{V_p} D_e \left[\frac{1}{\epsilon_p k_s} + \frac{f_e a_t}{K_L a_i}\right]; \quad \alpha_{gs} = \frac{V_p}{S_x}\frac{\epsilon_p k_{gs}}{D_e} \tag{4d}$$

Partial differential equations and complete sets of boundary conditions are given in Table A (Appendix) for various particle shapes. Equations A-1, A-6 and A-11 can be solved analytically only for $m = 1$. The solutions also are given in Table A. However, the mixed boundary conditions in Eq. 4 render the expression of A_n, B_n, or D_n as a function of α_{gLS}, α_{gs} and f_e difficult. Mills and Dudukovic (1979, 1980) and Herskowitz (1981) proposed solutions to this problem. Mills and Dudukovic developed a dual series method of solution coupled with a method of weighted residuals which yielded approximate solutions. Herskowitz expressed the boundary condition 4 in terms of Fourier cosine series. Then the coefficients could be calculated from sets of linear algebraic equations.

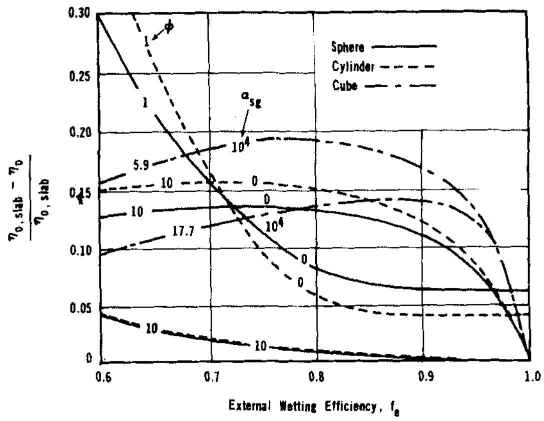

Figure 3. Deviation of effectiveness factors of spherical, cylindrical, and cubical particles ($\alpha_{gLs} = 1.0$).

Fortunately, carrying out the integration in Eq. 2a, with the expression for C substituted from Table 1 (for $m = 1$) yields simple results:

$$\eta_o = \frac{A_1(\alpha_{gLS}, \alpha_{gs}, f_e, \phi)}{\phi}[1 - \exp(-2\phi)] \quad \text{for slab} \tag{5a}$$

$$\eta_o = \frac{B_1(\alpha_{gLS}, \alpha_{gs}, f_e, \phi)}{\phi} I_1(2\phi) \quad \text{for cylinder} \tag{5b}$$

$$\eta_o = \frac{D_1(\alpha_{gLS}, \alpha_{gs}, f_e, \phi)}{\phi} I_1(3\phi) \quad \text{for sphere} \tag{5c}$$

Although the constants A_1, B_1, D_1 are a function of the number of terms in the linear algebraic equations, analysis indicates that only 20 to 40 terms are required to achieve a change in η_o of less than 0.5%. The solutions in Eq. 5 cover all cases, ranging from a nonvolatile limiting reactant for which $\alpha_{gs} = 0$ to a gaseous limiting reactant with negligible gas-solid mass transfer resistance for which $\alpha_{gs} \rightarrow \infty$.

A simple solution of Eq. 3 ($m = 1$) for a cubical shape was published by Herskowitz et al. (1979). The solution was restricted to values of $f_e = 1/6, 2/6, 3/6, 4/6, 5/6$, or 1 so that intermediate values had to be evaluated graphically. A comparison between the values of η_o for the various shapes presented by Herskowitz (1981) is shown in Figure 3. The figure shows that the effect of particle shape on η_o is not significant. Similar results were reported by Mills et al. (1981).

Several rivulets separated by gas-covered regions may flow on the particle surface. Capra et al. (1981) tackled this problem for a first-order reaction and cylindrical particles. They report that the intraparticle concentration profiles are strongly affected by the distribution and the size of the rivulets but the overall effectiveness factor is only slightly affected. Calculations based on the model proposed by Herskowitz (1981) gave similar results. Therefore neither particle shape nor the number of rivulets flowing on the surface seriously affect the overall effectiveness factor. The evaluation of η_o from the models mentioned above requires extensive computation work. Hence simple, approximate solutions were developed.

Ramachandran and Smith (1979) derived an approximate solution for η_o in partially wetted particles. The basic assumption was that η_o may be expressed as a weighted average of η_L (the effectiveness factor for a particle completely covered by liquid) and η_g (the effectiveness factor for a particle completely covered by gas) as follows:

$$\eta_o = f_e \eta_L + (1 - f_e)\eta_g \tag{6}$$

This approximate method applied for slab geometry agreed well with the numerical solution which did not involve the assumption of Eq. 6.

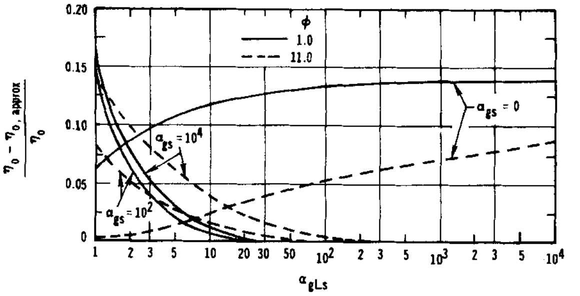

Figure 4. Comparison of exact and approximate solutions for η_o (slab geometry and f_e = 0.7).

This approach was further developed and extended to spherical geometry by Tan and Smith (1980). Mills and Dudukovic (1980) derived similar expressions for slab and spherical geometries and for cylindrical particles. These expressions are listed in Table 1.

Comparison between the approximate and exact solutions for a slab, a cylinder and a sphere were carried out by Tan and Smith (1980), Mills and Dudukovic (1980), Mills et al. (1981), Capra et al. (1981), and Herskowitz (1981). The discrepancy was less than 10% over a wide range of parameters. Larger deviations existed only for low values of the Thiele modulus ($\phi < 1$). Furthermore, the approximate solutions were lower than the exact solutions. This is illustrated in Figure 4 for a slab. While the approximate models for partially wetted particles are based on assumptions which may not fit the physical situation, they are of important practical value. The concentration profiles computed by Capra et al. (1981) depend on the *size and distribution* of the rivulets, while η_o does not. Therefore, a simple model is adequate for the analysis of partially wetted particles and the prediction of the quantity of interest, the overall effectiveness factor.

All models presented thus far have been for first-order reactions, Goto et al. (1981) solved the effectiveness factor problem for nonlinear kinetics. First, a numerical solution of Eq. A-11 with the appropriate boundary conditions given in Table A was computed for a spherical particle and substituted into Eq. 2a to evaluate η_o. Then an approximate solution was obtained by utilizing an assumption similar to Eq. 6. Thus, for a limiting gaseous reactant

$$\eta_o = f_e(C_{S,L}/C_L)^m \eta_L + (1 - f_e)(C_{s,g}/C_L)^m \eta_g \tag{7}$$

where $C_{S,L}$ and $C_{s,g}$ are the surface concentration on the liquid and the gas-covered parts. $C_{S,L}$, $C_{s,g}$, n_L and n_g were evaluated from the numerical solution of Eq. A-11 for completely wetted and completely dry particles. A further simplification was introduced by employing Bischoff's (1965) approximation to obtain explicit solutions of n_L or n_g for any kinetics. A comparison of the three methods indicates that Bischoff's approximation introduces little error and simplifies greatly the computation task. For the case of a limiting nonvolatile reactant, the following expression was derived:

$$\eta_o = (C_{S,L}/C_L)^m \eta_L \tag{8}$$

where the particle size in the Thiele modulus and in the modified Biot number are divided by f_e.

The possibility of partial internal wetting was considered by Dudukovic (1977) and Mills and Dudokovic (1979) for liquid limiting reactants. Martinez et al. (1981) extended these models to include gas-phase reaction in dry zones. The numerical solution shows, as expected, that lowering the internal wetting efficiency increases the overall effectiveness factor due to negligible intraparticle mass transfer resistance in dry pores. It should be pointed out that the solution requires two additional parameters, the fraction of the particle external surface in contact with dry pores and the average depth of the dry pores. The internal wetting efficiency is calculated from these two parameters. An approximate, explicit expression proposed for η_o gives results which agree well with the exact solution.

Sicardi et al. (1980) proposed to reconcile discrepancies between wetting efficiencies measured by tracer and "chemical" methods by including the effect of stagnant liquid zones. They divide the wetted external surface into a dynamic and a stagnant zone. Then a nonvolatile reactant in the liquid is transferred to the solid through dynamic and static areas. It is also transferred between the two zones, giving rise to three mass transfer coefficients. These coefficients were evaluated as a function of the liquid rate. Predicted rates of reaction considering only the dynamic areas were lower than those which included the static zones.

The effect of the wetting efficiency on the selectivity of consecutive first-order reactions was examined by Herskowitz (1981a). The exact solution previously described was employed. For the case of a volatile reactant and a nonvolatile intermediate product the effect was significant.

INTERPHASE MASS TRANSFER

Since gas-liquid and the liquid-solid mass transfer resistances can be important in trickle-bed reactors, a number of experimental studies have been made. Shah (1979) has critically reviewed the correlations reported before 1977. The reviews of Goto et al. (1977), Charpentier (1976) and van Landeghem (1980) are also available.

In the last few years several important contributions have been recorded. However, the complex problem of gas-solid mass transfer which can be important for partially wetted pellets, has not been studied. Since this resistance is relatively small, gas-solid transport is often assumed to occur at near-equilibrium conditions.

Gas-Liquid Mass Transfer

The overall gas-liquid mass transfer coefficient may be expressed, according to the two-film concept, in terms of the liquid side and the gas side mass transfer coefficients:

$$\frac{1}{K_L a_i} = \frac{1}{H^* k_g a_i} + \frac{1}{k_L a_i} \tag{9}$$

For slightly soluble gases such as hydrogen or oxygen the values of H^* are larger than unity. Then $H^* k_g a_i$ is at least one order of magnitude larger than $k_L a_i$ over the range of liquid and gas rates used in trickle-bed (Goto et al., 1977) and $K_L a_i$ is approximately equal to $k_L a_i$.

The liquid-side mass transfer coefficient $k_L a_i$ may be obtained by absorption measurements with or without chemical reaction in the liquid phase. Fukushima and Kusaka (1977, 1977a) measured $k_L a_i$ and the interfacial area a_i using the process of oxygen absorption into sodium sulfite solution with cobaltous chloride as a homogeneous catalyst. The data were correlated in terms of the gas and liquid Reynolds numbers, the liquid holdup, the column and particle diameter and a shape factor, as follows:

$$\frac{k_L a_i d_p^2}{D_L(1 - h_e)} = \beta_1 S_p^{\beta 2} Re_L^{*\beta 3} Re_g^{*\beta 4} Sc^{1/2} (d_p/d_t)^{\beta_5} \tag{10a}$$

$$\frac{a_i d_p}{(1 - h_e)} = \gamma_1 S_p^{\gamma 2} Re_L^{*\gamma 3} Re_g^{*\gamma 4} (d_p/d_t)^{\gamma_5} \tag{10b}$$

TABLE 2. CONSTANTS IN EQ. 10

Flow Regimes	β_1	β_2	β_3	β_4	β_5	γ_1	γ_2	γ_3	γ_4	γ_5
Gas-Continuous	2.0	0.2	0.73	0.2	0.2	3.9×10^{-3}	−0.1	0.4	0.0	−2.0
Pulsing	0.11	0.0	1.0	0.4	−0.3	2.2×10^{-4}	−0.3	0.66	0.20	−2.5
Spray	0.037	0.0	0.48	0.9	−0.3	7.5×10^{-5}	−0.2	0.15	0.66	−2.5
Dispersed-Bubble	6.1×10^{-5}	−0.6	2.1	0.2	−1.5	2.8×10^{-7}	−0.9	1.8	0.0	−3.3

The constants β and γ, which depend on the flow regime, are given in Table 2. These correlations were obtained with relatively large particles (1.28 and 2.54 cm spheres and 1.16 cm Raschig rings) but a comparison with previously measured k_La_i and a_i yielded reasonable agreement.

Recently, Seirafi and Smith (1980) measured k_La_i by a dynamic method. The mass transfer coefficients were calculated from the zeroth and the first moments obtained from the analysis of experimental breakthrough curves. The experiments were conducted in a trickle-bed reactor in which benzene was absorbed from water on 0.108 cm activated carbon particles. Values of k_La_i calculated from the Fukushima and Kusaka correlation agree well with those reported by Seirafi and Smith in the pulsing-flow regime.

However, the Fukushima and Kusaka correlation could not predict the interfacial areas measured by Morsi et al. (1982) for small packings. The latter measurements were carried out by chemical methods for organic and aqueous solutions with 0.116 cm glass beads and 0.24 cm catalyst ($Co/Mo/Al_2O_3$) spheres. Furthermore, the values of a_i obtained for the aqueous solution data may not be useful for predicting the interfacial area in organic solutions. Further work is required to confirm those results. Morsi et al. (1980) also presented data, collected by similar methods, for 0.648 cm Raschig rings, which indicate that the nature of the liquid phase has little effect on the interfacial area. The agreement between these data and the predictions of the Fukushima and Kusaka correlation is good. Morsi et al propose a modification of the Gianetto et al. (1970) correlation:

$$a_i = 7.75 \times 10^5 \epsilon_B \delta_{Lg}/a_t$$

for

$$3 \times 10^{-5} < \epsilon_B \delta_{Lg}/a_t < 7 \times 10^{-4} \qquad (11)$$

This equation, which is applicable in the gas-continuous flow regime, could not correlate the aqueous solution data, probably because of their anticoalescent characteristics. δ_{Lg}, the two-phase pressure drop, may be estimated from the Midoux et al. (1976) correlation.

The study published by Mahajani and Sharma (1979) with 0.4 cm particles (pellets and granular) also indicates that there is little effect of liquid characteristics (organic or aqueous) on the interfacial area. They measured the absorption of CO_2 (from lean gas mixtures) in aqueous solutions of NaOH, MEA in n-butanol, and CHA in p-xylene containing 10% isopropanol. In the gas-continuous flow regime the interfacial area was a weak function of the liquid and gas rates. Similar conclusions could be drawn from the k_La_i data reported in this study. Furthermore, the k_La_i values obtained for the aqueous solution agree well with those reported by Smith and Seirafi. Mahajani and Sharma correlated their values with a Sherwood-Holloway type equation,

$$\frac{k_La_i}{D_L} = 8.08 \left(\frac{L_m}{\mu_L}\right)^{0.41} Sc_L^{1/2} \qquad (12)$$

which is in excellent agreement with the Goto and Smith (1975) correlation.

The application of correlations of gas-liquid mass transfer coefficients for organic solutions and small packings was examined by Turek and Lange (1981). They measured the absorption of hydrogen in α-methyl styrene at low liquid rates ($0 - 4.6 \times 10^{-4}$ m/s) and for small particles (0.054, 0.09 and 0.3 cm). The correlation that fits their data,

$$\frac{k_La_i}{D_L} = 16.8 Ga^{-0.22} Re_L{}^{0.25} Sc^{1/2} \qquad (13)$$

gives much lower values than the Goto and Smith correlation. Clearly, further experimental work should be done to obtain reliable correlations of k_La_i for organic solutions and small particles, which are frequently used in catalytic, trickle-bed reactors.

Turek and Lange also calculated k_La_i values from rate data obtained from α-methyl styrene hydrogenation on a Pd catalyst. These values were much higher than those predicted by Eq. 13. This is not surprising since at the low liquid rates employed partial wetting of the bed probably had a major effect on the observed reaction rate.

Liquid-Solid Mass Transfer

Liquid-solid mass transfer coefficients in trickle-beds have been measured by three methods:

a. Dissolution of slightly soluble solids into the liquid.
b. Electrochemical reaction.
c. Chemical reaction with significant liquid-solid mass transfer resistance.

Method (a) has been by far the most widely used. Specchia et al. (1978) and Satterfield et al. (1978) have summarized the work published before 1978. Since then several important contributions have been reported. They are summarized in Table 3.

In the studies conducted by Satterfield and Specchia the same system was used, allowing for a direct comparison. Mass transfer coefficients measured at zero gas flow rate were in good agreement. Specchia et al. (1978) correlated their data, along with those of Goto and Smith (1975), in terms of modified Sherwood and Reynolds numbers as previously suggested by *van Krevelen and Krekels* (1948). Thus:

$$Sh'_L = 2.79(Re'_L)^{0.70} Sc_L^{1/3} \quad 0.1 < Re'_L < 20 \qquad (14)$$

where

$$Re'_L = \frac{u_L \rho_L}{\mu_L a_t}; \quad Sh'_L = \frac{k_s a_s}{a_t}\left(\frac{d_p}{D_L}\right)$$

This correlation agrees well with a *similar correlation* proposed by Satterfield et al. (1978):

$$\mathrm{Sh}'_\mathrm{L} = 0.815(Re^*_L)^{0.822} Sc_L^{1/3} \quad Re^*_L < 60 \qquad (15)$$

where

$$Re^* = \frac{u_L \rho_L d^*_p}{\mu_L}$$

Herskowitz et al. (1979) calculated liquid-solid mass transfer coefficients from global rates of reaction measured in a trickle bed. Their data agree reasonably well with the correlations expressed in Eqs. 14 and 15.

However, the study of gas rate effects on k_sa_s in the gas-continuous flow regime produced marked differences. Specchia et al. (1978) reported that k_sa_s almost tripled when the gas superficial velocity changed from zero to 0.5 m/s. Over the same range Satterfield et al. (1978) found no effect of the gas rate. These latter results are supported by measurements carried out in a trickle bed packed with 0.635 cm Berl saddles coated with a molten mixture of benzoic acid and fluorescent dye (Reuther et al., 1980). Reuther correlated k_sa_s values measured in the gas-continuous flow regime in terms of a modified Sherwood number as a function of a modified Reynolds number:

$$\epsilon_B Sh''_L = 0.0819(Re''_L)^{0.777} Sc^{1/3}; \quad Re''_L < 55 \qquad (16)$$

where

$$Sh''_L = \frac{k_s a_s}{D_L a_t^2}; \quad Re''_L = \frac{\mu_L \rho_L}{\mu_L a_t h_e}$$

Comparison with the previous correlations shows that the Specchia correlation underestimates k_sa_s by about 30% while the Satterfield et al. correlation gives excellent agreement.

Recently Yoshikawa et al. (1981) measured liquid-solid mass transfer coefficients in beds of very small particles (0.46 to 1.3×10^{-3} m). They employed an ion-exchange reaction (Na^+ ions with $R{-}H^+$ resin particles) followed by an instantaneous irreversible neutralization reaction. The coefficients were only slightly affected by the gas flow rate in the gas-continuous flow regime. The following correlation was proposed for the range, $0.46 < d_p < 1.3 \times 10^{-3}$ m, $0 < Re_g < 12$, $0.5 < Re_L < 50$:

$$\frac{\epsilon_B Sh'}{Sc^{1/3}} = (1.0 + 0.003 Re_L Re_g^{1/2})(0.765 Re_L^{0.18} + 0.365 Re_L^{0.616}) \qquad (16a)$$

TABLE 3. LIQUID-SOLID MASS TRANSFER STUDIES

Reference	Packing		Liquid		Gas		Correlations in the Pulsing Regime
	Shape	Size, cm	Type	L_m, kg/m²·s	Type	G_m, kg/m²·s	
Specchia et al. (1978)	Cylinders of benzoic acid	0.3 and 0.6	Water, water with surfactant, water with glycerol	1.6–8.3	Air	0–1.9	$\ln[Sh'_L Sc_L^{-1/3}] = 1.84 + 0.311 \ln(We'_L \times 10^3) - \dfrac{6.33}{[\ln(We'_L \times 10^3)]^2}$ (3-1)
Satterfield et al. (1978)	Cylinders of benzoic acid	0.3 and 0.6	Water	0.48–25	Air, helium, argon, nitrogen	0–1.9	$Sh'_L Sc_L^{-1/3} = 0.334\, Ko^{0.202}$ (3-2)
Chou et al. (1979)	Nickel plated brass spheres	0.78	Water	8.4–23.5	Air	0.12–0.45	$\epsilon_B Sh'_L Sc_L^{-1/3} = 0.72\, Re_L^{0.54} Re_g^{0.16}$ (3-3)
Ruether et al. (1980)	Berl saddles	0.635	Water	2.1–94.4	Air	0.33–1.77	$\epsilon_B Sh''_L Sc_L^{-1/3} = 0.68\, (Re'')_L^{0.416}$ $Re''_L > 100$ (3-4)

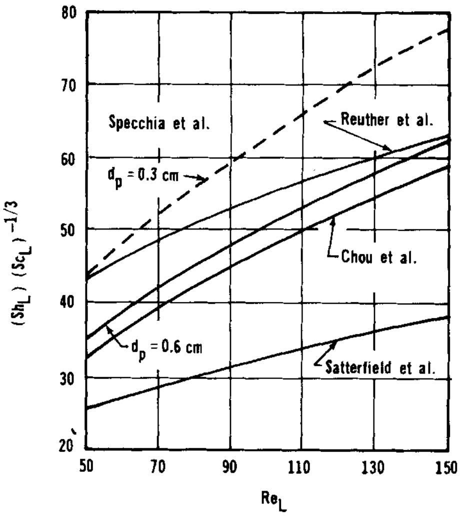

Figure 5. Comparison of liquid-solid mass transfer correlations for the water-air system; $Re_g = 100$, $\epsilon_B = 0.38$, $d_p = 6.0 \times 10^{-3}$ m.

This correlation predicts larger values of Sh′ than the prior results and is recommended for estimating liquid-solid mass transfer coefficients in beds of very small particles.

The transition from the gas-continuous regime to the pulsing flow regime causes an abrupt increase in the liquid-solid mass transfer coefficient, as reported by Satterfield et al. (1978), Chou et al. (1979), and Reuther et al. (1980). In contrast, Specchia found a gradual change. Correlations of the Sherwood number as a function of the Weber, Kolmogoroff, and Reynolds numbers in the pulsing flow regime are listed in Table 3.

A comparison of the correlations in the pulsing flow regime is shown in Figure 5. The external holdup and the two-phase pressure drop were calculated from the Specchia and Baldi (1977) correlations. In the case of large particles the agreement between three correlations is reasonable. It should be pointed out that Chou et al. (1979) measured local liquid-solid mass transfer coefficients from a single sphere using an electrochemical technique. The Satterfield et al. (1978) correlation gives significantly lower values; their experimental values were much lower than those published by Specchia et al.

For smaller particles, the Specchia correlation predicts higher values than the other correlations. This correlation is based on data measured over a wide range of operating parameters, and it is recommended for estimating $k_s a_s$. However, it should be tested in beds of small particles and with organic liquids used in catalytic trickle beds.

HEAT TRANSPORT EFFECTS

When trickle-bed reactors are used for desulfurization or oxidation of small fractions of a stream, the concentrations of reacting species are so small that significant temperature changes do not occur. When the concentrations are large, as in reforming, temperature gradients may become important. Catalyst particles in trickle-beds are usually completely filled with liquid. Then intraparticle temperature gradients are negligible due to the low effective diffusivities in the liquid phase, as pointed out by Satterfield (1975) and Baldi (1980). However, if the limiting reactant and the solvent are volatile, vapor phase reaction may occur in the gas-filled pores causing significant intraparticle temperature gradients. Such effects have been reported by Sedriks and Kenney (1973) and more recently by Hanika et al. (1975). In the latter, the hydrogenation of cyclohexene to cyclohexane was studied at atmospheric pressure and 60°C, which is close to boiling point of cyclohexane (80.5°C). Moreover, the liquid superficial velocity was very low (1×10^{-4} m/s) while the gas superficial velocity was much higher (2.5×10^{-2} m/s). This resulted in poor wetting effi-

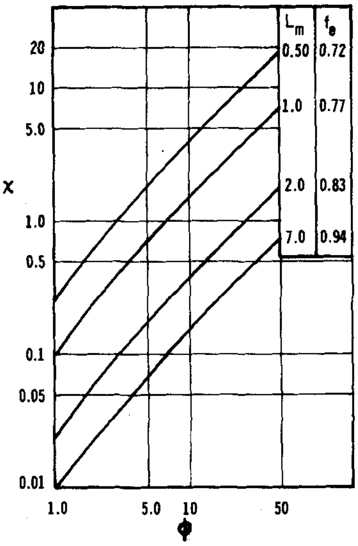

Figure 6. Effect of wetting efficiency on the overall effectiveness factor: $Sc_L = 100$; $d_p = 1.5 \times 10^{-3}$ m; $\epsilon_p = 0.5$; $\epsilon_B = 0.4$; $\tau = 2$; $\mu_L = 8 \times 10^{-4}$ kg/(m)(s); $C_L^* = 1.0$.

ciency and extensive evaporation. Under those conditions temperature differences up to 15°C were measured. In runs carried out at lower temperatures only liquid phase reaction was observed with temperature differences of less than 0.5°C.

Interphase heat transfer resistances should also be considered. A heat balance in the liquid phase may be expressed as follows:

$$(h_{Ls}a_t/\rho_p)(T_s - T_f) = (-\Delta H)r_0 \qquad (17)$$

or

$$T_s - T_f = \frac{(-\Delta H)r_o}{h_{Ls}a_t/\rho_p} \qquad (18)$$

There is no correlation available for estimating h_{Ls} in trickle beds. An approximate value may be obtained from the Whitaker (1972) correlation; typical values of $Pr_L = 10$, $\lambda_L = 0.126$ J/(m)(s)(K) and $\rho_p = 1{,}500$ kg cat/m^3, a Reynolds number as low as unity, and $d_p = 1.5 \times 10^{-3}$ m, yield $h_{Ls}a_t/\rho_p = 335$ J/(kg cat)(s)(K). In hydrogenation reactions, the rate of reaction may be as high as 1×10^{-6} kg mol/(kg cat)(s) (Herskowitz et al., 1979; Hanika et al., 1975). Substituting those values in Eq. 18 yields $T_s - T_f = 0.4$ K. Hanika reports $T_s - T_f \simeq 0.5$ K.

If the particles are only partially wetted, heat may be transferred from the liquid in the pores to the gas phase. A similar calculation with $Pr_{H_2} = 0.7$, $\lambda_{H_2} = 0.168$ J/(m)(s)(K), $Re_{H_2} = 10$, and $f_e = 0.6$ gives $h_{gs}a_{gs}/\rho_p = 251$ J/(kg cat)(s)(K). The temperature drop in this case is also negligible.

EFFECTS OF COUPLED MASS TRANSPORT AND PARTIAL WETTING

The significance of partial wetting on the global rate of reaction depends on several factors, such as intra and interparticle mass transfer resistances, and the volatility of the limiting reactants and of the solvent. If the limiting reactant is nonvolatile, the effect of the wetting efficiency on the overall effectiveness factor ($0.6 < f_e < 1.0$) is not large, as pointed out by Mills and Dudukovic (1979) and Herskowitz (1981). Moreover, errors in estimating the wetting efficiency would not change greatly the calculated values of η_o. Hence, the available data on the wetting efficiency as a function of the operating parameters provides accurate enough information for calculating η_o.

If the limiting reactant is volatile, but interphase mass transfer resistances are not significant, the effect of f_e on η_o also is negligible. If mass transfer resistances are important the overall effectiveness factor may be greatly affected by the wetting efficiency. As an illustration, a set of operating conditions is selected to calculate the difference between the overall effectiveness factors of a partially wetted and a completely wetted particle, expressed as follows:

$$\chi = \frac{\eta_o - \eta_o(f_e = 1)}{\eta_o(f_e = 1)} \qquad (19)$$

The wetting efficiency is given by the expression:

$$f_e = 0.77L_m^{0.1} \qquad (20)$$

while the gas-liquid and liquid-solid mass transfer coefficients are calculated from the Goto and Smith (1975) and Specchia et al. (1978) correlations, respectively. Using the operating parameters listed in Figure 6 in these correlations, expressions for k_s and K_La_i as a function of the liquid superficial velocity L_m are obtained. These expressions along with Eq. 20 are substituted into Eq. 4d to yield:

$$\frac{1}{\alpha_{gLs}} = \frac{1}{1.05L_m^{0.3}} + \frac{1}{6.91L_m^{0.6}} \qquad (21)$$

The overall effectiveness factor is calculated from the approximate solution for a spherical particle given in Table 2. The gas-solid Biot number α_{gs} is assumed to be very large.

The plots in Figure 6 clearly indicate that the effect of partial wetting is very significant at high values of the Thiele modulus ϕ and at low liquid superficial flow rates. Moreover small changes in f_e may cause large changes in η_o. Therefore, a reliable correlation of the wetting efficiency is required. Considering the progress that has been made, operating at $L_m < 10$ kg/(m^2)(s) and $\phi \gg 1$ would require experimental measurements of the wetting efficiency in the reaction system. Furthermore, testing for significant mass transport resistance by measuring the rate of reaction as a function of the liquid flow rate may lead to pitfalls due to the opposing effects of the liquid rate (the mass transfer rate from the "dry" surface increases with decreasing liquid rate while the mass transfer rate from the wetted surface decreases with decreasing liquid rate). If $\phi < 1$ the overall effectiveness factor is little affected by the liquid flow rate and the wetting efficiency.

Recently, Lee and Smith (1981) have proposed criteria of negligible transport effects and of partial wetting in terms of observable quantities.

REACTOR DESIGN: FLOW REGIMES

Multiple flow regimes are observed in studying hydrodynamics in trickle-bed reactors. Shah (1979), Gianetto et al. (1978), Hofmann (1978), and Satterfield (1975) have summarized the available data and have presented various types of flow regime maps in terms of operating parameters.

Basically, four flow regimes exist: the gas-continuous flow at low gas and liquid rates, dispersed-bubble flow at higher liquid rates, pulsing flow at increasing gas rates, and spray flow at very high gas rates. The boundaries of the flow patterns were determined by visual observations (Talmor, 1977), sharp increase in the pressure fluctuations (Chou et al., 1977; Sicardi et al., 1979), sudden changes in the gas-liquid mass transfer coefficients (Fukushima and Kusaka, 1977) and variations in the apparent electric conductivity (Matsuura et al., 1979).

In several studies (Fukushima and Kusaka, 1977; Matsuura et al., 1979) the air-water system was investigated. However Chou et al., (1977), Kobayashi et al. (1979), Morsi et al. (1978 and 1982), Sicardi et al. (1979) have indicated that the effect of physical properties of the fluids on the transition from the gas-continuous to the pulsing-flow regime is very significant. Chou et al also reported a major effect of particle wettability. Sicardi et al. pointed out possible effects of particle shape, surface roughness and size, and the reactor-to-particle diameter ratio. Some of these factors have been considered in the preparation of the flow regime maps.

Chou et al., Baldi and Specchia (1977), Morsi et al. (1978 and 1982) plot $L_m\lambda\psi/G_m$ vs. G_m/λ as suggested by Midoux et al.

(1976), where $\lambda = \{(\rho_g/\rho_a)(\rho_L/\rho_w)\}^{1/2}$ and $\psi = (\delta_w/\delta_L)[(\mu_L/\mu_w)(\rho_w/\rho_L)^2]^{0.33}$. Morsi et al. defined three categories of liquids: non-foaming, foaming and viscous, and prepared the flow map accordingly. Talmor (1977) proposed $(G_m/L_m)\,(\rho_L/\rho_g)_{avg}$ and $(1 + 1/Fr_m)/(We_m + 1/Re_m)$ as coordinates in the flow regime map, so that effects of particle shape and size and the reactor-to-particle diameter ratio could also be included.

The gas-continuous and the pulsing flow regimes are encountered in laboratory, pilot and industrial trickle-bed reactors. Accordingly, Baldi and Specchia (1977) have defined two distinct flow regimes: poor-interaction and high-interaction. Based on this criterion Sicardi et al. (1979) have prepared a modified flow map for non-foaming systems which is reproduced in Figure 7.

In contrast with the extensive experimental work, little has been published on the development of general correlations for predicting transitions from the gas-continuous to the pulsing-flow regime. Sicardi et al. (1979, 1980a) have adopted the method put forward by Dukler (1977), for describing two-phase flow in tubes, to explain pulse formation in trickle-beds. They postulate that the packed bed consists of straight parallel channels (with a diameter of $4\epsilon_B/a_t$) in which the liquid and the gas flow concurrently. Pulsing inception was assumed to be caused by the formation of large waves which block the channels. A general correlation was derived to relate the ratio of the wave amplitude to the mean height of the liquid film and the pressure drop at the pulsing inception. However, this is not a predictive model at this stage in its development, so that flow-regime maps are still necessary for estimating flow-pattern transition. The plot suggested by Sicardi et al., shown in Figure 7, is recommended for this purpose.

REACTOR DESIGN: PRESSURE DROP AND LIQUID HOLDUP

The total liquid holdup, h_t, which is the fraction of the total volume of the bed filled with liquid, consists of the static holdup h_s plus the dynamic holdup h_d. The static holdup is the volume fraction of the liquid that remains after draining the bed and, for porous particles, it consists of intraparticle holdup h_{is} and the interparticle static holdup h_{es}. *For completely liquid-filled particles*, h_{is} is computed as follows:

$$h_{is} = \epsilon_p(1 - \epsilon_B) \tag{22}$$

The interparticle (external) holdup h_e (the sum of h_d and h_{es}) has a significant effect on interparticle transport parameters. It also affects the pressure drop in the column since it reduces the effective void fraction.

Hutton and Leung (1974), and more recently Matsuura et al. (1979a), developed models which define a gravity-viscosity regime (at low liquid rates) and a gravity-inertia regime (at high liquid rates) to relate the pressure drop and the external liquid holdup. Matsuura et al employed their model to correlate dynamic holdup (h_d) and pressure drop (δ_{Lg}) data obtained for three glass sphere packings (1.2, 2.6, and 4.3 × 10^{-3} m) in the water-air system for all flow regimes, as follows:

$$h_d = 13.5Re_L^{1/3}(Ga_L^*)^{-1/3} + 1.20Re_L(Ga^*)^{-1/2} \tag{23}$$

$$\delta_{Lg} = \left[4f_t\,\frac{1 - \epsilon_B}{\epsilon_B h_d^2}\,\frac{\rho_L u_L^2}{2d_p} - \rho_L g\right] h_e/\epsilon_B \tag{24}$$

where

$$Ga^* = \rho_L^2 g d_p^3\{1 - \epsilon_B/(\rho_L h_e g)\delta_{Lg}\}/\mu_L^2 \tag{25}$$

$$f_t = 1.2 \times 10^3\{\rho_L u_L d_p h_e/[\mu_L(1 - \epsilon_B)h_d]\}^{-1.1} \tag{26}$$

Recalling that

$$h_d = h_e - h_{es} \tag{27}$$

and using the correlation proposed by Van Swaaij et al. (1969),

$$h_{es} = h_{es}(E\ddot{o}) \tag{28}$$

where

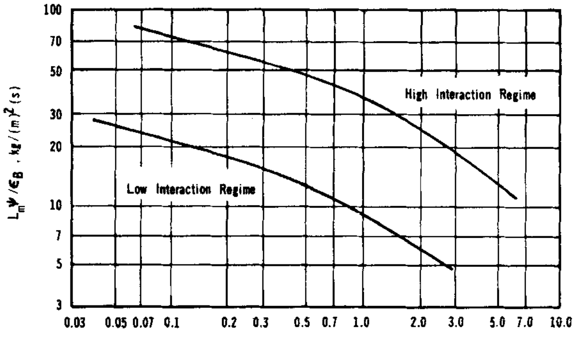

Figure 7. Flow map for non-foaming system, Sicardi et al. (1979).

$$E\ddot{o} = \frac{\rho_L g d_p^2}{\delta_L}, \tag{29}$$

Equations 23 to 29 can be solved simultaneously to yield values of the liquid holdups and the pressure drop.

Similar correlations have been derived by Specchia and Baldi (1977) for the low-interaction regime:

$$h_d/\epsilon_B = 3.86Re_L^{0.545}(G_a')^{-0.42}\left(\frac{a_t d_p}{\epsilon_B}\right)^{0.65} \tag{30}$$

$$\delta_{Lg} = C_1\,\frac{[1 - (\epsilon_B - h_e)]^2}{(\epsilon_B - h_e)^3}\,\mu_g u_g + C_2\,\frac{1 - (\epsilon_B - h_e)}{(\epsilon_B - h_e)^3}\,\rho_g u_g^2 \tag{31}$$

where

$$Ga_L' = d_p^3\rho_L(\rho_L g + \delta_{Lg})/\mu_L^2 \tag{32}$$

C_1 and C_2 depend on particle shape and size and must be evaluated experimentally. However, for the high interaction regime, they proposed empirical equations:

$$h_d/\epsilon_B = 0.125(Z/\psi^{1.1})^{-0.312}\left(\frac{a_t d_p}{\epsilon_B}\right)^{0.65};\quad 1 < Z/\psi^{1.1} < 500 \tag{33}$$

for non-foaming systems, and

$$h_d/\epsilon_B = 0.0616(Z/\psi^{1.1})^{-0.172}\left(\frac{a_t d_p}{\epsilon_B}\right)^{0.65};\quad 0.6 < Z/\psi^{1.1} < 80 \tag{34}$$

for foaming systems. The corresponding pressure drop equations are

$$ln\, f_{Lg} = 7.82 - 1.30\, ln(Z/\psi^{1.1}) - 0.0573[ln(Z/\psi^{1.1})]^2 \tag{35}$$

where

$$f_{Lg} = \frac{\delta_{Lg} d_e}{2u_g\rho_g};\ d_e = \frac{2}{3}\,\frac{\epsilon_B}{1 - \epsilon_B}\,d_p;\quad Z = Re_g^{1.167}/Re_L^{0.767} \tag{36}$$

for foaming and non-foaming systems.

Shah (1979) and Gianetto et al. (1978) have published excellent reviews of holdup and pressure drop correlations. More recently Morsi et al. (1980) have presented correlations for non-foaming, foaming, and viscous liquids in the low and high interactions regimes.

Interesting results for pressure drop and liquid holdup in a trickle-bed packed with small particles (0.05, 0.1 and 0.18 × 10^{-2} m) were found by Kan and Greenfield (1978, 1979). They observed multiple values of the pressure drop and the total liquid holdup at the same gas and liquid rates in the water-air system. When the gas flow rate was increased from zero, at constant liquid rate, to a maximum value and then decreased, two curves were obtained, the latter being lower than the former, as illustrated in Figure 8. Under similar conditions the total liquid holdup increased by as much as 10%. Their analysis of these results is based on the assumption that in beds of small packings, the liquid bridges between the particles tend to break down so that flow channels in the flow direction are formed. This reduces the tortuosity of gas flow path,

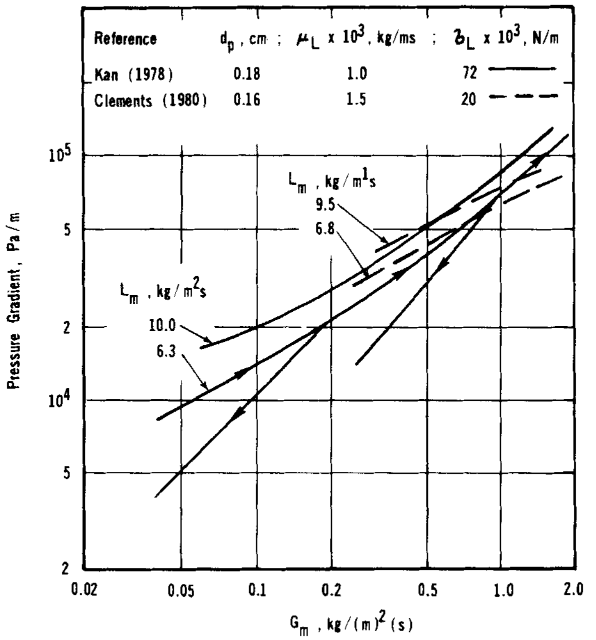

Figure 8. Comparison of pressure drop data measured in trickle beds packed with small particles.

thereby lowering the pressure drop. The channels are stable with decreasing gas rate due to the high surface tension of the water. However, when the surface tension was lowered from 72 to 38 × 10^{-3} N/m, multiple states were still observed. No multiple states were observed in the high-interaction regime. Various correlations were used to correlate the pressure drop and liquid holdup data. The Specchia and Baldi (1977) correlation given in Eq. 30, but with modified constants, was found to be the best. It should be pointed out that this equation correlated well the data obtained with increasing and with decreasing gas flow.

Clements and Schmidt (1980a,b) have also studied pressure drop and liquid holdup in a trickle-bed packed with various small packings (0.16×10^{-2} and 0.29×10^{-2} m spheres and 0.08×10^{-2} m extrudate). Silicone liquids that covered a wide range of viscosities [$1.5 \times 10^{-3} - 8 \times 10^{-3}$ kg/(m)(s)] and had a surface tension of 18–20 × 10^{-3} N/m were used. Although many of the pressure drop curves were obtained by a series of increasing gas rates followed by a series of decreasing gas rates, no multiple states were observed. However, most of the data were measured in the high-interaction regime. Furthermore, the liquid surface tension was low. The pressure drop vs. the gas rate plotted in Figure 8 is in good agreement with the data published by Kan and Greenfield. Clements and Schmidt correlated their data as a function of the group $Re_g We_g / Re_L$ as follows:

$$\delta_{Lg}/\delta_g = 0.024 d_p \mu_L \left(\frac{\epsilon_B}{1-\epsilon_B}\right)^3 \left(\frac{Re_g We_g}{Re_L}\right)^{-1/3} \tag{37}$$

$$h_d = 0.84 \left(\frac{Re_g We_g}{Re_L}\right)^{-0.034} \tag{38}$$

Estimated values of δ_{Lg} from the Specchia and Baldi (1977) correlation, Eq. 31, are in reasonable agreement with δ_{Lg} values measured by Clements and Schmidt in the high-interaction regime. This equation together with Eqs. 30 to 34 are recommended for calculating the pressure drop and the liquid holdup in trickle-beds. For small particles the modified constants published by Kan and Greenfield should be used. The effect of the physical properties of the liquid in small particles should be further investigated.

Recently Mills and Dudukovic (1981) correlated dynamic holdup data obtained from dynamic measurements using a tracer (Colombo et al., 1976; Mills and Dudukovic, 1981) and from direct measurements of the flowing liquid in the bed (Goto and Smith, 1975) for small particles. They proposed the following correlation, for the dynamic liquid saturation h_d/ϵ_B, which is applicable for low gas rates where the effect of the gas rate is negligible:

$$h_d/\epsilon_B = \tanh\left[0.731 Re_L^{-0.333} Fr_L^{0.708} We_L^{-0.346} \left(\frac{a_t d_p^2}{\epsilon_B^2}\right)^{0.924}\right] \tag{39}$$

where d_p in the group $a_t d_p^2/\epsilon_B^2$ should be evaluated in m × 10^2.

REACTOR DESIGN: LIQUID DISTRIBUTION

The liquid distribution in absorption columns has been extensively studied. The application of this information to trickle beds is of limited value because the operating conditions are usually different. Hence, the following discussion refers only to trickle-bed studies.

Experimental Data

The liquid distribution has been usually measured by collecting the liquid in annular collectors located at the bottom of the bed. All the experimental investigations, except one, were carried out in the water-air system as listed in Table 4. Various liquid initial distributions were employed.

Three important aspects of the liquid distribution should be considered:

1. the bed depth required for achieving equilibrium liquid distribution (that is, the distribution that does not change with bed depth). This bed depth depends on the gas and liquid rates, physical properties of the liquid, particle size and shape, column diameter and especially the feed distribution at the top of the packed bed.
2. the equilibrium liquid distribution which depends on the gas and liquid rates, physical properties of the liquid and particle size and shape.
3. the wall flow which is the liquid flowing near the column wall, due to the higher bed porosity. This depends on the liquid physical properties, the particle shape and, particularly, on the ratio of column to packing diameter.

Clearly, a much shorter bed depth is required for reaching equilibrium liquid distribution if a uniform feed distribution rather than a point source is used (Prchlik et al., 1975; Herskowitz and Smith, 1978). If the initial distribution is known, the models presented later may be employed to calculate this bed depth.

The equilibrium liquid distribution has been found to be essentially uniform at low liquid rates ($u_L < 0.9 \times 10^{-3}$ m/s) in the low-interaction flow regime (Specchia et al., 1974; Sylvester and Pitayagulsan, 1975; and Herskowitz and Smith 1978). Increasing the liquid superficial velocity beyond 0.01 m/s and with no gas flow, Specchia et al. measured a parabolic profile with a minimum at the center of the column. In the same range Weekman and Myers (1964) reported a maximum in the liquid distribution at the center of the column and a minimum in the middle section. Sylvester and Pitayagulsarn (1975) found the liquid distribution to be unstable when the liquid superficial velocity was higher than 0.01 m/s and the gas superficial velocity was lower than 0.033 m/s.

At the onset of the pulsing-flow regime, a significant increase in the liquid flow at the center of the column was measured (Specchia et al.; Sylvester and Pitayagulsarn). Increasing further the gas flow rate, Specchia et al. and Weekman and Myers reported a slight change in the liquid distribution while Sylvester and Pitayagulsarn measured a nearly uniform distribution. These apparently contradictory results may have been caused by the effect of the collector on the measured liquid distribution, as pointed out by Specchia et al. and Herskowitz (1978).

Wall flow has been measured as a function of the particle size and shape, the column diameter (Prchlik et al., 1975b; Herskowitz and Smith, 1978) and the liquid physical properties (Prchlik et al. 1978). Prchlik et al. (1975a) reported that for $d_t/d_p > 25$ the wall flow at equilibrium was less than 10% of the total flow in the bed.

TABLE 4. EXPERIMENTAL STUDIES OF LIQUID DISTRIBUTION IN TRICKLE-BED REACTORS

Reference	$u_L \times 10^2$, m/s	$u_g \times 10^2$, m/s	Liquid Source	Collecting Device (# of Annular Sections)	Packing		$d_t \times 10^2$
					Shape	$d_p \times 10^3$, m	
Weekman and Myers (1964)	1.1	0–98	Uniform	3	Sphere	4.7	8.0
Stanek and Kolar (1968)	0–1.7	—	Point	8	Sphere	5.0, 6.0, 10, 15, 16	10.9
Stanek and Kolar (1973)	0–0.8	—	Point, Wall	13	Sphere	15, 20	29.1
Stanek and Kolar (1973a)	0.5–0.8	—	Point, Disc	13	Sphere	15, 20	29.1
Soukup et al. (1973)	0.03–0.45	—	Point	13	Pellet	10.3	25.0
Kolomaznik et al. (1974)	0.03–0.45	—	Ring	13	Pellet, Sphere	10.3, 5.6, 7.5 9.8	25.0
Specchia et al. (1974)	0.53–1.8	5.3–130	Uniform	5	Sphere	6.0	14.1
Sylvester & Pitayagulsarn (1975)	0.36–1.9	3.3–66	Uniform	6	Pellet	3.7	15.0
Prchlik et al. (1975)	0.03–0.45	—	Uniform, Wall Point	13	Pellet	10.3	25.0
Prchlik et al. (1975a)	0.03–0.45	—	Uniform, Wall Point	13	Pellet, Sphere	10.3, 5.6, 7.5, 9.8	25.0
Herskowitz & Smith (1978)	0.1–0.5	0.1–5.0	Uniform, Point	3, 4, 6	Granular Sphere Cylinder	2.6, 3.5, 7.2, 8.7, 11.1 3.0, 6.4, 9.5 9.0, 7.8, 5.8, 3.9	4.1, 11.4
Prchlik et al. (1978)	0.03–0.45	—	Point, Disc	13	Pellet	10.3, 5.6, 7.5	25.0

Herskowitz and Smith (1978) proposed that for $d_t/d_p > 18$ the wall flow is negligible. For $d_t/d_p < 18$, granular particles cause less wall flow than spherical or cylindrical particles. It should be pointed out that Prchlik et al. measured the wall flow in a section of the collector adjacent to the wall while Herskowitz and Smith calculated the wall flow from the liquid flow in the section near the wall. A negligible effect of the liquid physical properties on the wall flow measured at equilibrium was found by Prchlik et al. (1978). On the other hand, Herskowitz and Smith measured a negligible wall flow for $d_t/d_p = 12$ when the surface tension was lowered to 38×10^{-3} N/m. For d_t/d_p larger than about 20, the liquid distribution at equilibrium in laboratory and pilot trickle-bed reactors, operated in the low-interaction flow regime, is uniform (Herskowitz and Smith). In the transition regime a maximum in the center may occur, while in the high-interaction flow regime the liquid distribution is nearly uniform. No data on the liquid distribution in industrial reactors are available.

Theoretical Models

Most of the theoretical work has been based on a randon-walk mechanism for the trickle flow over a randomly packed bed. This approach yields a diffusion-type equation.

$$\frac{\partial u_z}{\partial z} = D_r \left(\frac{\partial^2 u_z}{\partial r^2} + \frac{1}{r} \frac{\partial u_z}{\partial r} \right) \tag{40}$$

where u_z is the vertical component of the local liquid velocity and D_r is the radial liquid-spread coefficient. Two boundary conditions express the axial symmetry at the center of the column and the initial liquid distribution as follows:

$$\frac{\partial u_z}{\partial r} = 0 \text{ at } r = 0; \; u_z = u_{z,i} \text{ at } z = 0 \tag{41}$$

The difficult problem is to formulate a boundary condition at the wall which is physically reasonable and mathematically tractable. A critical discussion of the various boundary conditions at $r = R$ is given elsewhere (Herskowitz, 1978).

A finite-difference model that considers the bed to consist of discrete spherical particles was developed by Jameson (1966). The final expressions included two parameters, the radial spreading factor $\underline{s}$ which represents the fraction of the liquid flow that moves radially, and the wall factor f_w which represents the fraction of wall flow that returns to the bed. Recently this model was modified by Herskowitz and Smith (1978). The two parameters D_r and s are related by the expression

$$s = \frac{4D_r}{d_p} \tag{42}$$

They may be evaluated from liquid distribution data (Stanek and Kolar, 1968; Kolomaznik et al., 1974; Herskowitz and Smith, 1978) or from tracer distribution data (Specchia et al., 1974). The results obtained in the various studies, compared in Table 5, show good agreement. They also indicate that the liquid spreads more quickly in granular packings compared with cylinders or spheres. For a particle diameter less than about 0.006 m the radial spreading factor is unity. Changing the surface tension of the liquid had no effect on the radial spreading factor as reported by Herskowitz and Smith (1978) and Prchlik et al. (1978). On the other hand, measurements of the liquid distribution performed with a mixture of hydrocarbons yielded a value of D_r lower by about 25% than the value obtained with water.

At zero or low gas rates and $u_L < 0.005$ m/s, D_r was found to be

TABLE 5. COMPARISON OF THE SPREADING FACTORS EVALUATED FROM VARIOUS STUDIES

Reference	Particle		$D_r \times 10^3$, m	s^*	s^{**}
	(Dia.) $\times 10^3$, m	Shape			
Stanek and Kolar (1968)	6.0	Spherical	1.38	0.92	0.92
Stanek and Kolar (1968)	10	Spherical	1.38	0.55	0.55
Stanek and Kolar (1968)	15	Spherical	1.38	0.37	0.37
Kolomaznik et al. (1974)	10	Cylindrical	2.0	0.80	0.62
Kolomaznik et al. (1974)	7.5	Cylindrical	1.8	0.96	0.85
Kolomaznik et al. (1974)	9.8	Spherical	1.4	0.57	0.57
Specchia et al. (1974)	6.0	Spherical	1.2	0.80	0.92

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* Calculated from Eq. 42.

** Reported by Herskowitz and Smith (1978).

constant (Specchia et al.; Stanek and Kolar, 1968; Herskowitz and Smith). At higher values of the liquid superficial velocity Stanek and Kolar reported that D_r depends on the liquid rate while Specchia et al. reported a constant value of D_r. On the other hand, Specchia et al. found that D_r decreases with increasing gas and liquid rates.

Recently Crine et al. (1979a) developed a different model, based on the percolation theory, which considers preferential flow paths in the bed, which have been reported in several studies. The liquid distribution predicted by the two models was different at low liquid rates but in reasonable agreement at high liquid rates. This model should be simplified and tested experimentally before it can be used for predictions. Additional experimental data, obtained with improved means of measuring the liquid distribution are needed for further testing of the various theoretical models.

REACTOR DESIGN: AXIAL DISPERSION

Axial dispersion in trickle-bed reactors has been extensively studied. Various models, which include up to six parameters, are summarized in the reviews of Gianetto et al. (1978) and Shah (1979). Gianetto et al. pointed out that a comparison of the parameters given in different studies is difficult, because their values depend on the method of analysis. In a subsequent paper, Sicardi et al. (1980b) confirmed this conclusion.

The simplest model is the piston-dispersion (PD) model. This approach, which includes the axial dispersion coefficient E_D as the only parameter, has been frequently used for predicting reactor performance (Goto et al., 1977; Hofmann, 1978). Schwartz and Roberts (1973) have compared predicted conversions for first-order reactions from the PD model and more complex, two-parameter models. The difference, even at high conversions, was small. Although more complex models may represent better the RTD data, the PD model offers the advantage of being more easily utilized in design. Furthermore, simple criteria may be derived for negligible axial dispersion, as proposed by Mears (1974).

Correlations of the axial dispersion coefficient as a function of the operating parameters have been published (Goto et al., 1977; Shah, 1979). A comparison between the correlations, carried out by Goto et al. (1977), indicates large discrepancies. This is not surprising, considering the scatter of the data. Recently Buffham and Rathor (1978) have investigated the effect of the viscosity on the axial dispersion coefficient (or the Peclet number). Changing the viscosity from 1.0×10^{-3} (Pa)(s) to 7.5×10^{-3} (Pa)(s) had little effect on E_D. Hence, a correlation of the Peclet number as a function of Froude number was proposed:

$$Pe_L = 0.45(Fr_L')^{0.27} \tag{43}$$

where:

$$Pe_L = \frac{u_L d_p}{L_e E_D}; \; Fr_L' = \frac{u_L^2}{L_e^2 d_p g}$$

Since $Fr_L' = Re_L^2 Ga_L^{-1}$, the dependency of Pe_L on Re_L and Ga_L agrees with previous correlations published by Michell and Furzer (1972) and Hochman and Effron (1969).

Kobayashi et al. (1979) proposed a correlation, based on RTD data obtained with several aqueous solutions, which gives a large dependency of Pe_L on Ga_L:

$$Pe_L = 60(Re_L''')^{0.63}(Ga'')^{-0.73} \tag{44}$$

This correlation predicts that the Peclet number depends strongly on the liquid viscosity, in contrast with the Buffham and Rathor results. It also predicts that at a certain value of the Reynolds number, the Peclet number depends strongly on the particle size, in contrast with the Hochman and Effron (1969) data (d_p = 0.00476 m) and the Schwartz et al. (1976a) data ($d_p = 6.0 \times 10^{-4}$ m). The Buffham and Rathor (1978) correlation predicts Peclet numbers which agree with the data of Hochman and Effron (1969) and Schwartz et al. (1976a). The liquid holdup data given in the original papers were used in the calculations. The Buffham and Rathor correlation is recommended for estimating the axial dispersion coefficient in the low-interaction regime.

Axial dispersion also has been evaluated in the high-interaction regime. Kobayashi et al. reported that the Peclet number measured in trickle-beds was close to the Peclet number predicted for a single-phase liquid flow. If this is true, axial dispersion in the high-interaction regime is essentially negligible. This conclusion is supported by a recent work published by Lerou et al. (1980).

REACTOR DESIGN: INTERPARTICLE HEAT TRANSFER

Radial heat transfer in single-phase-flow, packed-bed reactors has been reviewed by Specchia et al. (1980). Radial temperature profiles were calculated from a model which included two parameters: the effective radial thermal conductivity λ_{er} and the heat transfer coefficient at the hall h_w, both of which were considered to be independent of position in the bed. The effective radial thermal conductivity was expressed as the sum of two contributions: a stagnant effective thermal conductivity λ_e^o, which does not include radial transport of fluids and a contribution associated with the radial flow of gas $\lambda_{e,g}$.

The first study of the radial heat transfer in trickle-bed reactors was published by Weekman and Myers (1965) for the water-air system. A one-parameter model which neglected the heat transfer resistance at the wall was employed; all resistance to heat transfer was included in an overall effective thermal conductivity Λ_{er}. The overall effective thermal conductivity in the trickle-bed, Λ_{er}, was found to be 200 to 400% larger than for a liquid-full, single-flow reactor at the same liquid rate. However, as shown by Specchia and Baldi (1979), such a model cannot correlate adequately the data. Hence, the correlations have been extended to include contributions due to flowing gas and liquid, according to the expression

$$\lambda_{er} = \lambda_e^o + \lambda_{e,g} + \lambda_{e,L} \tag{45}$$

Accordingly, the correlations of λ_{er} given in Table 6 consist of three terms. Different correlations were derived for the low and high interaction regimes.

Several well-defined studies have been published. Hashimoto et al. (1976) measured the radial temperature profiles, including the wall temperature, at various bed depths. Air and water or a water-glycerine mixture were used. The reactor was packed with glass beads of 0.26 to 0.48×10^{-2} m dia. and 0.44×10^{-2} cm dia. alumina spheres. The data were analyzed by a two-parameter model. A correlation of the effective radial thermal conductivity λ_{er} which covers both the low and high interaction regimes was derived. This correlation, given in Table 6, is also combined of three terms. The last term, $\lambda_{e,L}$, was dominant. Its value, at a certain liquid rate, was larger than the value for liquid single-phase flow. Moreover a comparison of the Peclet number for radial heat transfer $Pe_H = L_m C_{p,L} d_p / \lambda_{e,L}$ with the Peclet number for radial mass transfer of liquid $Pe_M = d_p/D_r$ showed good agreement.

A similar study was recently published by Specchia and Baldi (1979). The data were also correlated with three terms. However, the first-term λ_e^o is not constant but a function of the bed void fraction and the thermal conductivities of the solid and the gas. Both λ_e^o and $\lambda_{e,g}$ were derived from a study of gas flow through packed beds (Specchia et al., 1980). The values of these two terms are much smaller than $\lambda_{e,L}$. The Specchia and Baldi and Hashimoto et al. correlations are in agreement for Peclet numbers for radial heat and liquid transfer. Then, in principle, the effective radial thermal conductivity may be calculated from the radial liquid spreading factor obtained from liquid distribution data.

Matsuura et al. (1979b) have also studied the effect of the operating parameters on the effective radial thermal conductivity. They proposed a correlation similar to the Hashimoto et al. correlation. However, the coefficient $(\alpha\beta)_L$ was correlated as a function of the gas Reynolds number, independent of the liquid Reynolds number. Therefore, it predicts higher values of λ_{er}, as illustrated in Figure 9.

Comparison of the three correlations of λ_{er}, carried out in the

TABLE 6. CORRELATIONS OF RADIAL HEAT TRANSFER PARAMETERS IN TRICKLE BEDS

Reference	Effective Radial Thermal Conductivity	Wall Heat Transfer Coefficient
Weekman and Myers (1965)	$\frac{\Lambda_{er}}{\lambda_L} = \frac{2.90 \times 10^{-3}}{\lambda_L} + 0.000285 \left(\frac{L_m d_t}{\mu_L}\right) Pr_L$ (6-1)	
Hashimoto et al. (1976)	$\frac{\lambda_{er}}{\lambda_L} = \frac{1.1 \times 10^{-4}}{\lambda_L} + 0.095 Re_g Pr_g \frac{C_{p,g}\lambda_g}{C_{p,g}\lambda_L} + (\alpha\beta)_L Re_L Pr_L$ (6-2)	
Muroyama et al. (1977)		$\frac{h_w d_p}{\lambda_L} = 0.012\, Re_L^{1.7} Pr_L^{1/3}$ (6-3) low interaction regime $\frac{h_w d_p}{\lambda_L} = 0.092 (Re_L'')^{0.8} Pr_L$ (6-4) high interaction regime
Matsuura et al. (1979b)	$\frac{\lambda_{er}}{\lambda_L} = 1.5 + (\alpha\beta)_g' Re_g Pr_g \frac{C_{p,g}^*}{C_{p,g}} \frac{\lambda_g}{\lambda_L} + (\alpha\beta)_L' Re_L Pr_L$ (6-5)	
Matsuura et al. (1979c)		$h_w = h_{wo} + h_{ws} + \frac{1}{\frac{1}{h_w^*} + \frac{1}{h_{wt,g} + h_{wt,L}}}$ (6-6)
Specchia and Baldi (1979)	$\frac{\lambda_{er}}{\lambda_L} = \left\{\epsilon_B + \frac{1 - \epsilon_B}{0.220\epsilon_B^2 + \frac{2\lambda_g}{3\lambda_s}} + \frac{Re_g Pr_g C_{p,g}^*/C_{p,g}}{8.65[1 + 19.5(d_e/d_t)^2]}\right\} \frac{\lambda_g}{\lambda_L} + \frac{\lambda_{e,L}}{\lambda_L}$ (6-7) $(\alpha\beta)_L = \left\{\frac{1}{1.90 + 0.0264(d_e L_m/h_e \mu_L)(\mu_L/\mu_o)} + 0.197\right\} \frac{d_e}{d_p}$	$\frac{h_w d_e}{\lambda_L} = 0.057 (Re_L'')^{0.89} Pr_L^{1/3}$ (6-8) low interaction regime

d_p, cm	$(\alpha\beta)_g'$	$(\alpha\beta)_L'$	$h_{wo}d_p/\lambda_L$	$h_{ws}d_p/\lambda_L$	Range of h_d
0.12	0.412	$0.201(1 + 2.83 \times 10^{-2} Re_g)$	0.09	$1.10\, h_d/\epsilon_B$ $21.\, h_d/\epsilon_B - 9.95$	$0 < h_d/\epsilon_B < 0.5$ $0 < 2\, h_d/\epsilon_B < 1$
0.26	0.334	$0.167(1 + 1.34 \times 10^{-2} Re_g)$	0.21	$1.70\, h_d/\epsilon_B$ $18.8\; h_d/\epsilon_B - 6.50$	$0 < h_d/\epsilon_B < 0.38$ $0.38 < h_d/\epsilon_B < 1.0$
0.43	0.190	$0.152(1 + 6.32 \times 10^{-3} Re_g)$	0.43	$3.40\, h_d/\epsilon_B$ $16.6\; h_d/\epsilon_B - 3.30$	$0 < h_d/\epsilon_B < 0.25$ $0.25 < h_d/\epsilon_B < 1$

$$h_w^* d_p/\lambda_L = \begin{cases} 4.0\, Pr_g^{1/3} Re_g^{1/2}\, \lambda_g/\lambda_L & \text{low interaction regime} \\ 2.6\, Re_L^{1/2} Pr_L^{1/3} & \text{high interaction regime} \end{cases}$$

$$\frac{h_{wt,g} d_p}{\lambda_L} = 0.5 (\alpha\beta)_g Re_g Pr_g \lambda_g/\lambda_L; \frac{h_{wt,L} d_p}{\lambda_L} = 0.5\, (\alpha\beta)_L' Re_L Pr_L; \quad \text{high interaction regime}$$

$$\frac{h_{wt,g} d_p}{\lambda_L} = 0.054 Re_g Pr_g \frac{C_{p,g}^*}{C_{p,g}} \frac{\lambda_g}{\lambda_L}; \quad h_{wt,L} = 0 \quad \text{low interaction regime}$$

$$\frac{\lambda_{e,L}}{\lambda_L} = \frac{h_e^{0.87}}{0.041} Re_L^{0.13} Pr_L; \quad \text{low interaction regime}$$

$$\frac{\lambda_{e,L}}{\lambda_L} = \frac{h_e^{-0.29}}{338} Re_L^{0.325} Pr_L (a_t d_p/\epsilon_B)^{2.7}; \quad \text{high interaction regime}$$

high interaction regime, indicates a significant disagreement between the predictions at high Reynolds numbers. The Hashimoto et al. correlation, which was obtained with small particles and gives conservative estimates of λ_{er}, is recommended for estimating the effective radial thermal conductivity. Calculations carried out at low Reynolds number (the low interaction regime) showed good agreement between the Hashimoto et al. and the Matsuura et al. correlations.

The heat transfer coefficient at the wall, h_w, has also been correlated as a function of the Reynolds and Prandtl numbers. Muroyama et al. (1977) proposed correlations for the low and high interactions regimes. Matsuura et al. (1979c) developed a model which includes five contributions to h_w:

1. The apparent wall heat transfer coefficient h_{wo} for a no-flow situation; h_{wo} is a function of particle size.
2. The apparent wall heat transfer coefficient h_{ws}, which accounts for the heat transfer between the fluid and the wall near the contact surface between particles and the wall. This was correlated as a function of the liquid holdup h_d.
3. The true heat transfer coefficient h_w^*, correlated as a function of the gas-phase Reynolds and Prandtl numbers for the low inter-

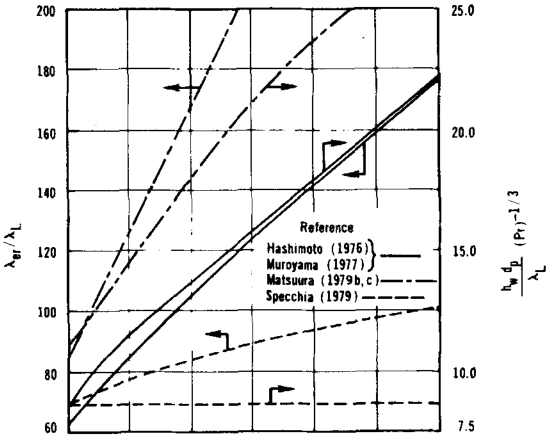

Figure 9. Comparison of correlations for radial heat transfer parameters (water-air system): $d_p = 4.8 \times 10^{-3}$ m; $Re_g = 65$; $Pr_L = 7.7$; $Pr_g = 0.73$; $d_t = 0.074$ m; $\epsilon_B = 0.375$.

action regime, and the liquid-phase dimensionless numbers for the high interaction regime.

4. The apparent heat transfer coefficients h_{wg} and h_{wL}, accounting for heat transfer due to radial gas and liquid mixing, respectively.

The correlations of h_w for the low-interaction and high-interaction regimes are given in Table 6.

In contrast with these investigations, Specchia and Baldi (1979) reported a constant value of $h_w = 2.1$ kJ/(m^2)(s)(K) in the high-interaction regime. The correlations are compared in Figure 9. The Muroyama et al. correlation is recommended for estimating h_w. This was obtained with small particles normally used in trickle beds. The complex result proposed by Matsuura et al. may not apply for other fluids and different operating conditions. The Specchia and Baldi proposal is probably not applicable for small packings.

The axial temperature profile in an adiabatic trickle-bed reactor has been measured by Hanika et al. (1976). They studied the hydrogenation of cyclohexene to cyclohexane; the latter is a relatively volatile solvent. Only a small change in temperature with bed depth was measured for low concentrations of the reactant in the feed. However, at high concentrations the temperature increased due to the much greater heat release in the reactor. The liquid superficial velocity was very low (9.4×10^{-5} m/s) so that the wetting efficiency was low, enhancing the gas-phase reaction.

A temperature rise with bed depth has also been observed in commercial trickle-beds that operate adiabatically. The temperature can be controlled by the addition of quenching streams. Shah (1979) summarized several simulation studies of trickle-bed reactors with one or more quenches. Recently, Yan (1980) presented a dynamic model of a trickle-bed hydrocracker with a quenching system.

REACTOR MODELS

Various models for correlating and predicting the performance of trickle-bed reactors have been proposed (Goto and Smith, 1978, 1978a). These references develop and solve mass conservation equations for gas and liquid phases and account for mass transfer processes for first-order reactions. While some models do not take into account mass transfer effects, in many cases such resistances cannot be neglected. Shah (1979), Hofmann (1978) and Goto et al. (1977) have reviewed the various models. In the latter review a model, which includes mass transfer effects for both linear and nonlinear kinetics, was used to analyze several reactions in trickle beds. The appropriate mass balances yielded a set of second-order, nonlinear differential equations that had to be solved numerically.

Ramachandran and Smith (1979a) proposed a mixing-cell method that assumes that the reactor consists of a number of stirred tanks in series, in each of which the liquid is completely mixed and the gas is in plug flow. The design equations which result from the mass balances in a cell are nonlinear, algebraic equations. An analytical solution is presented for a first-order reaction. The degree of backmixing is represented by the number of cells ($N = 1$ for a slurry reactor and $N = \infty$ for a plug flow reactor). This model can be modified to include liquid maldistribution or partial wetting of the particles, but assumes complete liquid wetting.

A mixing-cell model was adopted by Herskowitz (1981b) to examine the effect of the wetting efficiency on the reactor performance. This model was based on calculating global rates of reaction in a partially wetted particle (Herskowitz, 1981). The outlet concentrations of the reactants involved in a first-order reaction were determined from analytical expressions as a function of the mass transfer coefficients, the Thiele modulus, the wetting efficiency, and the bed depth. The model was applied to the oxidation of sulfur dioxide in an aqueous solution catalyzed by activated carbon. A significant effect of wetting efficiency was found. Unfortunately, no experimental data are available for further testing of this model.

The effect of liquid distribution on the performance of the reactor was also investigated by means of a cell model. Hanika et al. (1978) employed the Dean & Lapidus (1960) approach to examine the effect of the initial distribution, the reaction order, the reaction rate, and the feed rate. Effects of mass transfer resistances, partial wetting and even wall flow were neglected. The predictions depend on the initial liquid distribution. Herskowitz and Smith (1978a) proposed a model for the distribution of a tracer (which included effects of the wall flow) which could be extended to include chemical reaction.

Recently, Stanek et al. (1981) published a more complete model that accounted for liquid maldistribution and heat effects. The approach is based on the diffusion Eq. 40. Extensive computations were carried out and indicated two important aspects: the liquid maldistribution caused by poor initial distribution and by wall flow. In laboratory or pilot-scale reactors, the liquid is usually well distributed and a calming zone is used to achieve uniform distribution. Furthermore, the ratio of column to particle diameters is normally larger than 15 so that no significant wall flow is expected. In commercial reactors, the liquid distribution is more complex and has not been investigated. The initial distribution, which is required in the calculations, may be difficult to obtain in a practical case. This model is useful as an interim procedure, but it neglects important aspects such as mass transfer resistances and partial wetting. Further experimental work in reacting systems, particularly under non-isothermal conditions, is needed for testing the various models for deriving criteria for the importance of factors such as heat and mass transfer, partial wetting, and liquid distribution. Considering the complexity of trickle beds, only those factors that have a significant effect on the reactor performance should be included in the model.

The hazards of using space velocity for scaleup of fixed-bed (gas-solid) catalytic reactors are well known. Trickle-bed reactors introduce such additional complications as liquid distribution and wetting efficiency. Hence, it seems unlikely that simple parameters, such as liquid space velocity, can be used for reliable scaleup, except in very special cases. The recommended procedure is, first, to establish in the laboratory the rate of reaction for single catalyst pellets which will include the effect of wetting efficiency. If there is a soluble gaseous reactant, the rate should account for mass transfer from both the gas and liquid-covered surfaces of the pellet. This basic rate data then can be used with intrareactor mass and, if necessary, energy conservation expressions to design the large-scale reactor. This second step should include the liquid distribution. The required mass and energy transport rates will limit application of this approach; the necessary data will more likely be available for operation in the trickling-flow regime.

ACKNOWLEDGMENT

The financial assistance of National Science Foundation Grant CPE-8026101 is gratefully acknowledged. Also, we would like to thank P. L. Mills and M. P. Dudukovic for their helpful comments.

NOTATION

A_n = constants in Eq. A-5
a_{gs} = gas-covered specific surface area per unit column volume, $f_e a_t$, m^{-1}
a_i = gas-liquid interfacial area for mass transfer, m^{-1}
a_t = external area of particle per unit volume of column, m^{-1}
B_n = constants in Eq. A-10
C = intraparticle concentration, dimensionless, C_i/C_L
C_i = intraparticle concentration, kmol/m^3
C_L = bulk liquid concentration (nonvolatile reactant) or reactant concentration in equilibrium with its concentration in the bulk gas (volatile component), kmol/m^3

APPENDIX: TABLE A. SOLUTIONS OF EQ. 3 FOR VARIOUS PARTICLE SHAPES

Particle Shape	Mass Balance	Boundary Conditions	Solution
Slab	$\frac{\partial^2 C}{\partial x^2}+\frac{\partial^2 C}{\partial y^2}-\phi^2 C=0$ (A-1)	$\frac{\partial C}{\partial y}=0;\ y=0,1$ (A-2) $\frac{\partial C}{\partial x}=0;\ x=1$ (A-3) $-\left(\frac{\partial C}{\partial x}\right)_{x=0}=\alpha_{gLs}(C_L^*-C);\ 0<y<f_e$ $-\left(\frac{\partial C}{\partial x}\right)_{x=0}=\alpha_{gs}(1-C);\ f_e<y<1$ (A-4)	$C=\sum_{n=1}^{\infty}A_n\cos[(n-1)\pi y]\{\exp(-\sqrt{(n-1)^2\pi^2+\phi^2 x})$ $+\exp(\sqrt{(n-1)^2\pi^2+\phi^2}(x-2))\}$ (A-5)
Cylinder	$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)+\frac{1}{r^2}\frac{\partial^2 C}{\partial \theta^2}$ $-\phi^2 C=0$ (A-6)	$\frac{\partial C}{\partial \theta}=0;\ \theta=0,\pi$ (A-7) C finite; $r=0$ (A-8) $\left(\frac{\partial C}{\partial r}\right)_{r=1}=\alpha_{gLs}(C_L^*-C);\ 0<\theta<f_e\pi$ (A-9) $\left(\frac{\partial C}{\partial r}\right)_{r=1}=\alpha_{gs}(1-C);\ f_e\pi<\theta<\pi$	$C=\sum_{n=1}^{\infty}B_n I_{n-1}(2\phi r)\cos[(n-1)\theta]$ (A-10)
Sphere	$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right)$ $+\frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial C}{\partial \theta}\right)$ $-\phi^2 C=0$ (A-11)		$C=\sum_{n=1}^{\infty}D_n I_{n-1}(3\phi r)P_{n-1}(\cos\theta)$ (A-12)

C_L^* = bulk liquid concentration, defined in Eq. 4c, dimensionless
$C_{L,b}$ = bulk liquid concentration, kmol/m^3
$C_{p,L}, C_{p,g}$ = specific heat, liquid and gas, kcal/(kg)(K)
$C_{p,g}^*$ = specific heat of saturated air, kcal/(kg)(K)
$C_{s,L} C_{s,g}$ = concentration on the liquid-covered and gas-covered surface, kmol/m^3
C_1, C_2 = constants in Eq. 31
D_e = effective diffusivity in the liquid-filled pores of the catalyst, m^2/s
D_L = diffusivity in liquid phase, m^2/s
D_r = radial liquid spread coefficient, m
D_n = constants in Eq. A-12
d_p = particle diameter, m
d_p^* = diameter of a sphere with the same external surface area of a particle, m
d_e = equivalent particle diameter, defined in Eq. 36, m
d_t = column diameter, m
E_D = axial dispersion coefficient, m^2/s
$E\ddot{o}$ = Eötvos number, defined in Eq. 29
Fr_L = Froude number, $a_t L_m^2/\rho_L^2 g$
Fr_L' = modified Froude number, $u_L^2/h_e^2 d_p g$
Fr_m = two-phase Froude number,

$$\frac{(L_m/\rho_L + G_m/\rho_g)^2}{g\left\{\dfrac{\epsilon_B d_t}{1 + 3(1 - \epsilon_B)d_t/2d_p}\right\}}$$

f_e = wetting efficiency, external, dimensionless
f_{Lg} = two-phase friction factor defined in Eq. 36, dimensionless
f_t = two-phase friction factor defined in Eq. 26, dimensionless
Ga_L = Galileo number, $d_p^3 \rho_L^2 g/\mu_L^2$
Ga_L^* = modified Galileo number, defined in Eq. 25
Ga_L' = modified Galileo number, defined in Eq. 32
G_m = superficial gas mass velocity, kg/(m^2)/(s)
g = acceleration of gravity, m^2/s
H^* = Henry's constant, dimensionless
$(-\Delta H)$ = heat of reaction, Kcal/kmol
h_d = dynamic holdup, dimensionless
h_e = external holdup, $h_d + h_{es}$, dimensionless
h_{es} = external static holdup, dimensionless
h_{is} = intraparticle holdup, dimensionless
h_s = static holdup, $h_{is} + h_{es}$, dimensionless
h_t = total holdup, dimensionless
h_w = wall heat transfer coefficient, kJ/(m^2)(s)(K)
$h_{wo}, h_w^*, h_{ws}, h_{wt,g}, h_{wt,L}$ = parameters in Eq. 6-6 in Table 6
K_L = liquid-phase mass-transfer coefficient (gas-liquid transfer) m/s
Ko = liquid-phase Kolmogoroff number, $\delta_{Lg} u_L (d_p^*)^4 \rho_L^2/h_e \mu_L^3$
k_g = gas-side mass transfer coefficient, m/s
k_L = liquid-side mass transfer coefficient, m/s
k_{gs} = gas-solid mass transfer coefficient, m/s
k_s = liquid-solid mass transfer coefficient, m/s
k_v = kinetic rate constant, m^3/(kg)(s)
L_m = liquid superficial mass velocity, kg/m$^2 \cdot$ s
m = order of reaction
n = normal direction
Pe_L = Peclet number, $u_L d_p/h_e E_D$
Pe_L' = modified Peclet number, $u_L d_p/\{1 + 4d_p/6d_t(1 - \epsilon_B)\}h_e E_D$
Pe_H = Peclet number for radial heat transfer, $L_m C_{p,L} d_p/\lambda_{e,L}$
Pe_M = Peclet number for radial liquid transfer, d_p/D_r
Pr_L, Pr_g = Prandtl number, liquid and gas
Re_L, Re_g = Reynolds number, liquid and gas, $\dfrac{u_L d_p \rho_L}{\mu_L}$ and $\dfrac{\mu_g d_p \rho_g}{\mu_g}$
Re_L' = modified Reynolds number, $u_L \rho_L/\mu_L a_t$
Re_L'' = modified Reynolds number, $u_L \rho_L/\mu_L a_t h_e$
Re_L''' = modified Reynolds number, $u_L \rho_L d_p/\mu_L h_e[1 + 4d_p/6d_t(1 - \epsilon_B)]$
Re_L^* = modified Reynolds number, $u_L \rho_L d_p^*/\mu_L$
Re_m = two-phase Reynolds number, $\{\epsilon_B d_t/[1 + 3(1 - \epsilon_B)d_t/2d_p]\}(L_m + G_m)^2/(\mu_L L_m + \mu_g G_m)$
r = radial distance, m
r_o = overall rate of reaction, kmol/(kg)(s)
S_p = shape factor, s_x/d_p^2
S_D = gas-covered external particle surface, m^2
S_x = external particle surface, m^2
S_w = liquid-covered external particle surface, m^2
s = spreading factor
Sc_L = Schmidt number
Sh_L = Sherwood number, $\dfrac{k_s d_p}{D_L}$
Sh_L' = modified Sherwood number, $\dfrac{k_s a_s}{a_t}\dfrac{d_p}{D_L}$
Sh_L' = modified Sherwood number, $\dfrac{k_s a_s}{D_L a_t^2}$
T_s = temperature on particle surface, K
T_f = temperature in the bulk fluid, K
V_p = volume of particle, m^3
u_L, u_g = superficial velocity, liquid and gas, m/s
u_z = vertical component of the local liquid velocity, m/s
$u_{z,i}$ = initial liquid velocity, m/s
We_L = Weber number, $L_m^2/\delta_L \rho_L a_t$
We_L' = modified Weber number $u_L^2 \rho_L d_p/h_e^2 \delta_L$
We_g = gas Weber number, $(u_g^2 d_p \rho_g/\delta_L)$
We_m = two-phase Weber number,

$$\frac{d_t(L_m + G_m)(L_m/\rho_L + G_m/\rho_g)}{\{1 + 3(1 - \epsilon_B)d_t/2d_p\}\delta_L}$$

Z = parameter defined in Eq. 36
z = axial coordinate, m

Greek Letters

α_{gs} = Biot number for mass transfer on the gas-covered surface of the particle, defined in Eq. 4d, dimensionless
α_{gLs} = Biot number for mass transfer on the liquid covered surface of the particle, defined in Eq. 4d dimensionless
$(\alpha\beta)_L, (\alpha\beta)_L', (\alpha\beta)_g'$ = parameters defined in Table 6
$\beta_1 \beta_2 - \beta_5$ = constants given in Table 2
$\gamma_1, \gamma_2 - \gamma_5$ = constants given in Table 2
δ_{Lg}, δ_g = two-phase and gas-phase frictional pressure drop, N/m^3
ϵ_B = bed void fraction, dimensionless
ϵ_p = particle porosity, dimensionless
η_o, η_L, η_g = overall, liquid and gas effectiveness factor, dimensionless
λ = parameter $[(\rho_g/\rho_{\text{air}})(\rho_L/\rho_{\text{water}})]^{0.5}$
λ_{er} = effective radial thermal conductivity, kJ/(m)-(s)(K)
$\lambda_e^o, \lambda_{e,g}, \lambda_{e,L}$ = contributions to λ_{er}
Λ_{er} = effective radial thermal conductivity evaluated by Weekman and Myers, kJ/(m)(s)(K)
μ_L, μ_g = liquid and gas viscosity, kg/(m)(s)
μ_w = water viscosity, kg/(m)(s)
ρ_L, ρ_g = liquid and gas density, kg/m^3
ρ_a = air density kg/m^3
ρ_p = particle density, kg/m^3
δ_L = liquid surface tension, kg/s^2

δ_w = water surface tension, kg/s^2
ϕ = Thiele modulus, $V_p/S_x\sqrt{\rho_p k_v C^{m-1}/D_e}$
χ = variable defined in Eq. 19
ψ = parameter, $(\delta_w/\delta_L)[(\mu_L/\mu_w)(\rho_w/\rho_L)^2]^{0.33}$

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Manuscript received May 14, 1982; revision received October 25, and accepted October 28, 1982.