LITERATURE CITED

Bellman, R. E., H. H. Kagiwada, R. E. Kalaba, and M. C. Prestrud, *Invariant Imbedding and Time-Dependent Transport Processes*, American Elsevier, New York (1964).

Bellman, R. E., R. E. Kalaba, and J. A. Lockett, *Numerical Inversion of the Laplace Transform: Applications to Biology, Economics, Engineering and Physics*, American Elsevier, New York (1966).

Blair, D. W., J. O. L. Wendt, and W. Bartok, "Evolution of Nitrogen and other Species during Controlled Pyrolysis of Coal," Sixteenth Symposium (International) on Combustion, p. 475, The Combustion Institute, Pittsburgh, Pa. (1977).

Filon, L. N. G., "On a Quadrature Formula for Trigonometric Integrals," *Proc. Royal Soc. Edinburgh*, 49, 38 (1928).

Hahn, W. A., "Use of the Laplace Transform for the Time Resolution of Rapid Processes Applied to Coal Volatilization," M.S. thesis, Univ. Ariz., Tucson (1977).

———, and F. P. Plachco, "Solid-Liquid Extraction in Co- or Countercurrent," *Lat. Am. J. Chem. Eng. Appl. Chem.*, 7, 3 (1977).

Krylov, V. I., and N. S. Skoblya, *Handbook of Numerical Inversion of Laplace Transforms*, IPTS Press, Wierner Bindery, Ltd., Jerusalem, Israel (1969).

Marquardt, D. G., *J. Soc. Indust. Appl. Math.*, 3, 431 (1963).

Seinfeld, J. M., and L. Lapidus, *Mathematical Models in Chemical Engineering*, Vol. 3, Prentice-Hall, Englewood Cliffs, N.J. (1974).

Sy, F., and E. N. Lightfoot, "Transient Creeping Flow Around Fluid Spheres," *AIChE J.*, 17, 177 (1971).

Wen, C. Y., and L. T. Fan, *Models for Flow Systems and Chemical Reactors*, p. 130ff, Marcel Dekker, New York (1975).

Manuscript received August 8, 1977; revision received June 30, and accepted July 19, 1978.

JOURNAL REVIEW

Hydrodynamics and Solid-Liquid Contacting Effectiveness in Trickle-Bed Reactors

A. GIANETTO, G. BALDI, V. SPECCHIA, and S. SICARDI

Istituto di Chimica Industriale,
Politecnico, 10100 Torino, Italy

The term trickle-bed reactor usually means a reactor in which a liquid phase and a gas phase flow concurrently downward through a bed of catalytic pellets.

Trickle-bed reactors or similar apparatuses are used in the chemical, petrochemical, and petroleum industries, as well as in the field of wastewater treatment (trickling filters).

Considerable attention has therefore been recently directed to their fundamental mechanisms. These are rather complicated, owing to the three phases involved.

The subject as a whole has been reviewed in three papers (Satterfield, 1975; Hofmann, 1977; Hofmann, 1978); in addition, Laurent et al. (1974) and Charpentier (1976) have reviewed gas-liquid mass transfer in packed beds.

Most recent works on trickle-bed reactors deal with their hydrodynamics, modeling, and solid-liquid contacting effectiveness. Although in these works comparisons are made between the results obtained from different sources, a more extensive, critical analysis of these three topics seems worthwhile.

HYDRODYNAMICS

The hydrodynamics studies considered in this section concern the flow regimes, liquid distribution on the packing, pressure drop, and liquid holdup. The following parameters must be considered: gas and liquid flow rates, physical properties of the liquid phase, foaming characteristics of the system, and packed-bed geometry.

Hydrodynamic Regimes

Two-phase flow regimes. Many studies have been carried out for two-phase concurrent downward flow with nonfoaming systems (Larkins et al., 1961; Weekman and Myers, 1964; Sato et al., 1973; Charpentier and Favier, 1975; Midoux et al., 1976; Chou et al., 1976; Specchia and Baldi, 1977). For an air-water system at low liquid flow rates ($L < 3$ to 5 kg/m^{2}s), a gas continuous channeled or trickling flow occurs at low gas flow rates; then, by increasing the gas flow rate, a spray flow appears.

At L between 5 and 35 kg/m^{2}s, on increasing the gas flow rate, gas continuous channeled flow, pulsing flow, and spray flow occur in succession.

When $L > 35$ kg/m^{2}s, and the gas flow rate is low, a dispersed bubble flow can be observed, followed by a pulsing flow when the gas flow rate is increased.

The hydrodynamic regimes set up in a packed bed when foam appears have been defined by Charpentier and Favier (1975) and Midoux et al. (1976). Trickling flow, foaming flow, foaming-pulsing flow, pulsing flow, and spray flow can be observed.

0001-1541-78-1620-1087-$02.05. © The American Institute of Chemical Engineers, 1978.

Flow regime maps. Almost all the data refer to the air-water system; Charpentier and Favier (1975) and Midoux et al. (1976) have also tested hydrocarbons to study liquid systems similar to those employed industrially.

Various flow maps have been presented. Charpentier and Favier (1975) plotted the dimensionless group $L\lambda\psi/G$ as a function of G/λ, where λ and ψ, originally proposed by Baker (1954) for two-phase flow in empty horizontal pipes, depend only on the physical properties of the gas and the liquid. They did not take the packing characteristics into account.

Gianetto et al. (1970) observed that at a constant gas flow rate, the transition from trickling to pulsing flow occurred at higher liquid flow rates as the bed void fraction increased. The same phenomenon has been noted by Chou et al. (1976). The data of Sato et al. (1973) show a nonmonotonic effect of the bed void fraction. The low columns/packing diameter ratio adopted for the beds with a high void fraction, however, casts doubt on this finding.

By considering the bed void fraction ϵ in Figure 1, a flow map is proposed where $L\lambda\psi/G$ is plotted as a function of $G/\lambda\epsilon$ for foaming and nonfoaming systems, using the results obtained by several workers (Table 1) in the form of smoothed curves.

For the transition from trickling to pulsing flow for nonfoaming systems (full lines), all the data, except those of Chou et al. (1976), which show a large scatter, are in a good agreement; almost all the data refer to particles similar to catalyst pellets in shape and size. The transition data obtained by Charpentier et al. (1969) with large Raschig rings, in fact, do not agree satisfactorily with the full lines in Figure 1.

The results of Chou et al. (1976) and Specchia and Baldi (1977) for the same transition in foaming systems (dashed lines) are also shown in the same figure; the transition line of Charpentier and Favier (1975) for foaming systems coincides with the plotted curve for nonfoaming systems. As can be seen, there is little agreement between the sources.

Packing wettability has a significant effect on the transition from trickling to pulsing flow. Only Chou et al. (1976) have used silicone coated glass beads, and the transition occurred at higher gas and liquid flow rates than those necessary for uncoated beads.

On the basis of the gas-liquid interaction, Midoux et al. (1976) and Specchia and Baldi (1977) have suggested that only two main hydrodynamic regimes are involved: a low interaction regime, including the trickling flow only, and a high interaction regime, comprising all the other flow regimes for both foaming and nonfoaming systems.

As a conclusion, the flow map shown in Figure 1 can be assumed as reliable for determining the transition conditions between low and high interaction regime for nonfoaming systems in a bed of catalyst pellets. As regards foaming systems, the flow map is not reliable owing to the few available data and their scatter. Furthermore, the

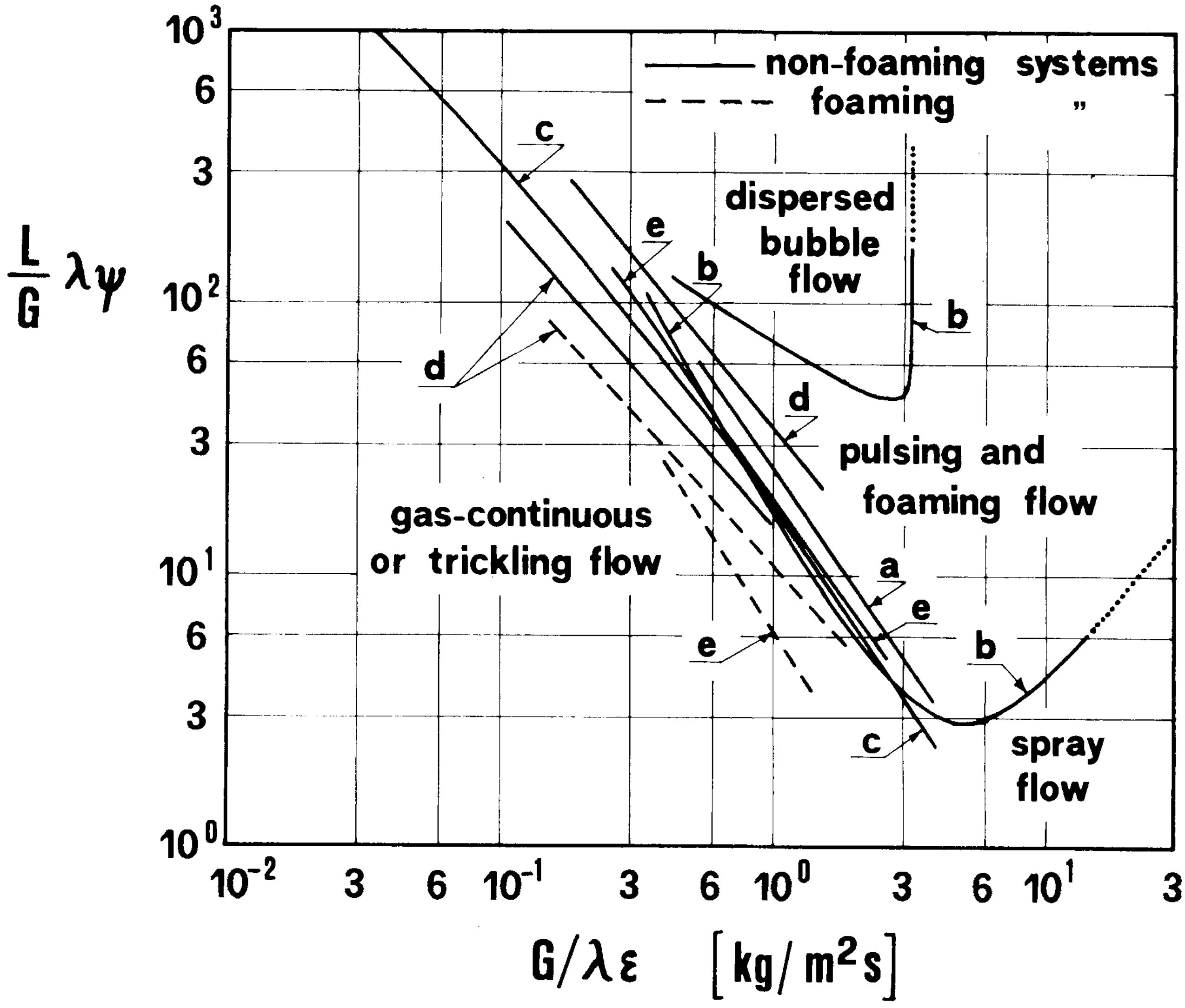

Fig. 1. Regime flow map for foaming and non-foaming systems (for the sources of the lines, see Table 1).

TABLE 1. LITERATURE DATA FOR THE FLOW MAP PLOTTED IN FIGURE 1: TWO-PHASE CONCURRENT DOWNWARD FLOW FOR FOAMING AND NONFOAMING SYSTEM

References	Line in Figure 1	Packing	Porosity	Gas-liquid system
Gianetto et al. (1970)	a	6 mm glass spheres	0.41	Air-Sodium hydroxide aqueous solutions
		6 mm glass rings	0.71	Air-Sodium hydroxide aqueous solutions
		6 mm ceramic rings	0.50	Air-Sodium hydroxide aqueous solutions
		6 mm Berl saddles	0.59	Air-Sodium hydroxide aqueous solutions
Sato et al. (1973)	b	8 mm glass spheres	0.39	Air-water
Charpentier and Favier (1975)	c	3 mm catalyst spheres	0.39	Air-water; air-cyclohexane
		1.8 × 6 mm catalyst cylinders	0.39	Air-water
		1.4 × 5 mm catalyst cylinders	0.37	Nitrogen-cyclohexane or gasoline or petroleum ether; carbon dioxide-gasoline or petroleum ether; helium-gasoline
Chou et al. (1976)	d	2.9 mm glass beads	0.39	Air-methanol and ethanol aqueous solutions; air-water with surfactants
Specchia and Baldi (1977)	e	6 mm glass spheres	0.40	Air-water
		5.4 × 5.4 mm glass cylinders	0.37	Air-water; air-glycerol aqueous solutions
		2.7 × 2.7 mm glass cylinders	0.38	Air-water

physical parameters employed (density, viscosity, and surface tension) are probably not sufficient to define when a gas-liquid system is foaming; the foam formation is very likely connected with the physicochemical conditions of the interfacial surface. The coalescence tendency of the gas bubbles might probably play an important role on the foam stability. Studies on this argument would be worthwhile.

Distribution and Radial Spread of the Liquid

The radial liquid distribution for two-phase concurrent flow in packed beds is related to the profile across the column section of the liquid flow rate per unit empty area; it may affect the uniform wetting of the catalyst and hence the performance of trickle-bed reactors.

The liquid velocity profile has been generally obtained by measuring the liquid flowing from several annular collectors at the bottom of the column. Table 2 lists the liquid distribution studies in the literature, together with the column diameter, bottom collecting device, and packings employed. Almost all these packings are those generally used in absorption towers.

Generally the liquid velocity profile, after a certain bed depth from the feed point, reaches a steady distribution (which does not change by increasing the bed depth). This calming bed depth depends on the packing shape and size, column diameter, gas and liquid flow rates, liquid physical properties, and the design of the liquid inlet distributor; the calming depth is shorter for a uniform inlet distribution than for a point source feed. Without gas flow rate, or at very low gas flow rate, several authors (Jameson, 1966; Dutkai and Ruckenstein, 1968; Brignole et al., 1973; Onda et al., 1973; Herskowitz and Smith, 1977*a*) determined experimentally for various types of packing the bed depth necessary to reach the steady liquid distribution.

For two-phase concurrent flow in the high interaction regime, Reiss (1967) found a calming bed depth of about 0.6 m for a 0.4 m diameter column packed with $2.5 \cdot 10^{-2}$ m Raschig rings.

In this paper, only the liquid distribution in a fully developed flow is considered; in these conditions, the liquid velocity does not depend anymore on the axial coordinate. The results from different sources are sufficiently in agreement.

In order to analyze the liquid distribution in a packed bed, it is necessary to divide the column section into two zones; the packing zone, occupying almost all the column section, and the wall zone, which consists of a thin annular section near the wall (usually the width of the wall zone is considered to be about one half the packing size). The flow on the packing and that at the wall, in fact, have different behavior, since the void fraction of the wall zone is higher than that of the packing (Schwartz and Smith, 1953).

At very low gas and liquid flow rates, that is, in the gas continuous regime, the liquid distribution on the packing is substantially uniform for particles with $D_p \leqq 6$ mm and for $12 \leqq D_c/D_p \leqq 48$, irrespective of packing shape, but not for larger particles (Specchia et al., 1974; Sylvester and Pitayagulsarn, 1975; Baldi and Specchia, 1976; Herskowitz and Smith, 1977*a*, *b*). By contrast, Weekman and Myers (1964) determined a nonuniform liquid distribution for 4.7 mm beads. Hochman and Effron (1969) carried out liquid residence time distribution measurements at various positions in a column sections with 4.7 mm pellets for the nitrogen-methanol system and found a uniform liquid velocity within 10% across the whole column section.

At large gas flow rates, the liquid velocity profile on the packing depends on the gas superficial velocity. For beads and saddles, a marked increase in the liquid velocity at the center of the column was noted on approaching the pulsing flow regime, a further increase in the gas flow rate again led to a liquid redistribution (Specchia et al., 1974; Sylvester and Pitayagulsarn, 1975; Baldi and Specchia, 1976). A less marked increase of the liquid velocity at the center was obtained with 6 mm rings and no increase at all with large rings (Reiss, 1967; Sylvester and Pitayagulsarn, 1975; Baldi and Specchia, 1976).

In connection with the liquid distribution, a radial spread factor D_R has been defined, which takes account of the tendency of the liquid to move radially in the catalytic bed.

The distribution of the local liquid flow rate per unit empty area v in a developing flow can be expressed by the following equation (Porter and Jones, 1963):

$$\frac{\partial v}{\partial z} = D_R \frac{\partial}{r\,\partial r}\left(r \frac{\partial v}{\partial r}\right) \qquad (1)$$

To determine D_R experimentally, the liquid flow rate is generally fed axially at the top of the bed, and the radial distribution of v is measured at a certain height of the bed.

On the other hand, Porter et al. (1968) proposed a tracer method; the radial and axial concentration profile

Table 2. Liquid Distribution Studies for Two-Phase Concurrent Downward Flow in Packed Beds

References	Column diameter and collecting device	Packing
Weekman and Myers (1964)	80 mm; 3 annular zones	4.7 mm glass beads
Reiss (1967)	400 mm; 4 annular zones	12-75 mm Raschig rings
Specchia et al. (1974)	141 mm; 5 annular zones	6 mm glass beads
Sylvester and Pitayagulsarn (1975)	150 mm; 6 annular zones	3 × 3 mm cylindrical pellets 6 mm Raschig rings 6 mm Intalox saddles
Baldi and Specchia (1976)	141 mm; 5 annular zones	6 mm Berl saddles 6 and 12.5 mm Raschig rings
Herskowitz and Smith (1977 a, b)	40.8 mm; 3 annular zones	2.58, 3.52, 7.15, 8.75 and 11.1 mm granular activated carbon 6.35 and 9.53 mm ceramic balls
	114 mm; 4 and 6 annular zones	3 mm glass beads 6.35 × 6.35, 4.76 × 4.76 and 3.18 × 3.18 mm alumina cylinders

All studies were carried out with the air-water system under isothermal conditions at room temperature.

of a tracer injected axially in a fully developed flow was expressed as follows:

$$\frac{\partial c}{\partial z} = D_R \frac{\partial}{r\,\partial r}\left(r \frac{\partial c}{\partial r} \right) \tag{2}$$

They also showed that both methods give the same values for D_R. This result probably means that the radial liquid mixing in a packed bed is mainly due to a convective transport, while the diffusion phenomena have a little significance.

Measurements of D_R, carried out by Specchia et al. (1974) and Baldi and Specchia (1976) with the tracer method for various packings and all the hydrodynamic regimes, showed that it depends on the same parameters as those controlling the liquid distribution. For 12.5 mm rings, a concurrent gas flow did not affect D_R values. For 6 mm beads, saddles, and rings, D_R values decreased as the gas flow rate increased, particularly at high liquid velocities. The decrease of D_R was greater percentwise on passing from rings to saddles and then to beads.

This D_R decrease probably occurs because a concurrent gas flow breaks off the liquid bridges between the packing particles, so that the radial component of the liquid rivulets is reduced.

Herskowitz and Smith (1977*a*, *b*) defined a model for liquid distribution similar to that of Jameson (1966) by considering another spreading factor s as the fraction of the local axial liquid flow rate which moves in the radial direction. s was determined in a developing flow for the gas continuous flow regime only and was found to depend on particle shape and size; it was greater on passing from spherical to cylindrical and to granular particles and decreased when the particle size increased; however, for all particles of less than about 6 mm in equivalent diameter D_p^*, a maximum s value of 1 was obtained. D_p^* is the diameter of a sphere with the outer surface area of the particle.

It is possible to compare D_R and s and then the experimental results obtained with different methods. By transforming Equation (1) into a finite-differences representation based on radial and axial increments equal to D_p^*, a relationship similar to that developed by Herskowitz and Smith emerges on assuming

$$s = 4\, D_R/D_p^* \tag{3}$$

For $s = 1$, from Equation (3), one obtains

$$D_R = D_p^*/4 \tag{4}$$

For beads of 6 mm nominal size, the D_R value in the gas continuous regime calculated from Equation (4) is 1.25 mm; it is in close agreement with the experimental D_R value of 1.15 mm obtained by Specchia et al. (1974).

As regards the wall zone, Herskowitz and Smith (1977*a*, *b*) measured in the gas continuous regime a wall factor f_w which accounts for the fraction of the excess flow at the wall (that is, the difference between the actual liquid flow rate at the wall and the flow rate expected for uniform flow), which is directed back into the bed. f_w mainly depends on the number of contact points between the particles and the wall and hence on the ratio between the column and the particle equivalent diameter D_c/D_p^*; for the air-water system and for $D_c/D_p^* > 18$, irrespective of the packing shape, a maximum f_w value of 1 (that is, a wall liquid velocity equal to the superficial velocity) was obtained. As expected, for $D_c/D_p^* < 18$, f_w was affected by the particle shape; it was greater on passing from cylindrical to spherical and to granular particles.

Moreover, Herskowitz and Smith (1977*a*) found for cylindrical and spherical particles and for $D_c/D_p^* < 18$ that f_w increased tending to 1 by lowering the liquid surface tension with surfactants. Probably a lower surface tension improves the solid wettability at the contact points between the packing particles and the wall and makes easier the return of the liquid into the bed; in this way, the segregated liquid flow rate at the wall is reduced.

Specchia et al. (1974) and Baldi and Specchia (1976) measured the influence of the gas flow rate on the liquid wall flow. For all the packing tested, they found a liquid velocity at the wall greater than the superficial velocity in the low interaction regime; in the high interaction regime, on increasing the gas flow rate, the liquid velocity at the wall decreased tending to an asymptotic value, attained at very high gas flow rates. In these asymptotic conditions, the liquid wall velocity was practically equal to the liquid superficial velocity for packing particles with $D_p^* < D_c/18$ (6 mm beads and Berl saddles), whereas the liquid wall velocity was higher than the liquid superficial velocity for particles with larger D_p^* (6 and 12.5 mm Raschig rings).

As a conclusion of this review on the liquid distribution in trickle-bed reactors, it can be observed that there is a lack of experimental results in hydrodynamic regimes

Table 3. Pressure Drop Correlations for Two-Phase Concurrent Downward Flow in Packed Beds

References	Correlations and range of conditions
Larkins et al. (1961)	$\log\left(\frac{\delta_{LG}}{\delta_L+\delta_G}\right)=\frac{0.416}{(\log\chi)^2+0.666} \qquad (5)$ $0.05<\chi=(\delta_L/\delta_G)^{0.5}<30 \qquad (6)$ 9 mm Raschig rings, 9 mm stoneware spheres and 3 mm glass spheres; nonfoaming systems for all hydrodynamic regimes
Turpin and Huntington (1967)	$\ln f_{LG}=7.96-1.34\ln Z+0.0021(\ln Z)^2+0.0078(\ln Z)^3 \qquad (7)$ $f_{LG}=\delta_{LG}D_e/2\,v_G^2\,\rho_G \qquad (8)$ $D_e=\frac{2}{3}D_p\frac{\epsilon}{1-\epsilon} \qquad (9)$ $0.2<Z=(Re_G)^{1.167}/(Re_L)^{0.767}<500 \qquad (10)$ 7.5 to 8.1 mm tabular alumina; air-water for all hydrodynamic regimes
Sato et al. (1973)	$\left.\begin{array}{ll}\log\left(\frac{\delta_{LG}}{\delta_L+\delta_G}\right)=\frac{0.70}{[\log(\chi/1.2)]^2+1} & (11)\\ \left(\frac{\delta_{LG}}{\delta_L}\right)^{0.5}=1.30+1.85(\chi)^{-0.85} & (12)\end{array}\right\}\ 0.1<\chi<20$ 2.6 to 24.3 mm glass spheres; air-water for all hydrodynamic regimes
Midoux et al. (1976)	$\left(\frac{\delta_{LG}}{\delta_L}\right)^{0.5}=1+\frac{1}{\chi}+\frac{1.14}{(\chi)^{0.54}} \qquad (13)$ $0.1<\chi<80$ 3 mm glass and catalyst spheres, 1.8 × 6 and 1.4 × 5 mm catalyst cylinders; nonfoaming systems for all hydrodynamic regimes, and foaming systems for the low interaction regimes $\left(\frac{\xi_{LG}}{\xi_L}\right)^{0.5}=1+\frac{1}{\chi'}+\frac{6.55}{(\chi')^{0.43}} \qquad (14)$ $0.05<\chi'=(\xi_L/\xi_G)^{0.5}<100 \qquad (15)$ $\xi_{LG}=\frac{1}{\epsilon}\left[\frac{L}{\rho_L}+\frac{G}{\rho_G}\right]\left(\frac{\Delta H}{\Delta z}\right)_{LG}+\frac{L+G}{\epsilon\rho_e} \qquad (16)$ $\xi_L=\frac{L}{\epsilon}\left[\frac{1}{\rho_L}\left(\frac{\Delta H}{\Delta z}\right)_L+\frac{1}{\rho_e}\right] \qquad (17)$ $\xi_G=\frac{G}{\epsilon}\left[\frac{1}{\rho_G}\left(\frac{\Delta H}{\Delta z}\right)_G+\frac{1}{\rho_e}\right] \qquad (18)$ 3 mm glass and catalyst spheres and 1.4 × 5 mm catalyst cylinders; foaming systems for the high interaction regime
Specchia and Baldi (1977)	$\delta_{LG}=k_1\frac{[1-\epsilon(1-\beta_r-\beta_f)]^2}{\epsilon^3(1-\beta_r-\beta_f)^3}\mu_G v_G+k_2\frac{1-\epsilon(1-\beta_r-\beta_f)}{\epsilon^3(1-\beta_r-\beta_f)^3}\rho_G v_G^2 \qquad (19)$ 6 mm glass spheres, 5.4 × 5.4 and 2.7 × 2.7 mm glass cylinders, 6.4, 10.3, and 22 mm Raschig rings; foaming and nonfoaming systems for the low interaction regime $\ln f_{LG}=7.82-1.30\ln(Z/\psi^{1.1})-0.0573[\ln(Z/\psi^{1.1})]^2 \qquad (20)$ $0.6<Z/\psi^{1.1}<500$ $\psi=\frac{\sigma_{\text{water}}}{\sigma_L}\left[\frac{\mu_L}{\mu_{\text{water}}}\left(\frac{\rho_{\text{water}}}{\rho_L}\right)^2\right]^{1/3} \qquad (21)$ 6 and 3 mm glass spheres, 5.4 × 5.4 and 2.7 × 2.7 mm glass cylinders, 3.2 × 3.2 mm catalyst cylinders, 6.4, 10.3, and 22 mm Raschig rings; foaming and nonfoaming systems for the high interaction regime

other than the gas continuous flow when particles with the same shape and size as the catalyst are used. The effects of the physical properties of the fluids must also be investigated, mainly viscosity and surface tension of the liquid and density of the gas phase. Moreover, more attention must be devoted to the foaming systems.

Pressure Drop

Pressure drop is an important parameter in the design of two-phase concurrent reactors because it affects the energy supply; it has been used to correlate the gas-liquid and solid-liquid mass transfer (Reiss, 1967; Gianetto et al., 1970; Sato et al., 1972; Gianetto et al., 1973; Lemay et al., 1975).

An extensive literature exists on the two-phase frictional pressure drop δ_L, and many correlations have been proposed; the most significant, together with their range of validity, are listed in Table 3.

Unfortunately, most results have been obtained with laboratory or pilot columns, so that these correlations need to be checked with data from industrial apparatuses.

Following the Lockhart and Martinelli approach (1949) for concurrent two-phase flow in empty tubes, δ_{LG} correlations were first suggested by Larkins et al. (1961) and then by Sato et al. (1973). In these correlations, δ_{LG} is considered as a function of the pressure drop of each phase flowing alone through the whole section (δ_L and δ_G) and of the parameter χ defined by Equation (6) in Table 3.

Next, Midoux et al. (1976) used a modified parameter χ', defined by Equation (15); this was suggested by Charpentier et al. (1969) on the basis of an energy balance.

To employ the χ or χ' correlations, it is necessary to know the single phase pressure drops. Accuracy can only be assured with experimental measurements, so their employment is rather cumbersome.

This difficulty was overcome by Turpin and Huntington (1967), who proposed the empirical correlation shown by Equation (7); a two-phase friction factor f_{LG} is expressed as a function of the parameter Z, defined by Equation (10) on the basis of the gas and liquid Reynolds numbers.

These correlations do not generally agree satisfactorily with each other. Moreover, generally, they do not take into account the different hydrodynamic regimes and hence the different gas-liquid interaction, nor do they consider foaming systems on the other hand.

Midoux et al. (1976) have studied several gas-hydrocarbon foaming and nonfoaming systems. For all regimes in nonfoaming systems and for the low interaction regime in foaming systems they have proposed the χ based correlation shown in Equation (13), which was sufficiently in agreement with that of Larkins et al. and Sato et al. and with the experimental data of Weekman and Myers (1964). For the high interaction regime in foaming systems, Midoux et al. correlated the parameter ξ_{LG}, proportional to the two-phase frictional power loss per unit packed column and defined by Equation (16), as a function of χ'; this correlation is shown by Equation (14).

For the low interaction regime in both foaming and nonfoaming systems, an approach similar to that of Hutton and Leung (1974) has been proposed by Specchia and Baldi (1977); δ_{LG} is calculated as due to the gas flowing in a bed restricted by the presence of the liquid, and the influence of the concurrent gas flow on the liquid holdup has been taken into account. The correlation is shown by Equation (19). The coefficients k_1 and k_2 depend on packing shape and size and must be evaluated from the pressure drop δ_w of the gas flowing alone through a wetted packing, that is, when only the residual holdup is present in the bed. k_1 and k_2 calculated in this way differ significantly from those for a dry packing, as determined by Hutton and Leung. The model of Specchia and Baldi fits the experimental results better than the correlation suggested by Hutton and Leung.

For the high interaction regime in both foaming and nonfoaming systems, Specchia and Baldi (1977) proposed the empirical correlation shown by Equation (20), based on f_{LG} and Z. The experimental data for foaming systems were correlated by introducing the parameter ψ, defined by Equation (21). Equation (20) takes into account quite a wide range of operative conditions, fluid physical properties, and packing shape and size; it can be used in practice, since only easily available parameters are needed.

Liquid Holdup

General. Liquid holdup is the liquid volume contained in a unit column volume; liquid saturation is the liquid volume contained in a unit void volume of column.

Almost all the holdup data refer to laboratory columns; the only data on commercial reactors seem to be those of Ross (1965) obtained in a 2 m ID desulfurization reactor, where the holdup was about two-thirds that of a pilot reactor.

If the bed particles are porous, as in trickle-bed reactors, the total saturation β_t is the sum of the internal (the liquid held in the pore volume of the catalyst) and external contributions.

The external liquid saturation is divided into residual saturation β_r and free draining (or operative) saturation β_f. The former is the fraction of the liquid that remains in the bed after it has been completely wetted and drained; the latter is defined as the fraction of liquid that collects from the bottom of the column when draining, after a sudden shutoff of the liquid feed. β_f is affected by the liquid and gas flow rate, the fluid physical properties, and the packing characteristics.

β_t can be determined for porous and nonporous particles by a weighing method or by a dynamic tracer technique (Charpentier et al., 1971; Sato et al., 1973; Midoux et al., 1976; Colombo et al., 1976). The latter, however, gives poor results, especially for porous particles, if the tracer concentration in the tail of the response curve is not determined with accuracy.

Residual liquid saturation β_r. The residual saturation β_r depends on the liquid physical properties and particle shape, size, and wettability.

Charpentier et al. (1968) gave a graphical plot of $\epsilon\beta_r$ as a function of the Eötvos number ($E\ddot{o} = \rho_L g D_p^2/\sigma_L$) from their own data and those of other authors; the interpolating line was subsequently confirmed by Charpentier and Favier (1975) on several hydrocarbons, using catalyst cylinders.

For $E\ddot{o} < 4$, $\epsilon\beta_r$ is generally about 0.05; at higher $E\ddot{o}$ values, it decreases.

Verhoeven and Van Rompay (1974) also plotted $\epsilon\beta_r$ data as a function of the Eötvos number for a reactor for the catalytic hydrodesulfurization of petroleum fractions; their values were much higher than those of Charpentier et al. (1968), probably because the internal saturation of the catalyst pores was included.

Mersmann (1972) correlated β_r as a function of the Bond number ($Bn = \rho_L g/a_v^2\,\sigma_L$) for 0.57 and 1.13 mm glass beads. He found very high β_r values because of the large amount of the liquid held by capillary forces in his system.

Liquid saturation for free trickling liquid. Here the gas

TABLE 4. LIQUID SATURATION CORRELATIONS FOR FREE TRICKLING LIQUID

References	Correlations and range of conditions
Otake and Okada (1953)	$\epsilon\beta_f = 1.295\,(Re_L)^{0.676}\,(Ga_L)^{-0.44}\,(a_v D_p) \qquad (22)$ $10 < Re_L < 2\,000$ 6.4 to 22 mm spheres, 12.7 and 25.4 mm Raschig rings and Berl saddles
Mohunta and Laddha (1965)	$\epsilon\beta_f = 16.13\left(\frac{\mu_L v_L^3 N}{\rho_L g^2}\right)^{1/4}(N\,D_{pe})^{-1/2} \qquad (23)$ 6.3, 9.5, and 12.7 mm Raschig rings, 6.3 and 9.5 mm Lessing rings, 12.7 mm spheres; water and aqueous solutions of carboxy-methyl-cellulose
Satterfield and Way (1972)	$\epsilon\beta_{te} = A(v_L)^{1/3}\,(\mu_L)^{1/4} + B \qquad (24)$ 1.6 × 8 mm, 3.2 × 3.2 mm catalyst cylinders and 3 mm glass spheres; highly paraffinic hydrocarbon solvent and high viscosity paraffinic mineral oil
Wijffels et al. (1974)	$\beta^4{}_{te} = \left(\frac{200}{Re_L} + 1.75\right)\frac{v_L^2}{g\,D_p}\cdot\frac{1-\epsilon}{\epsilon^3} \qquad (25)$ 1, 3, 5, and 9.5 mm glass beads; water and cumene
Charpentier and Favier (1975)	$\beta_f = A'\,(L)^d \qquad (26)$ 3 mm glass and catalyst spheres, 1.8 × 6 and 1.4 × 5 mm catalyst cylinders; hydrocarbons
Specchia and Baldi (1977)	$\beta_f = 3.86(Re_L)^{0.545}\,(Ga_L)^{-0.42}\left(\frac{a_v D_p}{\epsilon}\right)^{0.65} \qquad (27)$ $0.3 < Re_L < 300$ 6.4, 10.3, 22, and 51 mm Raschig rings, 25 and 38 mm Berl and Intalox saddles, 4.13 and 4.8 mm glass beads, 6 mm glass spheres, 5.4 × 5.4 and 2.7 × 2.7 mm glass cylinders, 0.54 and 2.9 mm crushed particles, 1 mm carbon beads and 3.8 × 4.8 carbon cylinders; water, sugar aqueous solution, isopropanol solution, glycerol aqueous solutions and methanol

flow rate, if present, has a negligible effect on liquid flow behavior.

The most important correlations available are listed in Table 4. Some of these consider the total external saturation β_{te}, the others the free draining saturation β_f. Since β_f is affected by all the operative conditions, whereas β_r, which, under certain conditions, may be of the same order of magnitude, depends mainly on the liquid phase physical properties, it would seem advisable to consider β_f and β_r separately. For this reason, the correlations for β_{te} have poor theoretical support, since they consider the sum of two quantities that depend on different parameters.

The β_f correlations (except that of Charpentier and Favier, 1975) are, in fact, expressed as a function of Reynolds and Galileo numbers and of the packing geometry. β_{te} correlations, on the other hand, never employ the same dimensionless numbers.

The correlations of Satterfield and Way (1972), Wijffels et al. (1974), Charpentier and Favier (1975), and Specchia and Baldi (1977) consider the free liquid trickling on packings whose shape and size correspond to those of catalyst pellets.

Liquid saturation for two-phase flow. The most important correlations for β_f and β_{te} are listed in Table 5, together with the range of the operative conditions examined.

Larkins et al. (1961) and Sato et al. (1973) correlated β_f and β_{te}, respectively, [Equations (28) and (30)] on the basis of the parameter defined earlier.

Charpentier and Favier (1975) examined several foaming and nonfoaming systems. They correlated β_{te} as a function of χ' [Equations (33) and (34) for cylindrical and spherical packings, respectively]. Their data agree sufficiently well with those of Sato et al. (1973).

None of these correlations consider hydrodynamic regimes. This would seem advisable, however, as in the case of pressure drop.

For the high interaction regime, Clements (1976) proposed two correlations as a function of the group $We_G Re_G/Re_L$ (where We_G is the gas phase Weber number): one, Equation (35), for nonfoaming systems and one, Equation (36), for foaming systems. They were, however, verified with his own data only. When tested with those in the literature (Larkins et al., 1961; Charpentier et al., 1968; Charpentier and Favier, 1975; Specchia and Baldi, 1977), we found that the group did not take sufficient account of the effect of the packing geometry, especially for foaming systems.

Midoux et al. (1976) proposed one correlation, Equation (38), for all the hydrodynamic regimes for nonfoaming systems and for the low interaction regime for foaming systems, and another, Equation (39), for the high interaction regime for foaming systems. The β_{te} values calculated with Equation (38) were always lower than those of Sato et al. (1973).

Specchia and Baldi (1977) have proposed correlations of β_f that take into account the gas-liquid interaction and the foaming properties of the systems.

At the low interaction regime for both foaming and nonfoaming systems, the correlation for the free trickling liquid at $v_G = 0$ [Equation (27) in Table 4] was enlarged to $v_G \neq 0$ by considering the effect of the pressure gradient along the packed bed [Equation (40)]. A modified Galileo number, defined by Equation (41), was introduced.

For the high interaction regime, they proposed Equations (42) and (43) for nonfoaming and foaming systems, respectively. In both, β_f was considered as a function of $Z/\psi^{1.1}$, as used for δ_{LG} correlations, and of a dimensionless group that takes the packing properties into account. In the previous correlations, packing properties were not directly considered; Sato et al. (1973) only introduced the particle area per unit column volume.

The correlations of Specchia and Baldi are derived from a large array of literature and personal data.

Comments on Pressure Drop and Liquid Holdup Correlations

Pressure drop and liquid holdup are significant design parameters; pressure drop is, obviously, connected with the dissipated power in the reactor that cannot be neglected when a selection has to be made between various multiphase reactors for a given process and is an important factor in optimizing a trickle-bed reactor; the liquid holdup is particularly important when homogeneous side reactions can also take place.

Moreover, both pressure drop and liquid holdup have been used as correlating parameters for gas-liquid and solid-liquid mass transfer coefficients (Reiss, 1967; Gianetto et al., 1973; Lemay et al., 1975; Specchia et al., 1977) and for the radial effective thermal conductivity in the bed (Hashimoto et al., 1976).

These reasons justify the great amount of research work on these two topics. However, owing to the quite complex behavior of the two-phase flow in a packed bed, a reliable theoretical based model of this flow has not yet been given, and several empirical or semiempirical correlations have been proposed, so that doubts arise in selecting one of them.

As observed before, the authors' opinion is that it is not possible to correlate pressure drop and liquid holdup both in the low and high interaction regime with the same type of correlating equation because the hydrodynamic phenomena in the two regimes are quite different; furthermore, a distinction between foaming and nonfoaming systems in the high interaction regime should also be made.

In the authors' experience, the χ and χ' correlations of pressure drop and liquid holdup are not reliable in the low interaction regime, while they, together with the Z correlations, may give good results for nonfoaming systems in the high interaction regime. For foaming systems in the high interaction regime, too few data exist; the correlations that can be used with more confidence for this regime seem to be those proposed by Midoux et al. (1976) [Equations (14) and (39)]. For the low interaction regime, evidence does not exist that foaming and nonfoaming systems behave differently.

As a general suggestion, the most recent correlations seem more reliable than the oldest ones, especially if they consider experimental data from different sources. Anyway, these correlations should be employed in the range of physical properties of the phases, packing shape and size, and phase flow rates in which they were tested.

As a conclusion, it must be stressed that more experimental data of pressure drop and liquid holdup are needed concerning highly viscous liquids and low density gases, as used in industrial operations (for instance, hydrotreating of heavy oils). Furthermore, much work is necessary for foaming systems, since, as already said, the parameters affecting the foam formation are not yet well known.

HYDRODYNAMIC MODELS FOR GAS AND LIQUID FLOW

General

Many mathematical models for the hydrodynamics of the gas and liquid phases in trickle-bed reactors have been proposed in the literature.

They are used to transform into mathematical equations physical pictures of the gas and liquid flow in packed beds and provide numerical parameters to characterize the hydrodynamics of the flowing phases.

The models are usually verified on the basis of the residence times distribution function R.T.D.F. of the phases, and their characteristic parameters are generally identified by means of the following methods:

1. R.T.D.F. moments. This technique has the advantage of requiring only the solution of the differential equations of the model in the Laplace or Fourier domain, but the evaluation from the response curves of moments higher than the second is very difficult, owing to the uncertainty of the tails.
2. Numerical comparison of the experimental and theoretical R.T.D.F. curves in the time domain. The theoretical function which best fits the experimental data is obtained by determining the values of the parameters which give rise to the minimum mean-square deviation between the experimental and the calculated values of the response curves. This technique is more rigorous, but, if there are more than two involved parameters, the optimization techniques require complex iterative computations (Villermaux and Van Swaaij, 1969) and may give rise to ambiguous solutions.
3. Graphical comparison of particular values of the experimental and theoretical R.T.D.F. in the time domain. For example, with an impulse disturbance, one parameter can be identified by evaluation of the maximum of the response curves (Buffham et al., 1970). With the step decrease disturbance, the curve of the outlet tracer concentration vs. time in a semilog plot may be straight at high time values. Its slope has been used for the definition of one parameter (Bennet and Goodridge, 1970). These graphical techniques are not very rigorous but generally have the advantage of being quite immediate.

Some workers have reduced, with physical assumptions, the number of the parameters to be identified.

For example, sometimes it was assumed that the liquid holdup of dead zones was equal to the residual liquid holdup (Van Swaaij et al., 1969). In one case (Villermaux and Van Swaaij, 1969), the Peclet number has also been evaluated on the basis of physical arguments. This method is obviously not rigorous because it assumes the identification of a parameter independently from the experimental data on the R.T.D.F. of the phases.

Gas-Phase Models

Few papers have examined the gas R.T.D.F. in trickle-bed reactors, because in most cases the influence of axial gas dispersion on reactor performance is not very important. The gases most commonly used in trickle-bed operations (oxygen and hydrogen), in fact, are poorly soluble, and hence the mass transfer phenomena, if present, are confined to the liquid phase. In addition, the rate of consumption of the gaseous component is very low compared with its flow rate, and hence its concentration in the gas does not change significantly along the reactor.

On the other hand, the gas flow rate cannot be completely disregarded because it may affect the liquid hydrodynamics and hence the mass transfer in the liquid.

Hochmann and Effron (1969) and Dunn et al. (1977) have satisfactorily interpreted the gas phase R.T.D.F.

with the longitudinal dispersion model; the dispersion coefficient was found to increase on increasing the liquid and the gas flow rates.

Liquid-Phase Models

The models proposed for the interpretation of the liquid R.T.D.F. can be classified on the basis of their characteristic parameters.

Those discussed in this review are shown schematically in Figure 2. One of the parameters, the total holdup, is common to all the proposed models and can also be evaluated by direct experimental methods (that is, by drainage or weighing); for these reasons, many workers do not include it in the total number of characteristic parameters. But in a rigorous analysis, it must be defined from the response curves of the system, and hence it must be taken into account.

Two-parameter model. The piston dispersion (P.D.) model makes use of total holdup and longitudinal dispersion coefficient. In trickle-bed reactors, this coefficient is generally higher than in a full reactor and decreases as the liquid flow rate increases.

Correlations of the longitudinal dispersion coefficient determined with the P.D. model are available in the literature (Michell and Furzer, 1972*b;* Elenkov and Kolev, 1972).

Interpretation of the R.T.D.F. with this model is not very satisfactory because the physical phenomenon of the liquid trickling on the packing is too complex to be described by the dispersion coefficient only. This was pointed out by Charpentier et al. (1971), who observed that the Peclet numbers given by the P.D. model were very scattered. Michell and Furzer (1972*b*), too, noted that interpretation of the response curves at high time values is not satisfactory.

Three-parameter models. In the cross-flow or piston-exchange (P.E.) model, the liquid is assumed to be divided into two parts: one flowing in plug flow, the other stagnant and in contact with the flowing liquid. The parameters are: total liquid holdup, dynamic or static liquid holdup, and a mass transfer coefficient k_s^* between the two zones. The mathematical expression consists of two differential equations for the nonsteady mass balances in the two zones. The workers that used this model determined the dynamic holdup by the time delay τ_d between the output and input signals $\epsilon\beta_{fm} = v_L\tau_d/h$, where h is the reactor length and v_L the liquid superficial velocity. The mass transfer coefficient has been evaluated with the moment method (Hochman and Effron, 1969; Hoogendoorn and Lips, 1965).

The probabilistic time delay model (Buffham et al., 1970; Buffham and Gibilaro, 1970) supposes a main piston flow, with lateral streams delayed at different points along the column that cross liquid regions in plug flow or perfectly mixed and then come back to the main flow. The total liquid R.T.D.F. is determined by considering the probability that a certain number of delayed events occurs in the whole column. Thus, the parameters are total holdup, dynamic liquid holdup, and the mean time for these delayed events. If the lateral streams cross perfectly mixed zones, that is, the time delays for each event are exponentially distributed, this model coincides analytically with the P.E. model, and the mean time delay of the mixed zones τ_{dm} is connected with the mass transfer coefficient k_s^* of the P.E. model by the relationship: $\tau_{dm} = 1/k_s^*$.

In these three-parameter models, static holdup ($\epsilon\beta_{rm}$), that is, the difference between the total and the dynamic holdup, was found to practically coincide with the residual holdup ($\epsilon\beta_r$) given by Charpentier's correlation (Charpentier et al., 1968).

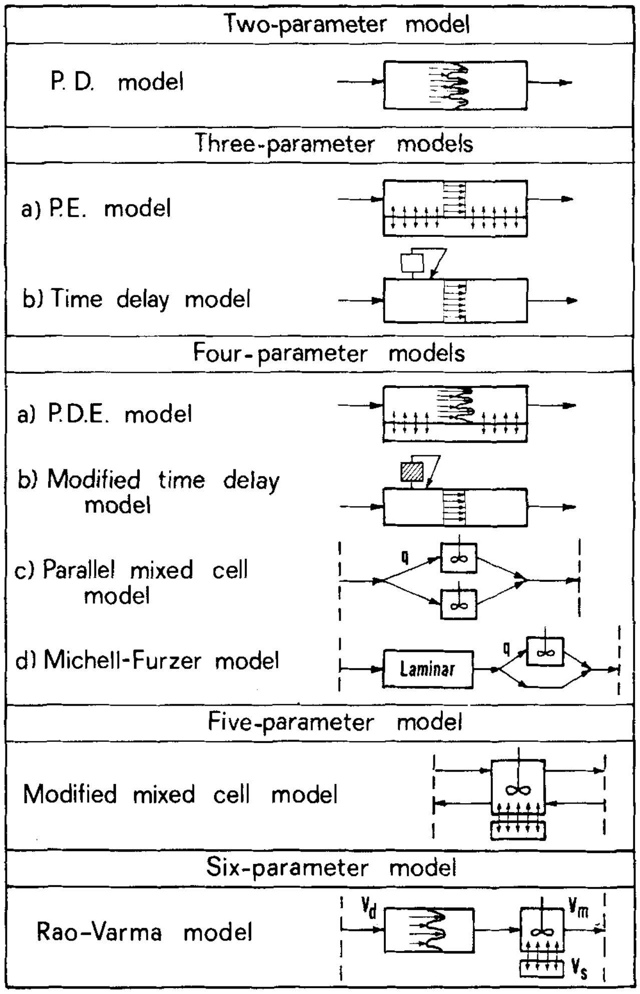

Fig. 2. Schematic drawing of the liquid phase hydrodynamic models.

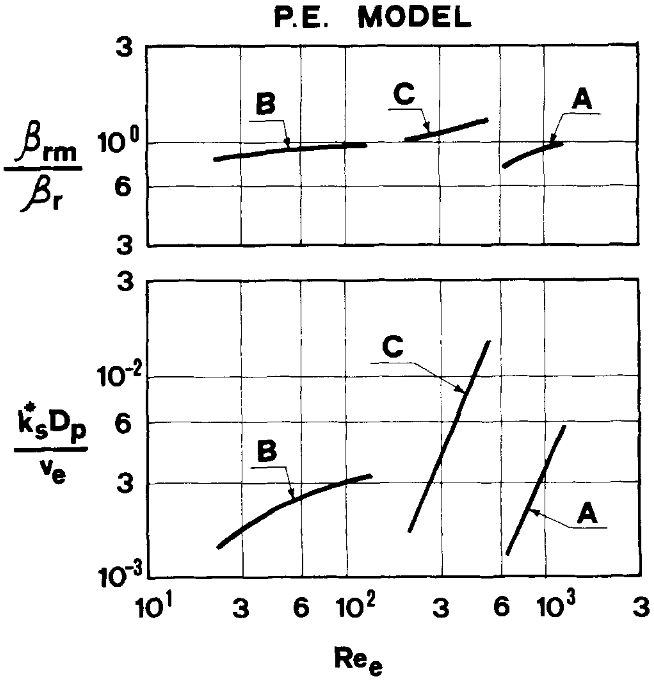

Fig. 3. Plot of β_{rm}/β_r and $k_s^*D_p/v_e$ as a function of Re_e for P.E. model (for the sources of the lines, see Table 6).

β_{rm}/β_r for the P.E. and the probabilistic time delay model is, in fact, about one, and is independent of the liquid flow rate (Figure 3).* Our experiments with a non-

---

* The literature sources for the curves shown in figures 3, 4, and 5 are listed in Table 6.

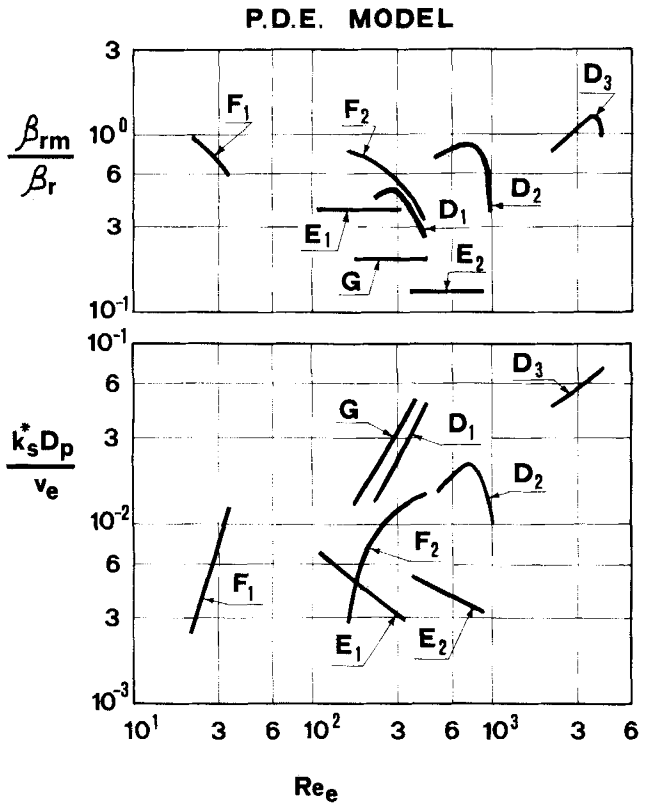

Fig. 4. Plot of β_{rm}/β_r and $k_s^*D_p/v_e$ as a function of Re_e for P.D.E. model (for the sources of the lines, see Table 6).

negligible gas flow rate showed that β_{rm}/β_r decreases as the gas flow rate increases.

Figure 3 also shows values of $k_s^*D_p/v_e$ as a function of Re_e obtained by workers using the same input signals (impulse disturbances) but different identification methods. $k_s^*D_p/v_e$ has been adopted by analogy with the mass transfer phenomenon. In formal terms, it may be considered as a Stanton number.

Four-parameter models. The P.D.E. (piston-dispersion-exchange) model is obtained from the P.E. model by assuming a plug flow with longitudinal dispersion. The mass transfer relationships between the flowing fluid and the stagnant zones are similar to those in the P.E. model. The liquid static holdup and k_s^* values given by this model are obviously different from those determined with the P.E. model because the P.D.E. model attributes the trend of the response curves to both mass transfer with the dead zones and longitudinal dispersion. The analytical solution in the time domain of the P.D.E. model for a closed-open system, as defined by Levenspiel (1962), was given by Villermaux and Van Swaaij (1969) and Popovic and Deckwer (1976) and for a closed-closed system by Bennet and Goodridge (1970).

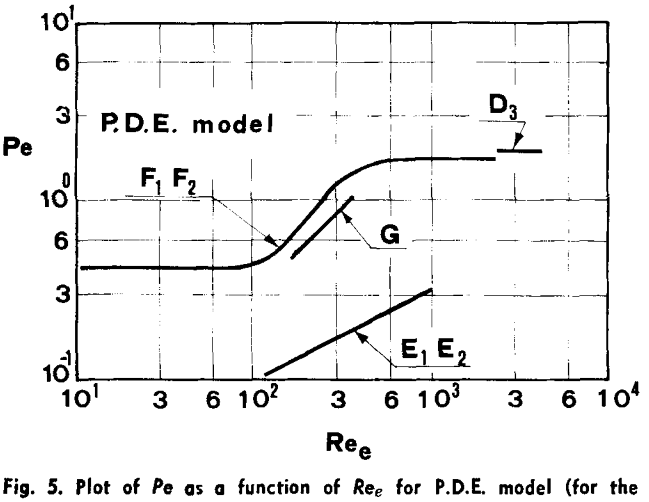

Fig. 5. Plot of Pe as a function of Re_e for P.D.E. model (for the sources of the lines, see Table 6).

Bennett and Goodridge (1970) suggested that a step decrease disturbance should be used to obtain the maximum amount of information, since it is thus possible to evaluate outlet stream concentration even at very high times (up to fourteenfold the mean residence time).

$k_s^*D_p/v_e$ as a function of Re_e evaluated with the P.D.E. model is shown in Figure 4. All the data, except those of Bennet and Goodridge (1970), were obtained by using a pulse disturbance. As concerns the identification, the data of Villermaux and Van Swaaij (1969) in Figure 4 were obtained by fixing the value of Pe a priori and then determining the other parameters; these data are thus not fully comparable with those of other workers. Matsuura et al. (1976) and Friebe (1966) identified all the characteristic parameters by mean-square deviations, whereas Bennet and Goodridge (1970) used the graphical identification method. The poor agreement in Figure 4 is probably due to the differences in the procedures adopted both for the experiments and for identification of the parameters.

β_{rm}/β_r values are shown in Figure 4. These ratios are generally lower than those evaluated with the P.E. model.

In Figure 5, Pe numbers are plotted as a function of Re_e.

The modified time delay model (Oorts and Hellinckx, 1974) supplements the original model of Buffham et al. (1970) with a parameter to take into account nonperfect mixing in the delayed lateral streams. The results seem to be very good; the mean-square deviations between the experimental and calculated values of the tracer concentrations in the response curves were lower than those obtained by the P.D.E. model.

Unfortunately, its validity at very high response times was not verified.

In the parallel mixed-cell model (Van Swaaij et al., 1969), the trickle bed is simulated by a cascade of elements provided by two perfect mixers in parallel; the liquid flow rate is distributed in the mixers according to the ratio $q/(1-q)$, and their liquid volumes are assumed as proportional to the dynamic and static liquid holdup.

The four parameters are total holdup, static holdup, q, and the number of elements in series (n). Since the static holdup is taken by the authors as equal to the residual holdup, the model becomes a three-parameter model. q and n were evaluated by the moment method.

In the cascade of laminar films with partial mixing and bypassing at the packing junctions (Michell and Furzer, 1972*a*), the parameters are total and dynamic liquid holdup, the fraction q of the liquid flow mixed at every junction, and the number n of elements in series. The dynamic holdup was evaluated from the correlations proposed in the literature. Since n was assumed equal to h/D_p, the model became a two-parameter one and was compared with the P.D. model. A relationship between q and the Pe number of the P.D. model was also proposed.

Five-parameter model. It is a modified mixed-cell model (Popovic and Deckwer, 1976).

This considers the liquid flowing through a series of perfectly mixed cells in which mass exchange with stagnant zones is also taken into account. The parameters are total and static holdup mass exchange coefficient k_s^*, n, and the backward flow rate. Popovic and Deckwer (1976) have demonstrated that this model is practically equivalent to the P.D.E. model.

Six-parameter model. A model proposed by Rao and Varma (1976) considers a series of n equal elements, in each of which the total liquid volume V_t is divided into three parts (see Figure 2): a zone characterized by plug flow with longitudinal dispersion (V_d), followed by a mixed volume (V_m) which exchanges mass with the stagnant volume (V_s). The six parameters of the model are total ($V_t = V_m + V_s + V_d$), dispersed (V_d) and static (V_s) volumes, dispersion coefficient (or the Peclet number), the fraction of feed that exchanges between the active and stagnant regions, and n. n was taken as equal to the ratio of bed height to the particle size, and hence the model became a five-parameter one. V_d/V_t and the fraction of feed that exchanges between V_m and V_s were found to be practically independent of the operative conditions. The other three parameters were identified by the mean-square deviations method.

The results of this model show about half of the total liquid holdup flow as a dispersed stream, while the static zones represent 5 to 14% of the total holdup.

Conclusions. At present, the following points need to be stressed:

1. Comparison and selection of the best model would only be possible if the same identification method were used for all parameters with the same sets of experimental data. However, the definition of the best model is a questionable matter. A suitable model, in fact, must not contain too many characteristic parameters. It must also give a good interpretation of the R.T.D.F., even at very high response times. Furthermore, the parameters should have the most realistic physical meaning. From a practical point of view, models with more than four parameters are not easy to use. A three-parameter model is probably sufficient for most calculations.

2. The information obtained with these models should be combined with the mass transfer and the chemical reaction relationships to define a complete design model for trickle-bed reactors.

Unfortunately, this association is difficult because hydrodynamic models for the liquid only give immediate information on interactions between the zones of the liquid but not on the liquid-solid contact, which is another important step when a liquid/solid reaction is involved. There is no doubt that the local liquid velocity and the holdup have an important role in liquid-solid contacting efficiency, but it is not easy to write reliable relationships between these phenomena.

For these reasons, results on the R.T.D.F. of the liquid in packed towers have so far been used to interpret absorption with chemical reaction in the liquid phase (Baldi and Sicardi, 1975; Sicardi and Baldi, 1976) and to develop pseudo homogeneous models of trickle-bed reactors, as will be explained in the next section (Mears, 1971).

3. Relationships can be probably found between the characteristic parameters of models based on a continuous system and the parameters of models based on a discrete number of elements in series. The relationships would help in comparing the results on the liquid hydrodynamics obtained by different workers.

SOLID-LIQUID CONTACTING EFFECTIVENESS

Reactor Models

Several factors can affect the performance of trickle-bed reactors: gas-liquid and liquid-solid mass transfer, heat transfer, axial dispersion, catalyst wetting, and effectiveness.

It is thus apparent that complete models for the trickle-bed reactors may be very complex. Such models have been described as heterogeneous, since mass transfer between phases is considered (Hofmann, 1977*b*).

Some workers have proposed simplified heterogeneous models that neglect the mass transfer resistance in the gas phase and the axial dispersion and assume a total wetting of the catalyst pellets (Sato et al., 1972; Specchia et al., 1976). On these assumptions, supposing a second-order reaction between a reactant fed with the gas phase (subscript 1) and another fed with the liquid phase (subscript 2), the following mass balance equations can be written:

gas phase:

$$v_G \frac{dc_{1G}}{dz} + (k_La_L)_1(Hc_{1G} - c_{1L}) = 0 \qquad (44)$$

liquid phase:

$$v_L \frac{dc_{1L}}{dz} + (k_Sa_S)_1(c_{1L} - c_{1S}) - (k_La_L)_1(Hc_{1G} - c_{1L}) = 0 \qquad (45a)$$

$$v_L \frac{dc_{2L}}{dz} + (k_Sa_S)_2\ (c_{2L} - c_{2S}) = 0 \qquad (45b)$$

solid phase:

$$(k_Sa_S)_1(c_{1L} - c_{1S}) - (1-\epsilon)k_r\,\eta\, c_{1S}c_{2S} = 0 \qquad (46a)$$

$$(k_Sa_S)_2(c_{2L} - c_{2S}) - (1-\epsilon)k_r\,\eta\, c_{2S}c_{1S} = 0 \qquad (46b)$$

Some experimental results obtained with relatively slow chemical reactions in laboratory trickle-bed reactors confirm the validity of the model based on Equations (44) to(46*b*) (Sato et al., 1972; Goto and Smith, 1975). Goto and Smith also found that the axial dispersion in the liquid phase was negligible, whereas the mass transfer rate was not. The role of mass transfer in trickle-bed reactors was examined by Goto et al. (1976).

Specchia et al. (1976) gave a criterion to evaluate the influence of mass transfer rate on the overall reaction rate as a function of the Thiele modulus; from this it can be seen that at low fluid flow rate, mass transfer phenomena cannot be neglected for a Thiele modulus roughly greater than 3.

For the evaluation of the mass transfer coefficients, some correlations are available (Satterfield, 1975; Charpentier, 1976; Specchia et al., 1978).

Usually a much simpler model is employed for hydrotreating reactions of gas oils, for which trickle-bed reactors are widely used. This model (Satterfield, 1975) which, according to Hofmann (1977*b*), may be called a pseudo homogeneous model since it takes into account only the liquid phase, assumes plug flow of the liquid flow rate; no mass transfer limitation; first-order irreversible reaction, with respect to the liquid reactant; no reaction heat effects; no homogeneous reaction; and total wetting of the pellets.

The relationship between the inlet (c_o) and the outlet (c_f) concentration of the liquid reactant is given by

$$\ln \frac{c_o}{c_f} = \frac{h\,k_v\,(1-\epsilon)\eta}{v_L} \qquad (47)$$

By introducing the liquid hourly space velocity LHSV, Equation (47) becomes

TABLE 5. LIQUID SATURATION CORRELATIONS FOR TWO-PHASE CONCURRENT DOWNWARD FLOW IN PACKED BEDS

References	Correlations and range of conditions
Larkins et al. (1961)	$\log \beta_f = 0.525 \log \chi - 0.109 (\log \chi)^2 - 0.774 \quad (28)$ $0.05 < \chi = (\delta_L/\delta_G)^{0.5} < 30$ 9 mm Raschig rings, 9 mm stoneware spheres and 3 mm glass spheres; nonfoaming systems for all hydrodynamic regimes
Turpin and Huntington (1967)	$\beta_f = 0.132 (L/G)^{0.24} - 0.017 \quad (29)$ $1 < (L/G)^{0.24} < 6$ 7.5 to 8.1 mm tabular alumina; air-water for all hydrodynamic regimes
Sato et al. (1973)	$\epsilon\beta_{te} = 0.40 (\chi)^{0.22} (a_v^*)^{1/3} \quad (30)$ $0.1 < \chi < 20$ $a_v^* = 6(1-\epsilon)/D^* \quad (31)$ $D^* = D_p \Big/ \left[1 + \frac{4 D_p}{6 D_c (1-\epsilon)} \right] \quad (32)$ 2.6 to 24.3 mm glass spheres; air-water for all hydrodynamic regimes
Charpentier and Favier (1975)	$\log \beta_{te} = 0.168 \log \chi' - 0.043 (\log \chi')^2 - 0.363 \quad (33)$ $0.05 < \chi' < 100$ for cylindrical packings (1.8 × 6 and 1.4 × 5 mm catalyst cylinders); foaming and nonfoaming systems for all hydrodynamic regimes $\log \beta_{te} = 0.175 \log \chi' - 0.047 (\log \chi')^2 - 0.280 \quad (34)$ $0.05 < \chi' < 100$ for spherical packings (3 mm glass and catalyst spheres); foaming and nonfoaming systems for all hydrodynamic regimes
Clements (1976)	$\epsilon\beta_f = 0.111 (We_G Re_G / Re_L)^{-0.15} \quad (35)$ 1, 1.9, and 3.4 mm extrudate; nonfoaming systems for the high interaction regime $\epsilon\beta_f = 0.245 (We_G Re_G / Re_L)^{-0.034} \quad (36)$

(Continued on opposite page)

$$\ln \frac{C_o}{C_f} = \frac{3\,600\, k_v (1-\epsilon)\eta}{\mathrm{LHSV}} \tag{48}$$

However, neither the heterogeneous nor the pseudo homogeneous model takes into account catalyst wetting or, more generally, the liquid-solid contacting effectiveness. Poor liquid-solid contacting can, in fact, arise from partial wetting of the pellets and uneven trickling of the liquid over the packing. This may be due to faulty design of the liquid distributor but, more generally, to a local uneven flow of the liquid trickling in the packed bed. Charpentier et al. (1968) noted that in an absorption tower the liquid flows in rivulets, films, and drops. There also exist semistagnant liquid pockets with a very low liquid renewal. This hydrodynamic feature results in different values for the local solid-liquid mass transfer, so that reactant concentrations at the solid-liquid interface may have very different values along the surface of a pellet. In the presence of negligible heat effects and a nonvolatile liquid reactant, even if the particles are totally wetted, this hydrodynamic behavior may give rise to poor utilization of the catalyst. If the previous models are used to examine a reaction in a trickle-bed reactor, this would lead to a underestimation of the kinetic rate constant.

In the case of the pseudohomogeneous model, Equation (48) must be rewritten as follows:

$$\ln \frac{C_o}{C_f} = \frac{3\,600\, k_{\mathrm{app}} (1-\epsilon)\eta}{\mathrm{LHSV}} \tag{49}$$

Satterfield (1975) defined the solid-liquid contacting effectiveness as k_{app}/k_v.

For hydrotreating reactions of gas oils in pilot reactors, it was generally found that k_{app} determined with Equation (49) increased on increasing the liquid flow rate (Ross, 1965; Henry and Gilbert, 1973; Montagna and Shah, 1975*a;* Paraskos et al., 1975). Bondi (1971) also found a positive effect of the gas flow rate. Koros (1976) has compared the values of the reaction rate constant for the catalytic decomposition of H_2O_2 on charcoal, determined in a trickle-bed reactor and in a slurry reactor (in which perfect liquid-solid contacting is generally assumed). The ratio between these values, which, according to Koros, represents the degree of catalyst utilization in the trickle-bed reactor, was always less than 1 and increased with the liquid flow rate. A good catalyst utilization ($\simeq 90\%$) was attained for a liquid superficial velocity greater than $4 \cdot 10^{-3}$ m/s.

All these workers attribute the variation of k_{app} with the liquid flow rate to the solid-liquid contacting effectiveness, which intuitively increases as v_L increases.

Mears (1971), on the contrary, ascribed this fact to axial dispersion.

(TABLE 5. CONTINUED)

	1, 1.9, and 3.4 mm extrudate; foaming systems for the high interaction regime $We_G = v_G^2 \rho_G D_p/\sigma_L \qquad (37)$
Midoux et al. (1976)	$\beta_{te} = \dfrac{0.66\,(\chi)^{0.81}}{1 + 0.66\,(\chi)^{0.81}} \qquad (38)$ $0.1 < \chi < 80$ 3 mm glass and catalyst spheres, 1.8 × 6 and 1.4 × 5 catalyst cylinders; nonfoaming systems for all hydrodynamic regimes and foaming systems for the low interaction regime $\beta_{te} = \dfrac{0.92(\chi')^{0.30}}{1 + 0.92(\chi')^{0.30}} \qquad (39)$ $0.05 < \chi' < 100$ 3 mm glass and catalyst spheres, 1.4 × 5 mm catalyst cylinders; foaming systems for the high interaction regime
Specchia and Baldi (1977)	$\beta_f = 3.86(Re_L)^{0.545}\,(Ga_L^*)^{-0.42}\left(\dfrac{a_v D_p}{\epsilon}\right)^{0.65} \qquad (40)$ $Ga_L^* = D_p^3\,\rho_L(\rho_L g + \delta_{LG})/\mu_L^2 \qquad (41)$ $3 < Re_L < 470$ 6 mm glass spheres, 5.4 × 5.4 and 2.7 × 2.7 mm glass cylinders, 6.4, 10.3, and 22 mm Raschig rings; foaming and nonfoaming systems for the low interaction regime $\beta_f = 0.125(Z/\psi^{1.1})^{-0.312}\left(\dfrac{a_v D_p}{\epsilon}\right)^{0.65} \qquad (42)$ $1 < Z/\psi^{1.1} < 500$ 6 mm glass spheres, 5.4 × 5.4 and 2.7 × 2.7 mm glass cylinders, 6.4, 10.3, and 22 mm Raschig rings; nonfoaming systems for the high interaction regime $\beta_f = 0.0616(Z/\psi^{1.1})^{-0.172}\left(\dfrac{a_v D_p}{\epsilon}\right)^{0.65} \qquad (43)$ $0.6 < Z/\psi^{1.1} < 80$ 3 and 6 mm glass spheres, 5.4 × 5.4 and 2.7 × 2.7 mm glass cylinders, 3.2 × 3.2 and 1.4 × 5 mm catalyst cylinders; foaming systems for the high interaction regime

(Continued from opposite page)

By contrast with these results, reaction rate constants in trickle-bed reactors greater than those in slurry reactors were measured in the presence of exothermic and fast reactions (hydrogenation of benzene, crotonaldehyde, α-methylstyrene). This was ascribed to the existence of dry zones of the catalyst, due to the reaction heat, giving rise to vaporization of liquid in the less effectively wetted zones. The enhancement of the reaction rate was explained as due either to gas-phase reaction in the dry zones of the catalyst faster than the liquid-phase reaction (Sedriks and Kenney, 1973; Satterfield and Ozel, 1973) or to better utilization of the catalyst volume due to diffusion into the pellets of the gas reactant through the dry pores faster than through the liquid filled pores (Germain et al., 1974).

Poor solid-liquid contacting can also give rise to hot spots in the reactor (Germain et al., 1974).

These conflicting data mean that solid-liquid contacting effectiveness plays a complex role, according to the reaction type, which must be considered in the design of trickle-bed reactors.

Scale-Up Criteria

Some scale-up criteria have been proposed to take into account variations of reactor performance with the

TABLE 6. LITERATURE DATA FOR P.E. AND P.D.E. MODELS PLOTTED IN FIGURES 3, 4, AND 5

References	Line	Packing	Gas-liquid system	Model
Hoogendoorn and Lips (1965)	A	12.5 mm Raschig rings	Air-water	P.E.
Buffham et al. (1970)	B	3.1 mm Raschig rings	Air-water	P.E.
Hochman and Effron (1969)	C	4.7 mm beads	Nitrogen-methanol	P.E.
Villermaux and Van Swaaij (1969)	D_1	6.4 mm Raschig rings	Air-water	P.D.E.
	D_2	10.3 mm Raschig rings	Air-water	P.D.E.
	D_3	22 mm Raschig rings	Air-water	P.D.E.
Bennet and Goodridge (1970)	E_1	6 mm Raschig rings	Air-water	P.D.E.
	E_2	9.4 mm Raschig rings	Air-water	P.D.E.
Matsuura et al. (1976)	F_1	1.2 mm beads	Air-water	P.D.E.
	F_2	4.3 mm beads	Air-water	P.D.E.
Friebe (1966)	G	6 × 10 mm cylinders	Air-water	P.D.E.

liquid flow rate. These criteria were developed on the basis of the pseudo homogeneous model described by Equation (49).

Mears (1971) considered the variation of k_{app} with the liquid flow rate as due to axial dispersion; he also gave a conservative criterion for the design of a reactor with a negligible axial dispersion effect. For small deviations from plug flow and for a first-order reaction, one can express the relationship between outlet and inlet concentrations as (Whener and Wilhelm, 1957)

$$\ln\frac{c_o}{c_f} = \frac{3\,600\,k_v(1-\epsilon)\eta}{\text{LHSV}} - \frac{3\,600^2\,k_v^2(1-\epsilon)^2\eta^2}{(\text{LHSV})^2}\,\frac{D_p}{h\,Pe'} \tag{50}$$

Paraskos et al. (1975) and Montagna and Shah (1975*a*) expressed Pe', according to Hochman and Effron (1969), as

$$Pe' \propto (\text{LHSV})^{\alpha}\,h^{\alpha} \tag{51}$$

with $1 > \alpha \geqq 0.5$. By combining Equations (50) and (51), we obtain

$$\ln\frac{c_o}{c_f} - \frac{3\,600\,k_v(1-\epsilon)\eta}{\text{LHSV}} \propto - \frac{(3\,600)^2\,k_v^2[(1-\epsilon)\eta]^2}{(\text{LHSV})^{2+\alpha}}\,\frac{D_p}{h^{1+\alpha}} \tag{52}$$

Equation (52) has been applied to interpret the results of several hydrotreating reactions of various gas oils (Paraskos et al., 1975; Montagna and Shah, 1975*a*). It gave a poor fit with the experimental data.

Henry and Gilbert (1973) proposed another scale-up criterion, based on the liquid holdup. For catalytic hydrodesulfurization and hydrodenitrogenation of gas oils, they defined a reaction rate per unit volume of the liquid held in the reactor, as for an homogeneous reaction, and wrote

$$k_{app} \propto k_v\,\epsilon\,\beta_{te} \tag{53}$$

For the total external holdup they adopted the relationship proposed by Satterfield et al. (1969) for the holdup of liquid trickling on a string of spheres:

$$\epsilon\,\beta_{te} \propto \left[\frac{v_L\,\rho_L\,D_p}{\mu_L}\right]^{1/3}\left[\frac{D_p^3\,g\,\rho_L^2}{\mu_L^2}\right]^{-1/3} \tag{54}$$

From Equations (49), (53), and (54), it follows that

$$\ln\frac{c_o}{c_f} \propto \frac{k_v(1-\epsilon)\eta}{(\text{LHSV})^{2/3}}\,(h)^{1/3}\,(D_p)^{-2/3}\left(\frac{\mu_L}{\rho_L}\right)^{1/3} \tag{55}$$

Mears (1974), on the other hand, considered

$$k_{app} \propto k_v\,\frac{a_w}{a_v} \tag{56}$$

where a_w/a_v is the fraction of the external pellets area that is effectively wetted. According to the correlation of a_w proposed by Puranik and Vogelpohl (1974) for packed absorption towers, Mears obtained

$$\ln\frac{c_o}{c_f} \propto \frac{k_v(1-\epsilon)\eta}{(\text{LHSV})^{2/3}}\,(h)^{0.32}(D_p)^{0.18}\left(\frac{\sigma_c}{\sigma}\right)^{0.21}\left(\frac{\mu_L}{\rho_L}\right)^{-0.05} \tag{57}$$

The approach used by Mears is more acceptable from a physical point of view than that of Henry and Gilbert (1973), since it considers the reaction rate is proportional to the wetted area of the catalyst, instead of to the liquid volume. However, it can be observed that the validity of the Puranik and Vogelpohl correlation has not been verified for beds of catalyst pellets.

Moreover, the catalytic reaction rate actually depends on the internal wetted area of the catalyst; the validity of Equation (56) is then limited to the case of a very fast reaction, when only a thin superficial layer of the catalyst pellets is effective.

In any case, for a given catalyst and given physical properties of the liquid phase, Equations (55) and (57) both lead to

$$\ln\frac{c_o}{c_f} \propto \frac{(h)^{\omega}}{(\text{LHSV})^{1-\omega}} \tag{58}$$

with a ω value very close to 0.33.

A test of the validity of these scale-up criteria was run by Paraskos et al. (1975) and Montagna and Shah (1975*a*) with hydroprocessing reactions of gas oils. They found that the conversion in laboratory trickle-bed reactors could well be expressed by an equation like Equation (58), but the ω values they determined with the same liquid phase changed with the type of reaction considered.

While Equation (49) suggests, for a given conversion degree and a given catalyst size, a scale-up criterion based on constant h/v_L, Equation (58) suggests to maintain constant $(h/v_L)v_L^{\omega}$, where v_L^{ω} should take account of the following phenomena:mass transfer, heat transfer, and catalyst effective wetting, not considered, or only partially considered, in the proposed criteria. However, the significance of these phenomena on the over-all reaction rate is strictly connected with the chemical reaction rate; this may be the reason of the variation of ω with the type of reaction found by Paraskos et al. (1975) and Montagna and Shah (1975*a*).

Effective Catalyst Wetting

In absorption packed towers, partial wetting of the packing has been observed (Shulman et al., 1955). A correlation for the effective wetted area for absorption packings has also been proposed (Puranik and Vogelpohl, 1974).

Very few data exist for the catalyst pellets in a trickle-bed reactor. Moreover, two kinds of wetting must be defined for porous catalysts.

1. Internal wetting, that is, the amount of internal area wetted by the liquid. It is a measure of the active area available for the liquid reactants, and hence of the maximum utilization of the catalyst volume, when internal mass transfer limitations are negligible. The active available area is connected with the pore filling, that is, the volume of liquid filling the catalyst pores divided by the total pore volume.

2. External effective wetting, that is, the amount of external area that is wetted by the flowing liquid. Although reaction occurs mainly on the internal area, a partial wetted external area may affect the reaction rate because of limitations to the supply rate of liquid reactants to the solid external surface, and of variations of the internal diffusion rate of these reactants. In a pellet completely enveloped by moving liquid, the maximum path of the molecules in the pores is of the order of the pellet radius; when the external area is only partially wetted, the maximum internal path increases, and the diffusion rate decreases. As a consequence, the catalyst effectiveness factor would change with the extent of the external wetting. This concept was recently developed by Colombo et al. (1976) and is the basis of a model proposed by Dudukovic

(1977). He assumes the catalyst effectiveness factor in a trickle-bed reactor η_{TB} expressed as follows:

$$\eta_{TB} = \eta_i \cdot \eta^* \tag{59}$$

Here η_i is the ratio between the wetted pellet volume V_{eff} and the total pellet volume V_p (pore filling), and η^* is the effectiveness factor of a pellet totally wetted (inside and outside) with the diameter proportional to $V_{\text{eff}}/S_{\text{eff}}$, where S_{eff} is the external wetted area of the pellet. For completely wetted pellets of irregular shape, Aris (1957) suggested the following expression for the effectiveness factor:

$$\eta = \frac{\tanh \phi}{\phi} \tag{60}$$

where the Thiele modulus ϕ, for a first-order reaction, is given by

$$\phi = \frac{V_p}{S_p} \sqrt{\frac{k_v}{D_i}} \tag{61}$$

By analogy, for a pellet partially wetted, a Thiele modulus ϕ_{TB} can be defined as

$$\phi_{TB} = \frac{V_{\text{eff}}}{S_{\text{eff}}} \sqrt{\frac{k_v}{D_i}} \tag{62}$$

If a ratio η_{CE} is introduced

$$\eta_{CE} = \frac{S_{\text{eff}}}{S_p} \tag{63}$$

where S_p is the total external area of a pellet, ϕ_{TB} can be expressed as

$$\phi_{TB} = \frac{\eta_i}{\eta_{CE}} \phi \tag{64}$$

and hence

$$\eta^* = f(\phi_{TB}) = \frac{\tanh\left(\frac{\eta_i}{\eta_{CE}} \phi\right)}{\frac{\eta_i}{\eta_{CE}} \phi} \tag{65}$$

Equations (62) and (65) can be written only on the assumption of symmetric concentration profiles within the partially wetted particles, which seems unrealistic.

From Equation (65), Equation (59) becomes

$$\eta_{TB} = \eta_{CE} \frac{\tanh\left(\frac{\eta_i}{\eta_{CE}} \phi\right)}{\phi} \tag{66}$$

When ϕ is very high (very fast reaction), one obtains

$$\eta_{TB} \simeq \frac{\eta_{CE}}{\phi} = \eta_{CE} \cdot \eta \tag{67}$$

This equation is similar to that used by Mears (1974) for his effective wetting scale-up criterion. For very low values of ϕ, it is obviously

$$\eta_{TB} \simeq \eta_i \tag{68}$$

In this model, which is not yet supported by experimental results, the two wetting parameters have been introduced: η_i and η_{CE}.

Pore filling η_i was measured with a tracer method by Colombo et al. (1976) in a trickle-bed reactor packed with $4 \cdot 10^{-3}$ and $1 \cdot 10^{-3}$ m porous carbon particles. They determined the total liquid holdup, inside and outside the particles, at various liquid flow rates; separately, they measured the external holdup by liquid drainage in the same bed. By comparison between these values, they concluded that pore filling was practically total ($\eta_i \simeq 1$), even at the lowest liquid superficial velocity ($5 \cdot 10^{-4}$ m/s). η_i values of about 0.80 were determined by Schiesser and Lapidus (1961). But these workers determined the external holdup and the external plus the internal holdup in different beds. Furthermore, their data, obtained with a tracer method, probably suffer a lack of accuracy in the response curve tails, as shown by the different η_i values determined with different inlet disturbances of the tracer concentrations. This was also demonstrated by Rothfeld and Ralph (1963).

Schwartz et al. (1976) found $\eta_i = 0.92$; the external holdup was again determined in a different bed of nonporous particles.

From these data, it appears that η_i can be considered reasonably close to 1, owing to capillary phenomena, if the following conditions do not occur: poor macroscopic liquid distribution, so that large zones of the bed are not irrigated by the liquid; and highly exothermic reaction, which may give rise to some evaporation of liquid in the pores near the zones of poor external wetting.

With regard to external wetting, Schwartz et al. (1976) tried to measure η_{CE} by using nonporous particles covered with a thin layer of porous material, and a tracer which could be adsorbed by this layer. They obtained the surprising result $\eta_{CE} = 0.7$, independent of the liquid flow rate.

It might be noted to this regard, that the pulse-response method was used for evaluating the wetting efficiency; with this technique, it is difficult to avoid errors when, as in this case, there are extensive tails in the response curve.

Specchia et al. (1978) determined η_{CE} by a chemical method: dissolution of pellets of phthalic anhydride into a reacting buffer solution. They found an increase of η_{CE} as the liquid and the concurrent gas flow rate increased. η_{CE} values equal to 1 were obtained at high liquid and gas flow rates. At $v_L > 6 \cdot 10^{-3}$ m/s, without gas flow rate, values greater than 0.8 were determined.

It may be observed that the interphase area determined with the chemical methods is highly dependent on the hydrodynamic model adopted (Baldi and Sicardi, 1975). The η_{CE} values determined by Specchia et al. (1978) are probably lower than the fraction of the external packing area actually wetted, especially at low liquid flow rates, when a significant part of the liquid holdup is almost stagnant and hence poorly effective in the solid-liquid mass transfer.

But a question arises about the meaning of η_{CE}. Is it the effective or the actual wetted fraction? If the former is valid, what is the meaning of effective, and what is the method for determining it?

Colombo et al. (1976) proposed another approach to the problem; they expressed the solid-liquid contacting effectiveness by the ratio between the apparent diffusivity $(D_i)_{\text{app}}$ of a tracer in a porous particle, determined in a trickle-bed reactor by assuming total wetting of the packing, and the intraparticle diffusivity D_i, determined in a full reactor. This ratio was found to increase as the liquid flow rate and the tracer molecular diffusivity increased, and the particle size decreased. At $v_L > 5 \cdot 10^{-3}$ m/s, $(D_i)_{\text{app}}/D_i$ was 1 for the highest diffusivity tracer (potassium chloride) and greater than 0.8 for the lowest diffusivity tracer (zinc sulfate).

The actual reaction rate in a trickle-bed reactor may be calculated from this diffusivity ratio. For a first-order reaction, assuming no influence of the gas-liquid and liquid-solid mass transfer, it can be written as (Colombo et al., 1976)

$$\frac{k_{app}}{k_v} = \frac{\eta_{TB}}{\eta} \tag{69}$$

where η_{TB} can be calculated from the Thiele modulus ϕ_{TB} defined through $(D_i)_{app}$

$$\phi_{TB} = \phi \sqrt{\frac{D_i}{(D_i)_{app}}} \tag{70}$$

Values of k_{app}/k_v calculated with Equations (69) and (70) using the experimental values of $(D_i)_{app}/D_i$ were found to agree closely with those considered usual by Satterfield (1975) on the basis of experimental values.

Unfortunately, the usefulness of the $(D_i)_{app}$ model for scale-up is limited by the fact that this diffusivity was also found to depend, for a given catalyst, on the molecular diffusivity of the diffusing component and not only on the hydrodynamics.

A complete answer to the solid-liquid contacting effectiveness will probably be given when the complex hydrodynamics of the liquid trickling in a packed bed is better known.

At the present state of the art, it may be suggested to adopt high enough liquid superficial velocities in order to avoid significant effects of poor liquid-solid contacting (poor catalyst utilization, hot spots, unstable reactor performance). A good wetting seems to be attained at $v_L > 6 \cdot 10^{-3}$ m/s.

NOTATION

A = empirical constant defined in Equation (24)
A' = empirical constant defined in Equation (26)
a_v = packing geometrical area per unit column volume, m^{-1}
a_v^* = packing geometrical area defined in Equation (31), m^{-1}
a_w = effectively wetted area of the packing, m^{-1}
B = empirical constant defined in Equation (24)
Bn = $\rho_L g/a_v^2 \sigma_L$ Bond number, dimensionless
c = concentration, kmole m^{-3}
c_G, c_L, c_S = concentration in gas phase, liquid phase, and solid-liquid interface, respectively v, kmole m^{-3}
D^* = modified particle diameter, defined in Equation (32), m
D_c = column diameter, m
D_e = equivalent diameter of the packing channels, defined in Equation (9), m
D_l = longitudinal dispersion, $m^2 s^{-1}$
D_i = internal diffusivity in a totally wetted pellet, $m^2 s^{-1}$
$(D_i)_{app}$ = internal diffusivity in the presence of partial wetting, $m^2 s^{-1}$
D_p = nominal packing diameter, m
D_p^* = diameter of a sphere with the same outer surface area of a packing particle, m
D_{pe} = diameter of a sphere having the same volume of the packing particle, m
D_R = radial liquid spread factor, m
d = exponent in Equation (26)
$E\ddot{o}$ = $\rho_L g \, D_p^2/\sigma_L$ Eötvos number, dimensionless
f_{LG} = two-phase friction factor defined in Equation (8), dimensionless
f_w = liquid wall factor, dimensionless
G = gas phase superficial mass velocity, kg $m^{-2} s^{-1}$
Ga_L = $D_p^3 \rho_L^2 g/\mu_L^2$ Galileo number, dimensionless
Ga_L^* = $D_p^3 \rho_L (\rho_L g + \delta_{LG})/\mu_L^2$ modified Galileo number, dimensionless
g = acceleration of gravity, m s^{-2}
H = Henry's constant, dimensionless
$(\Delta H/\Delta z)_{LG}$, $(\Delta H/\Delta z)_L$, $(\Delta H/\Delta z)_G$ = two-phase, liquid-phase, and gas-phase head loss per unit length of packing, dimensionless
h = bed length, m
k_1 = coefficient defined in Equation (19), m^{-2}
k_2 = coefficient defined in Equation (19), m^{-1}
k_{app} = apparent kinetic rate constant, s^{-1}
k_r = kinetic rate constant for second-order reaction, m^3 kmole^{-1} s^{-1}
k_s^* = mass transfer coefficient between static and dynamic zones, s^{-1}
k_v = kinetic rate constant for a first-order reaction, s^{-1}
$k_L a_L$ = volumetric gas-liquid mass transfer coefficient in the liquid phase, s^{-1}
$k_S a_S$ = volumetric liquid-solid mass transfer coefficient, s^{-1}
L = liquid phase superficial mass velocity, kg $m^{-2} s^{-1}$
LHSV = liquid hourly space velocity, h^{-1}
N = number of packing particles per unit empty volume, m^{-3}
n = number of elements in series, dimensionless
Pe = $v_e D_p/D_e$ = Peclet number based on the pellet size, dimensionless
Pe' = $v_L D_p/D_e$ = Peclet number based on the pellet size, dimensionless
q = fraction of liquid flowing in the mixed element, dimensionless
Re_e = $v_e \rho_L D_p/\mu_L$ = effective Reynolds number of the liquid phase, dimensionless
Re_G = $v_G \rho_G D_p/\mu_G$ = Reynolds number of the gas phase, dimensionless
Re_L = $v_L \rho_L D_p/\mu_L$ = Reynolds number of the liquid phase, dimensionless
r = radial coordinate, m
S_p = particle external area, m^2
S_{eff} = effectively wetted external area of a pellet, m^2
s = fraction of liquid flow rate in the radial direction, dimensionless
V_{eff} = wetted particle volume, m^3
V_m, V_d, V_s = volumes of mixed, dispersed, and stagnant zones, respectively, m^3
V_p = particle volume, m^3
v_G, v_L = gas phase and liquid phase superficial velocity, m s^{-1}
v_e = $v_L/\epsilon\beta_{fm}$ = effective liquid velocity, m s^{-1}
We_G = $v_G^2 D_p \rho_G/\sigma_L$ = gas-phase Weber number, dimensionless
Z = parameter defined in Equation (9), dimensionless
z = axial coordinate, m

Greek Letters

β_f = free draining or operating saturation obtained from drainage, dimensionless
β_{fm} = free draining or operating saturation determined from a model, dimensionless
β_r = residual saturation, dimensionless
β_{rm} = static saturation determined from a model, dimensionless
β_t = total (internal plus external) saturation, dimensionless
β_{te} = total external saturation, dimensionless
δ_{LG}, δ_L, δ_G = two-phase, liquid-phase, and gas-phase frictional pressure drop, kg $m^{-2} s^{-2}$
δ_w = pressure drop of the gas flowing through a wetted packing, kg $m^{-2} s^{-2}$
ϵ = bed void fraction, dimensionless
η = catalyst effectiveness factor for a pellet totally wetted, dimensionless
η^* = defined by Equation (22), dimensionless

η_{CE} = fraction of the external area of the pellet effectively wetted, dimensionless
η_R = pore filling, dimensionless
η_{TB} = effectiveness factor for a pellet partially wetted, dimensionless
λ = $[(\rho_G/\rho_{\rm air})(\rho_L/\rho_{\rm water})]^{0.5}$ = parameter defined by Charpentier and Favier (1975), dimensionless
μ_G, μ_L = gas and liquid phase viscosity, kg m^{-1} s^{-1}
$\mu_{\rm water}$ = viscosity of water, kg m^{-1} s^{-1}
ξ_{LG}, ξ_L, ξ_G = parameters defined in Equations (16), (17), and (18) respectively, dimensionless
$\rho_{\rm air}$ = air density, kg m^{-3}
ρ_e = density of the manometric liquid (generally water), kg m^{-3}
ρ_G, ρ_L = gas- and liquid-phase density, kg m^{-3}
$\rho_{\rm water}$ = density of water, kg m^{-3}
σ_c = critical surface tension, kg s^{-2}
σ_L = liquid-phase surface tension, kg s^{-2}
$\sigma_{\rm water}$ = surface tension of water, kg s^{-2}
τ_d = mean time delay, s
τ_{dm} = mean time delay of the delayed events, s
ϕ = $V_p/S_p \sqrt{k_v/D_i}$ = Thiele modulus for a totally wetted pellet, dimensionless
ϕ_{TB} = $V_{\rm eff}/S_{\rm eff} \sqrt{k_v/D_i}$ = Thiele modulus for a pellet partially wetted, dimensionless
χ = parameter defined in Equation (6), dimensionless
χ' = parameter defined in Equation (15), dimensionless
ψ = parameter defined in Equation (21), dimensionless

LITERATURE CITED

Aris, R., "On Shape Factor for Irregular Particles—I:the Steady State Problem. Diffusion and Reaction," *Chem. Eng. Sci.*, **6**, 262 (1957).

Baker, O., "Simultaneous Flow of Oil and Gas," *Oil Gas J.*, **53**, 185 (1954).

Baldi, G., and S. Sicardi, "A Model for Mass Transfer With and Without Chemical Reaction in Packed Towers," *Chem. Eng. Sci.*, 30, 617 (1975).

Baldi, G., and V. Specchia, "Distribution and Radial Spread of Liquid in Packed Towers with Two-phase Concurrent Flow: Effect of Packing Shape and Size," *Quad. Ing. Chim. Ital.*, **12**, 107 (1976).

Bennet, A., and F. Goodridge, "Hydrodynamic and Mass Transfer Studies in Packed Absorption Columns—Part I: Axial dispersion," *Trans. Inst. Chem. Engrs.*, **48**, T232 (1970).

Bondi, A., "Handling Kinetic from Trickle-Phase Reactors," *Chem. Tech.*, 185 (Mar., 1971).

Brignole, E. A., G. Zacheronek, and J. Mangosio, "Liquid Distribution in Packed Columns," *Chem. Eng. Sci.*, **28**, 1225 (1973).

Buffham, B. A., and L. G. Gibilaro, "A Unified Time Delay Model for Dispersion in Flowing Media," *Chem. Eng. J.*, **1**, 31 (1970).

———, and M. N. Rathor, "A Probabilistic Time Delay Description of Flow in Packed Beds," *AIChE J.*, **16**, 218 (1970).

Charpentier, J. C., C. Prost, W. P. M. Van Swaaij, and P. Le Goff, "Etude de la Rétention de Liquide das une Colonne à Garnissage Arrosé à Contre-courant et à Co-courant de Gaz-Liquide," *Chim. Ind. Génie Chim.*, **99**, 803 (1968).

———, and P. Le Goff, "Chute de Pression pour des Écoulements à Co-courant dans les Colonnes à Garnissage Arrosé: Comparaison avec le Garnissage Noyé," *Chem. Eng. Sci.*, **24**, 1777 (1969).

Charpentier, J. C., M. Bakos, and P. Le Goff, "Hydrodynamics of Two-Phase Concurrent Down Flow in Packed-Bed Reactors. Gas-Liquid Flow Regimes. Liquid Axial Dispersion and Dead Zones," Proc. 2nd Conf. on "Quelques Applications de la Chimie Physique," Veszprem, Hungary, Vol. 2, pp. 31-47 (1971).

Charpentier, J. C., and M. Favier, "Some Liquid Holdup Experimental Data in Trickle-Bed Reactors for Foaming and Nonfoaming Hydrocarbons," *AIChE J.*, **21**, 1213 (1975).

———, "Recent Progress in Two-Phase Gas-Liquid Mass Transfer in Packed Beds," *Chem. Eng. J.*, **11**, 161 (1976).

Chou, T. S., F. L. Worley, and D. Luss, "Flow Regime Transition in Trickle-Bed reactors," Submitted to Ind. *Chem. Eng. Process Design Develop.* (1976).

Clements, L. D., "Dynamic Liquid Holdup on Concurrent Gas-Liquid Downflow in Packed Beds," paper presented at Two-Phase Flow and Heat Transfer Symp. Workshop, Ft. Lauderdale, Fla. (Oct. 18-20, 1976).

Colombo, A. J., G. Baldi, and S. Sicardi, "Solid-Liquid Contacting Effectiveness in Trickle Bed Reactors," *Chem. Eng. Sci.*, **31**, 1101 (1976).

Duduković, M. P., "Catalyst Effectiveness Factor and Contacting Efficiency in Trickle-Bed Reactors," private communication (1977).

Dunn, W. E., T. Vermuelen, C. R., Wilke, and T. T. Word, "Longitudinal Dispersion in Packed Gas-Absorption Columns," *Ind. Eng. Chem. Fundamentals*, **16**, 116 (1977).

Dutkai, E., and E. Ruckenstein, "Liquid Distribution in Packed Columns," *Chem. Eng. Sci.*, **23**, 1365 (1968).

Elenkov, D., and N. Kolev, "Einfluss der Schuttung auf die Axialmischung der Flussigkeit in Füllkörpersäulen unterhalb des Flutpunktes," *Chemie Ing. Tech.*, **44**, 845 (1972).

Friebe, J., *Diss.*, Tech., Univ. Darmstadt (1966).

Germain, A. H., A. G. Lefebvre, and G. A. L'Homme, "Experimental Study of a Catalytic Trickle-Bed Reactor," Chemical Reaction Engineering II, ACS Monograph Ser., No. 133, p. 164 (1974).

Gianetto, A., G. Baldi, and V. Specchia, "Absorption in Packed Towers with Concurrent High Velocity Flows. I—Interfacial Areas," *Quad. Ing. Chim. Ital.*, **6**, 125 (1970).

———, "Absorption in Packed Towers with Concurrent High Velocity Flows. II—Mass Transfer," *AIChE J.*, **19**, 916 (1973).

Goto, S., and J. M. Smith, "Trickle-Bed Reactor Performance. Part II: Reactor Studies," *ibid.*, **21**, 714 (1975).

———, S. Watabe, and M. Matsubara, "The Role of Mass Transfer in Trickle-Bed Reactors," *Can J. Chem. Eng.*, **54**, 551 (1976).

Hashimoto, K., K. Muroyama, K. Fujiyoshi, and S. Nagata, "Effective Radial Thermal Conductivity in Cocurrent Flow of a Gas and Liquid Through a Packed Bed," *Intern. Chem. Eng.*, **16**, 760 (1976).

Henry, G. H., and J. B. Gilbert, "Scale-up of Pilot Plant Data for Catalytic Hydroprocessing," *Ind. Eng. Chem. Process Design Develop.*, **12**, 328 (1973).

Herskowitz, M., and J. M. Smith, "Liquid Distribution in Trickle-Bed Reactors. Part I: Flow Measurements," Submitted to *AIChE J.* (1977*a*).

———, "Liquid Distribution in Trickle-Bed Reactors. Part II: Tracer Studies," Submitted to *AIChE J.* (1977*b*).

Hochamn, J. M., and E. Effron, "Two-Phase Concurrent Downflow in Packed Beds," *Ind. Eng. Chem. Fundamentals*, **8**, 63 (1969).

Hofmann, H., "Hydrodynamics, Transport Phenomena and Mathematical Models in Trickle-Bed Reactors," *Intern. Chem. Rev.*, **17**, 71 (1978).

———, "Multiphase Catalytic Packed Bed Reactors," private communication (1977*b*).

Hoogendoorn, C. J., and J. Lips, "Axial Mixing of Liquid in Gas-Liquid Flow Through Packed Beds," *Can. J. Chem. Eng.*, **43**, 125 (1965).

Hutton, B. E. T., and L. S. Leung, "Concurrent Gas-Liquid Flow in Packed Columns," *Chem. Eng. Sci.*, **29**, 1681 (1974).

Jameson, J. B., "A Model for Liquid Distribution in Packed Columns and Trickle-Bed Reactors," *Trans. Inst. Chem. Engrs.*, **44**, T198 (1966).

Koros, R. M., "Catalyst Utilization in Mixed-Phase Fixed Bed Reactors," 4th ISCRE, Heidelberg, p. 372 (Apr. 6-8, 1976).

Larkins, R. P., R. R. White, and D. W. Jeffrey, "Two-Phase Concurrent Flow in Packed Beds," *AIChE J.*, **7**, 231 (1961).

Laurent, A., and J. C. Charpentier, "Aires Interfaciales et Coefficients de Transfert de Matiere dans les Divers Types d'Absorbeurs et de Reacteaurs Gaz-Liquide," *Chem. Eng. J.*, **8**, 85 (1974).

Lemay, Y., G. Pineault, and J. A. Ruether, "Particle-Liquid Mass Transfer in a Three-Phase Fixed Bed Reactor with Concurrent Flow in the Pulsing Regime," *Ind. Eng. Chem. Process Design Develop.*, **14**, 280 (1975).

Levenspiel, O., *Chemical Reaction Engineering*, Wiley, New York (1962).

Lockhart, R. W., and R. C. Martinelli, "Proposed Correlation of Data for Isothermal Two-Phase, Two-Component Flow in Pipes," *Chem. Eng. Progr.*, **45**, No. 1, 39 (1949).

Matsuura, A., T. Akehata, and T. Shirai, "Axial Dispersion of Liquid in Concurrent Gas-Liquid Downflow in Packed Beds," *J. Chem. Eng. Japan*, **9**, 294 (1976).

Mears, D. E., "The Role of Axial Dispersion in Trickle-Flow Laboratory Reactors," *Chem. Eng. Sci.*, **26**, 1361 (1971).

———, "The Role of Liquid Holdup and Effective Wetting in the Performance of Trickle-Bed Reactors," *Chem. Reaction Eng. II*, ACS Monograph Ser., No. 133, p. 268 (1974).

Mersmann, A., "Restflüssigkeit in Schüttungen," *Verfahrenstechnik*, **6**, 203 (1972).

Michell, R. W., and I. A. Furzer, "Trickle Flow in Packed Beds," *Trans. Inst. Chem. Engrs.*, **50**, 334 (1972*a*).

——————, "Mixing in Trickle Flow Through Packed Beds," *Chem. Eng. J.*, **4**, 53 (1972*b*).

Midoux, N., M. Favier, and J. C. Charpentier, "Flow Pattern, Pressure Loss and Liquid Holdup Data in Gas-Liquid Downflow Packed Beds with Foaming and Nonfoaming Hydrocarbons," *J. Chem. Eng. Japan*, **9**, 350 (1976).

Mohunta, D. M., and G. S. Laddha, "Prediction of Liquid Phase Holdup in Random Packed Beds," *Chem. Eng. Sci.*, **20**, 1069 (1965).

Montagna, A. A., and Y. T. Shah, "The Role of Liquid Holdup, Effective Catalyst Wetting and Backmixing on the Performance of a Trickle-Bed Reactor for Residue Hydrodesulfurization," *Ind. Eng. Chem. Process Design Develop.*, **14**, 479 (1975*a*).

——————, "Backmixing Effect in an Upflow Concurrent Hydrodesulfurization Reactor," *Chem. Eng. J.*, **10**, 99 (1975*b*).

Onda, K., H. Takeuchi, Y. Maeda, and N. Takeuchi, "Liquid Distribution in a Packed Column," *Chem. Eng. Sci.*, **28**, 1677 (1973).

Oorts, A. J., and L. J. Hellinckx, "A Modified Time Delay Model for Flow in Packed Columns," *Chem. Eng. J.*, **7**, 147 (1974).

Otake, T., and K. Okada, "Liquid Holdup in Packed Towers," *Kagaku Kogaku*, **17**, 176 (1953).

Paraskos, J. A., J. A. Frayer, and Y. T. Shah, "Effect of Holdup Incomplete Catalyst Wetting and Backmixing During Hydroprocessing in Trickle-Bed Reactors," *Ind. Eng. Chem. Process Design Develop.*, **14**, 315 (1975).

Popovic, M., and W. D. Deckwer, "Transient Behaviour of Reactors with Dispersion and Stagnant Zones," *Chem. Eng. J.*, **11**, 67 (1976).

Porter, K. E., and M. C. Jones, "A Theoretical Prediction of Liquid Distribution in a Packed Column with Wall Effect," *Trans. Inst. Chem. Engrs.*, **41**, 240 (1963).

———, V. D. Barnett, and J. J. Templeman, "Liquid Flow in Packed Columns, Part II: Spread of Liquid Over Random Packings," *ibid.*, **46**, 74 (1968).

Puranik, S. S., and A. Vogelpohl, "Effective Interfacial Area in Irrigated Packed Columns," *Chem. Eng. Sci.*, **29**, 501 (1974).

Rao, V. G., and Y. B. C. Varma, "A Model for the Residence Time Distribution of Liquid Phase in Trickle Beds," *AIChE J.*, **22**, 612 (1976).

Reiss, L. P., "Concurrent Gas-Liquid Contacting in Packed Columns," *Ind. Eng. Chem. Process Design Develop.*, **6**, 486 (1967).

Ross, L. D., "Performance of Trickle Bed Reactors," *Chem. Eng. Progr.*, **61**, No. 10, 77 (1965).

Rothfeld, L. B., and J. L. Ralph, "Equivalence of Pulse and Step Residence Time Measurements in a Trickle-Phase Bed," *AIChE J.*, **9**, 852 (1963).

Sato, Y., T. Hirose, F. Takahashi, and M. Toda, "Performance of Fixed-Bed Catalytic Reactor with Concurrent Gas-Liquid Flow," Pacific Chem. Eng. Congress, Session 8, Paper 8-3, p. 187 (1972).

——————, and Y. Hashiguchi, "Flow Pattern and Pulsation Properties of Concurrent Gas-Liquid Downflow in Packed Beds," *J. Chem. Eng. Japan*, **6**, 315 (1973).

Satterfield, C. N., A. A. Pelossof, and T. K. Sherwood, "Mass Transfer Limitations in a Trickle-Bed Reactor," *AIChE J.*, **15**, 226 (1969).

———, and P. F. Way, "The Role of the Liquid Phase in the Performance of a Trickle-Bed Reactor," *ibid.*, **18**, 305 (1972).

———, and F. Ozel, "Direct Solid Catalyzed Reaction of a Vapor in an Apparently Completely Wetted Trickle-Bed Reactor," *ibid.*, **19**, 1259 (1973).

Satterfield, C. N., "Trickle-Bed Reactors," *ibid.*, **21**, 209 (1975).

Schiesser, W. E., and L. Lapidus, "Further Studies of Fluid Flow and Mass Transfer in Trickle Beds," *ibid.*, **7**, 163 (1961).

Schwartz, C. E., and J. M. Smith, "Flow Distribution in Packed Beds," *Ind. Eng. Chem.*, **45**, 1209 (1953).

Schwartz, J. G., M. Duduković and E. Weger, "The Efficiency of Liquid-Solid Contacting in Trickle-Bed Reactors," 4th ISCRE, Heidelberg, p. 382 (Apr. 6-8, 1976).

———, E. Weger, and M. P. Duduković, "A New Tracer Method for Determination of Liquid-Solid Contacting Efficiency in Trickle-Bed Reactors," *AIChE J.*, **22**, 894 (1976).

Sedriks, W., and C. N. Kenney, "Partial Wetting in Trickle-Bed Reactors: the Reduction of Crotonaldehyde over a Palladium Catalyst," *Chem. Eng. Sci.*, **28**, 559 (1973).

Shulman, H. L., C. F. Ullricht, A. Z. Proulx, and J. O. Zimmermann, "Performance of Packed Columns—II: Wetted and Effective Interfacial Areas, Gas- and Liquid-Phase Mass Transfer Rates," *AIChE J.*, **1**, 253 (1955).

Sicardi, S., and G. Baldi, "A Model for Mass Transfer in Packed Towers: Mass Transfer with Controlling Resistance in the Gas Phase," *Chem. Eng. Sci.*, **31**, 651 (1976).

Specchia, V., A. Rossini, and G. Baldi, "Distribution and Radial Spread of Liquid in Two-Phase Concurrent Flows in a Packed Bed," *Quad. Ing. Chim. Ital.*, **10**, 171 (1974).

———, G. Baldi, and A. Gianetto, "Solid-Liquid Mass Transfer in Trickle Bed Reactors," 4th ISCRE, Heidelberg, p. 656 (Apr. 6-8, 1976).

——————, "Solid-Liquid Mass Transfer in Concurrent Two-Phase Flow Through Packed Beds," **17**, 362 (1978).

——————, "Pressure Drop and Liquid Holdup for Two-Phase Concurrent Flow in Packed Beds," *Chem. Eng. Sci.*, **32**, 515 (1977).

Sylvester, N. D., and P. Pitayagulsarn, "Radial Liquid Distribution in Concurrent Two-Phase Downflow in Packed Beds," *Can. J. Chem. Eng.*, **53**, 599 (1975).

Turpin, J. L., and R. L. Huntington, "Prediction of Pressure Drop for Two-Phase, Two-Component Concurrent Flow in Packed Beds," *AIChE J.*, **13**, 1196 (1967).

Van Swaaij, W. P. M., J. C. Charpentier, and J. Villermaux, "Residence Time Distribution in the Liquid Phase of Trickle Flow in Packed Columns," *Chem. Eng. Sci.*, **24**, 1083 (1969).

Verhoeven, L., and P. Van Rompay, "Simulation of a Trickle Bed Hydrodesulfurization Reactor," Proc. 7th Europ. Symp. Comput. Appl. in Chem. Ind., p. 90, Erlangen (1974).

Villermaux, J., and W. P. M. Van Swaaij, "Modele Representatif de la Distribution des Tempes de Sejour dans un Reactor Semi-Infini a Dispersion Axiale avec Zones Stagnantes. Application a l'Ecoulement Ruisselent dans des Colonne d'Anneaux Raschig," *Chem. Eng. Sci.*, **24**, 1097 (1969).

Weekman, V. W., Jr., and J. E. Myers, "Fluid-Flow Characteristics of Concurrent Gas-Liquid Flow in Packed Beds," *AIChE J.*, **10**, 951 (1964).

Wehner, J. E., and R. W. Wilhelm, "Boundary Conditions of Flow Reactor," *Chem. Eng. Sci.*, **6**, 89 (1957).

Wijffels, J. B., J. Verloop, and F. J. Zuiderweg, "Wetting of Catalyst Particles under Trickle Flow Conditions," Chem. Reaction Eng. II, ACS Monograph Ser. No. 133, p. 151 (1974).

Manuscript received November 29, 1977; revision received May 11, and accepted May 12, 1978.