terface (kg hydrate/m^3 solution)

ρ_s = solution density

σ = supersaturation [$= (\rho - \rho^*)/\rho^*$]

σ_c = parameter in BCF growth equation [Equation (14)]

σ_i = supersaturation at the crystal/solution interface [$= (\rho_i - \rho^*)/\rho^*$]

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Manuscript received March 23, 1976; revision received May 7 and accepted May 10, 1976.

A New Tracer Method for Determination of Liquid-Solid Contacting Efficiency in Trickle-Bed Reactors

A new tracer technique is reported for the determination of liquid-solid contacting efficiency and liquid holdup in trickle beds packed with small alumina particles. Holdup was a function of liquid mass velocity for both porous and nonporous packing. Contacting efficiency remained uniform at a level of 65%.

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SCOPE

A trickle bed consists of a fixed bed of catalyst particles with liquid, containing one or more of the reactants, trickling through the bed. A gas, containing the other reactant(s), is simultaneously passed through the bed. The major problems in the scale-up of trickle beds have been the difficulties in predicting the extent and effect on reactor performance of contacting between the solid catalyst and liquid, of mass and heat transfer within and to the catalyst particles, and of liquid backmixing. The progress to date on research in these areas was recently summarized in an excellent review paper (Satterfield, 1975).

Our objectives were to develop a method for evaluation of liquid-solid contacting which would be applicable to both porous and nonporous packing and to compare the experimental results obtained with the predictions of the available correlations over a range of liquid flow rates. A new two-tracer method was developed for this purpose. Hexane was used as the liquid phase and helium as the gas. Heptane was employed as the nonadsorbable tracer, and benzene and naphthalene were used as the adsorbable ones. The theory of chromatography was used to relate the first moments of the residence time distributions of the two types of tracers to liquid holdup and contacting efficiency.

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CONCLUSIONS AND SIGNIFICANCE

A tracer technique is developed for simultaneous evaluation of liquid-solid contacting and liquid holdup. The technique relies on the measurement of mean residence times for adsorbable and nonadsorbable tracers. This is the first method that allows direct measurements of contacting in beds packed with porous packing. Equations for adsorbable and nonadsorbable vaporizable tracers in gas-liquid-solid systems are developed and used in interpretation of the results.

The tracer determined holdups are found to be in good agreement with volumetrically determined ones. Holdup levels are higher than in previously published studies and less dependent on liquid flow rate. Contacting efficiency, based on total catalyst surface area, is uniform at the level of 65 and 66% for nonporous and porous packing, respectively, over a wide range of liquid flow rate (0.3 to 5 kg/m^{2}s). Both holdup and contacting efficiency are independent of gas flow rate when the latter is changed over a range from 1×10^{-4} to 2×10^{-3} kg/m^{2}s.

The experimental results are compared with the available correlations for holdup and contacting. Correlations obtained for adsorbers on the nonporous packing of large sizes and various shapes may not be applicable to trickle-bed reactors packed with small granuli. It is important to distinguish between particle scale and reactor scale incomplete contacting.

LIQUID HOLDUP AND CONTACTING EFFICIENCY: MEASUREMENT TECHNIQUES AND CORRELATIONS

Liquid Holdup

Liquid holdup is expressed as a fraction of reactor volume that is occupied by liquid. For porous packing, the total liquid holdup H_T consists of external holdup H_E and internal holdup H_I. The external holdup can be further divided into dynamic (free draining) holdup H_D and static (residual) holdup H_S. In the case of nonporous packing, total holdup is equal to external holdup:

$$H_T = H_E + H_I \tag{1}$$

$$H_E = H_D + H_S \tag{2}$$

Volumetric, gravimetric, and tracer methods are used most frequently in holdup measurements. Evaluation of holdup by tracer methods relies on the mean residence time of the liquid phase obtained from the first moment of the exit age distribution (residence time distribution) which is measured as a response to an impulse injection of a nonvolatile (relatively), nonadsorbing tracer (Danckwerts, 1953):

$$\bar{t}_L = \frac{H_T V}{Q_L} = \int_0^\infty tE(t)\,dt \tag{3}$$

where

$$E(t) = \frac{Q_L C_{TL\text{ex}}(t)}{M_T{}^i} \tag{3a}$$

When a step input of tracer is used, holdup is obtained from the cumulative age distribution:

$$\frac{H_T V}{Q_L} = \int_0^\infty [1 - F(t)]\,dt \tag{4}$$

where

$$F(t) = \frac{C_{TL\text{ex}}(t)}{C_o} \tag{4a}$$

Step and impulse tracer inputs were used by Lapidus (1957), who first used the tracer technique to determine holdup in trickle beds, and Schiesser and Lapidus (1961). They questioned the validity of the tracer measurements because of somewhat different results for holdup obtained for various forms of tracer inputs. However, the determination of the volume of the system, as presented by Equation (3), relies on the central volume principle which is theoretically sound (Stephenson, 1960). The principle simply states that the first moment of the residence time distribution for a linear system, where input and output occur by bulk flow only, is equal to the volume of the system divided by flow rate (Levenspiel, 1972). The validity of the tracer measurements and the equivalence of results for different tracer inputs has been demonstrated many times. In particular, Ross (1965) and Rothfeld and Ralph (1963) found good agreement for holdup in trickle-bed reactors when comparing results obtained with different tracer inputs.

Contacting Efficiency

Recent studies by Sedricks and Kenney (1973), Roberts and Yadwadkar (1972), Mears (1974), Weger and Schwartz (1974), and Satterfield (1975) indicate that it is not holdup but the catalyst area contacted by liquid (contacting efficiency) that primarily determines reactor performance. The analogous problem in packed-bed adsorbers is to determine the fraction of packing that is effectively wetted. An excellent summary and comparison of various correlations for packed beds was published by Hobler (1966). A number of the most frequently used correlations for nonporous packing in packed adsorbers (based on external wetted area) are presented in Table 1. However, because of the different shape, larger size, and nonporosity of the packing used, as well as different regimes of gas and liquid flow, the applicability of these contacting efficiency and holdup correlations to trickle-bed reactors is uncertain.

Different definitions of contacting efficiency have been used in the literature. There is no ambiguity in defining contacting efficiency for nonporous catalyst and/or adsorber packing as the fraction of external area contacted by liquid. On the other hand, for porous particles, the fraction of external area contacted η_{CE} the fraction of total external plus internal area contacted η_c and the fractions of pore volumes filled with liquid F_i are each distinguishable as possible estimates of the contacting efficiency.

All the experimental methods used to date to determine liquid-solid contacting have disadvantages. The indirect technique of Shulman et al. (1955) (via mass transfer rates) has the disadvantage that the packing must be constructed of, or coated with, a solid which either evaporates or dissolves. Thus, it is not possible to vary the interfacial properties of the system, such as contact angle or interfacial tension, over a wide range. Furthermore, it is highly unlikely that the wetting characteristics of the naphthalene particles reproduce those of alumina catalyst support, which is characteristic of many catalysts used in trickle-bed reactors. The assumption that the mass transfer coefficient is the same in gas-solid and gas-liquid-

TABLE 1. CONTACTING EFFICIENCY CORRELATIONS FOR NONPOROUS PACKING

Shulman et al. (1955):
$\eta_c = 0.24\left(\frac{L_m}{G_m}\right)^{0.25}$ (12.7, 25.4, 38.1 mm Raschig rings)
$\eta_c = 0.35\left(\frac{L_m}{G_m}\right)^{0.20}$ (12.7, 25.4 mm Berl saddles)
for
$5 \times 10^3 \leqq L_m \leqq 5 \times 10^4$ kg/m² hr
$5 \times 10^2 \leqq G_m \leqq 5 \times 10^3$ kg/m² hr
$13.4 < Re_L < 399.4$
Krauze and Serwinski (1971):
$\eta_c = 0.655\, L_m^{0.36}$ for $2.88 \times 10^2 \leqq L_m \leqq 1.98 \times 10^3$ kg/m² hr
$\eta_c = 0.585\, L_m^{0.17}$ for $2.98 \times 10^3 \leqq L_m \leqq 2.88 \times 10^4$ kg/m² hr
(5, 7, 10, 17 mm Raschig rings)
($0.75 < Re_L < 259.5$)
Onda et al. (1967):
$$\eta_c = 1 - \exp -1.45\, Re_L^{0.1}\, Fr_L^{-0.05}\, We_L^{0.2}\left(\frac{\sigma_c}{\sigma_L}\right)^{0.75}$$
for
$0.04 < Re_L < 500$
$1.2 \times 10^{-3} < We_L < 0.27$
$2.5 \times 10^{-9} < Fr_L < 1.8 \times 10^{-2}$
$0.3 < \sigma_c/\sigma_L < 2.0$
$8.0 < d_p < 50.8$ mm
$5.0 \times 10^2 \leqq L_m \leqq 3.0 \times 10^4$ kg/m² hr
(8, 17, 25, 35 mm Raschig rings; 12.7; 25.4 mm spheres; 12.7, 25.4, 38.1, 5.08 mm Berl saddles)
Puranik and Vogelpohl (1976):
$$\eta_c = 1.05\, Re_L^{0.047}\, We_L^{0.135}\, \frac{\sigma_L^{-0.206}}{\sigma_c}$$
(dynamic)
$$\eta_c = 1.045\, Re_L^{0.041}\, We_L^{0.133}\, \frac{\sigma_L^{-0.182}}{\sigma_c}$$
(total)
for
$2.1 \times 10^{-6} < We_L < 1.2 \times 10^{-2}$
$0.5 < Re_L < 85$
$7.7 \times 10^{-7} < Fr_L < 4.7 \times 10^{-3}$
$0.3 < \sigma_L/\sigma_c < 1.05$
$0.08 < a_W/a_T < 0.8$
$9 \times 10^2 < L_m < 4.32 \times 10^4$ kg/m² hr
$0.5 < \nu_L < 13$ cp
$25 < \sigma_L < 75$ dyne/cm
$10.0 < d_p < 37.5$ mm

solid systems, on which this technique relies, has not been verified.

The direct method of Krauze and Serwinski (1971), which is based on measurements of dyed areas, suffers from possible great inaccuracy in measuring such areas on small particles. The technique is cumbersome and time consuming. Each experiment at a given set of operating conditions requires a complete dismantling of the column to measure the area of individual particles contacted by the liquid. There is also the possibility of an experimental bias toward higher than actual contacting efficiencies if reactor scale contacting patterns change during the middle of a run. A liquid rivulet as it passes through the bed might contact a certain area of a particle, deposit indicator material, then change course and never contact that particular area again.

Neither the indirect nor direct technique can be used to measure the contacted area inside porous particles, and thus both are inapplicable to studies of contacting efficiency in trickle-bed reactors which are packed with porous catalysts.

The only previous method for estimating contacting efficiency in porous packing was developed by Lapidus (1957). Responses to a step input of tracer were measured in a 5 cm diameter trickle bed, first for beds of porous particles and then for beds of nonporous particles which were otherwise identical. Total holdups on porous and nonporous packing were obtained by use of Equation (4). The internal liquid holdup in the pores of the porous particles was then calculated by difference. Contacting efficiency was defined as the fraction of the catalyst pore volume that is filled with liquid:

$$F_i = \frac{H_I}{(1-\epsilon)\theta_p} = \frac{(H_T)_{\text{porous}} - (H_T)_{\text{nonporous}}}{(1-\epsilon)\theta_p} \tag{5}$$

Schiesser and Lapidus (1961) extended the above work by performing holdup measurements for both porous and nonporous alumina spheres in a 10 cm diameter trickle bed. The fractional pore filling was relatively constant at about 80% as the liquid rate was varied by a factor of about 2.5.

Several comments are appropriate concerning these tracer studies. First, since the fractional pore filling was calculated by taking the difference between the total and the external holdup, it was necessary to measure both holdups accurately to three significant figures. With tracer response curves that have pronounced tailing, this may be difficult. Second, the fractional pore filling, as determined in these studies, is not necessarily equal to the contacting efficiency, based on external geometric area. The fractional filling of the interior voids may or may not be directly related to the fraction of the external catalyst area that is contacted by liquid. The exact relationship between these parameters will depend on such factors as the pore structure of the catalyst and the surface properties of the gas-liquid-solid-system. Third, it has not been established that external holdup on porous and nonporous packing are the same at fixed operating conditions.

DEVELOPMENT OF THE NEW TRACER METHOD

The method reported here eliminates the disadvantages of the previously mentioned techniques, provides information on contacting and holdup simultaneously, and is applicable to both porous and nonporous packing. The method represents an extension of the principles of tracer chromatography to three-phase systems. If a pulse of tracer which does not absorb preferentially on the solid is injected into the liquid phase at the inlet at the top of the column, that is, trickle bed, and the concentration of tracer emerging from the column is measured at the exit, the total liquid holdup in the column can be obtained, as shown previously, from Equation (3), and the mean residence time of the tracer is equal to the mean residence time of the liquid:

$$\overline{t_T} = \frac{Q_L}{M_T^i}\int_o^\infty tC_{TL\text{ex}}(t)\,dt = \overline{t_L} = \frac{H_T V}{Q_L} \tag{6}$$

If, then, a tracer that adsorbs reversibly, linearly, and preferentially is similarly injected into the column operated at the same conditions as in the previous experiment, it can be shown (Schwartz, 1975) that

$$\overline{t_T}^* = \frac{Q_L}{M_T^i}\int_o^\infty tC_{TL\text{ex}}^*(t)\,dt = \frac{H_T V}{Q_L} + \frac{A_{io}K_a}{Q_L} \tag{7}$$

Equation (7) is generally applicable to two-phase systems consisting of one flowing and one stagnant phase where the tracer distributes itself with some partition coefficient K_a in both phases. The formula is valid for systems of all geometries provided that transport in the inflow and outflow stream is by bulk flow only (Duduković, 1972; Roberts et al., 1973). The catalyst area actually wetted (external and internal) A_w can be determined from Equation (7) when the adsorption equilibrium constant K_a is known from independent measurements. Contacting efficiency, based on total catalyst area A_T, is then evaluated:

$$\eta_c = \frac{A_w}{A_T} \tag{8}$$

An alternative method is to run the tracer tests on a liquid filled column at the same flow rates at which the experiments are performed in trickle flow. An explicit value of K_a is then unnecessary, and holdup and contacting efficiency can be obtained from the following formulas:

$$H_T = \frac{\bar{t}_T}{(\bar{t}_T{}^*)_{LF}} \tag{9}$$

$$\eta_c = \frac{\bar{t}_T{}^* - \bar{t}_T}{(\bar{t}_T{}^*)_{LF} - (\bar{t}_T)_{LF}} \tag{10}$$

It is usually difficult to find nonvolatile tracers that will closely resemble the carrier liquid and also have a linear adsorption isotherm. Therefore, an extension of the theory to account for vaporization is necessary. The zero$^{\text{th}}$ and first moment of the residence time distribution curve of a volatile tracer in the liquid phase will depend on the vapor-liquid equilibrium coefficient and on the rate constant for vaporization. Of primary interest in this paper is the maximal effect that tracer vaporization may have on holdup and contacting efficiency values. Both holdup and contacting efficiency are proportional to the mean residence time of the liquid and the sum of liquid mean residence time and catalyst contact time, respectively. The liquid mean residence time $\bar{t}_L$ is directly measured by the mean residence time of the nonvolatile nonadsorbing tracer $\bar{t}_T$ but not by the mean residence time of the volatile, nonadsorbing tracer $(\bar{t}_T)_e$. The difference between $\bar{t}_T$ and $(\bar{t}_T)_e$ will be largest if local equilibrium of the volatile tracer between vapor and liquid phase is established everywhere in the column, and this will cause the greatest error in holdup. Thus, in order to estimate the greatest effect of tracer volatility on holdup and contacting, it is necessary to study only the system where vapor and liquid are presumed to be in equilibrium.

The analysis of the trickle-bed column presented below is based on the following assumptions:

1. Temperature and pressure are essentially constant throughout the column.
2. The liquid, gas, and solid phase are treated as continua.
3. Longitudinal diffusional or dispersion effects are negligible.
4. Attainment of equilibrium in the radial direction in the liquid and gas phase is very fast.
5. The liquid and gas phase are homogeneously distributed in the column with a molar ratio Q.
6. The tracer molecules are completely distinguishable from all other molecules.
7. Holdup is not a function of position.
8. Local equilibrium is established for the tracer in the gas and liquid phase.
9. Adsorption on the solid is linear and reversible.

With these assumptions, one can write a combined equation of continuity for the liquid and gas phases in terms of tracer concentration together with an equation for the solid phase. These equations, with the appropriate initial and boundary conditions, are

$$(1 + K_{VL})\frac{\partial C_{TL}}{\partial t} = -\left(\frac{U_{SL}}{H_T} + K_{VL}\frac{U_{SV}}{h_T}\right)\frac{\partial C_{TL}}{\partial x} - ka\left(C_{TL} - \frac{C_{TS}}{K_a}\right) \tag{11}$$

$$\frac{\partial C_{TS}}{\partial t} = k\left(C_{TL} - \frac{C_{TS}}{K_a}\right) \tag{12}$$

$$C_{TL}(0, x) = C_{TS}(0, x) = 0 \tag{13}$$

$$C_{TL}(t, 0) = \frac{M_T{}^i}{Q_L + K_{VL}Q_V}\,\delta(t) \tag{14}$$

where

$$K_{VL} = \frac{C_{TV}}{C_{TL}} \tag{15}$$

Taking the Laplace transform, solving for $\overline{C_{TS}}$, and substituting into the equation for $\overline{C_{TL}}$, we obtain an ordinary first-order differential equation for $\overline{C_{TL}}(s, x)$. Upon integration and evaluation of the transform $\overline{C_{TL}}$ at the end of the trickle bed, the following result emerges (taking into account that $a = A_w/H_TV$):

$$\overline{C_{TL}}(s, L) = \frac{M_T{}^i}{Q_L + K_{VL}Q_V}\exp\left\{-\frac{1 + K_{VL} + \dfrac{kA_ws}{H_TV\left(s + \dfrac{k}{K_a}\right)}}{\dfrac{Q_L}{H_TV} + K_{VL}\dfrac{Q_V}{h_TV}}\right\} \tag{16}$$

The zero$^{\text{th}}$ and first moments of the tracer concentration curve are

$$\mu_o = C_{TL}(0, L) = \frac{M_T{}^i}{Q_L + K_{VL}Q_V} \tag{17}$$

$$\mu_1 = -\frac{d\overline{C}_{TL}}{ds}(0, L) = \frac{M_T{}^i}{Q_L + K_{VL}Q_V}\,\frac{1 + K_{VL} + \dfrac{K_aA_w}{H_TV}}{\dfrac{Q_L}{H_TV} + K_{VL}\dfrac{Q_V}{h_TV}} \tag{18}$$

The mean residence time of a volatile, adsorbable tracer in the column is

$$\bar{t}_{T_e}{}^* = \frac{\mu_1}{\mu_o} = \frac{H_TV}{Q_L}\,\frac{1 + K_{VL} + \dfrac{K_aA_w}{H_TV}}{1 + K_{VL}\dfrac{Q_V}{Q_L}\dfrac{H_T}{h_T}} \tag{19}$$

The same result as that given by Equation (19) would have been obtained if local equilibrium between liquid and solid was also assumed, but Equation (16) would have had a different form (Schwartz, 1975). This is due to the fact that the magnitude of the exchange rate between a moving and stationary phase does not affect the zero$^{\text{th}}$ and first moment of the tracer concentration curve and appears only in higher moments (Dudukovic, 1972; Roberts et al., 1973; Buffham, 1973). The exchange rate

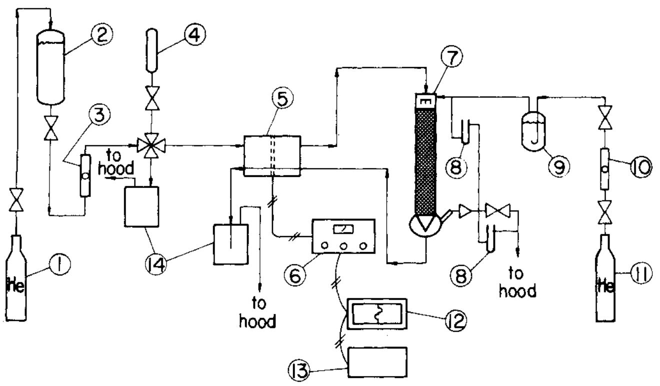

Fig. 1. Schematic diagram of the equipment for tracer-based measurement.

between two moving phases, however, does affect even the first two moments (Schwartz, 1975; Dudukovic et al., 1976). Once the assumption of local equilibrium between the moving phases is made, Equation (19) holds even for more complex models of the trickle bed, which account for dispersion effects (Dudukovic, 1972; Roberts et al., 1973). Thus, in that sense, Equation (19) represents a general result. If one assumes that $K_a = 0$, the mean residence time of a volatile, nonadsorbing tracer is obtained:

$$\bar{t}_{T_e} = \frac{H_T V}{Q_L} \frac{1 + K_{VL}}{1 + K_{VL}\dfrac{Q_V}{Q_L}\dfrac{H_T}{h_T}} \qquad (20)$$

This result is essentially the same as the one obtained by Perilloux and Deans (1972) for bubble-liquid chromatography.

For a given vaporization equilibrium constant K_{VL}, Equations (19) and (20) for volatile tracers present the largest possible departure from Equations (7) and (6), respectively, for nonvolatile tracers and reduce to the latter equations for $K_{VL} = 0$. The maximum possible effect of tracer vaporization on holdup is given by the difference in holdups evaluated from Equations (20) and (6). Similarly, the difference in the contacted area evaluated from Equations (19) and (7) gives the maximum effect of vaporization on contacting efficiency.

APPARATUS AND PROCEDURE

The measurements of holdup and contacting efficiency were made at a temperature of 25 ± 0.5°C in a trickle-bed column, consisting of a 38.1 cm insulated, borosilicate glass tube (1.35 cm I.D.) packed randomly with either porous or nonporous material to a height of 30.5 cm. The packing was packed dry with intermittent vibrations. Activated F-1 alumina (Alcoa), −20 to +28 mesh was used as porous packing ($S_g = 270$ m^2/g). Special samples of relatively nonporous alumina T-61/F-1 of the same mesh size were prepared by precipitating thin layers of porous F-1 alumina on the nonorous T-61 alumina. The specific surface area of these samples was 4 m^2/g. The liquid critical surface tensions on the two types of packing were approximately the same (Schwartz, 1975). Data were obtained on a number of repacked columns.

Pure *n*-hexane as the carrier liquid and pure helium, presaturated with hexane, as the gas phase were fed separately into the top of the column and then through 30.5 cm bed of packing supported by a 60 mesh stainless steel screen. After leaving the bottom of the test column, the two-phase system was separated in a 2 cm diameter glass bulb with gas leaving through a side port and liquid draining from the bottom. The operating pressure of the column was set by the back pressure metering valve (Whitey) through which the gas passed before it was vented to the atmosphere. Pressure drop through the column was small, that is, on the order of a few centimeters of water. A schematic diagram of the equipment for tracer based measurement is shown in Figure 1. The liquid flow rates ranging from 0.3 to 5 kg/m^{2}s (4 to 64 cm^3/min) were measured with a rotameter (Brooks) which was calibrated by using hexane. Liquid was introduced through a centrally located glass tube 0.2 cm in diameter.

Prior to entering the trickle-bed column, the liquid stream passed first through a six-port stainless steel sampling valve (Perkin-Elmer). A known volume and concentration of tracer solution from a separate supply tank was injected into the liquid feed stream via the sampling valve. The tracer was injected by switching a sample loop, with a volume of 0.606 cm^3, from the tracer stream to the main carrier stream. This was accomplished by the use of a grooved Teflon face plate on the six-port valve. Tracer introduced in this manner is proportional to the velocity of the flowing liquid which sweeps the sample loop and thus produces the correct flow averaged introduction of tracer (Turner, 1971; Buffham, 1972).

The stimulus pulse was measured repeatedly at each flow rate by use of a Waters Associates R-403 refractive index optical detector and was found to be reproducible and uniform. The first moment at a given flow rate never varied by more than 0.01 min, which is within the accuracy of time measurement for the system. The refractometer was operated with liquid flowing only through one side. Some carrier liquid was placed in the reference side, and this provided a stable signal. This mode of operation was also used for the measurements of the tracer concentration in the exit stream. The optical module of the detector was connected to a control module which supplied power to the light source and amplified the signal from the photo detector module. The output signal from the detector's control module was fed in parallel to a Beckman Model 1005 strip chart recorder and to a digital voltmeter-printer unit (Data Technology/Hecon).

Figure 2 can be used to describe the operation of the differential refractometer. The trickle-bed effluent liquid stream containing the tracer passes through the photo detector cell, where the difference in refractive index between the effluent stream and reference liquid is continuously measured. The change in refractive index is directly related, according to Snell's law, to the change in concentration of the effluent liquid stream as the tracer pulse passes through the detector. Calibrations were performed to determine the relationship between changes in refractive index and changes in concentration at different liquid flow rates.

Further details about the experimental system may be found in the original study (Schwartz, 1975). The selection of appropriate tracers is also described there. Heptane was used as nonadsorbing tracer for all runs; benzene was originally used as an adsorbing tracer. Typical injection and response curves are presented in Figure 3. Separate batch experiments were performed to determine the adsorption of the tracers on the porous Alcoa F-1 and the nonporous Alcoa T-61-F-1 alumina. It was found that heptane does not adsorb on either alumina, while a linear adsorption isotherm was observed for benzene at low concentrations. The composite isotherms for benzene are presented in Figures 4 and 5. All measurements were made with

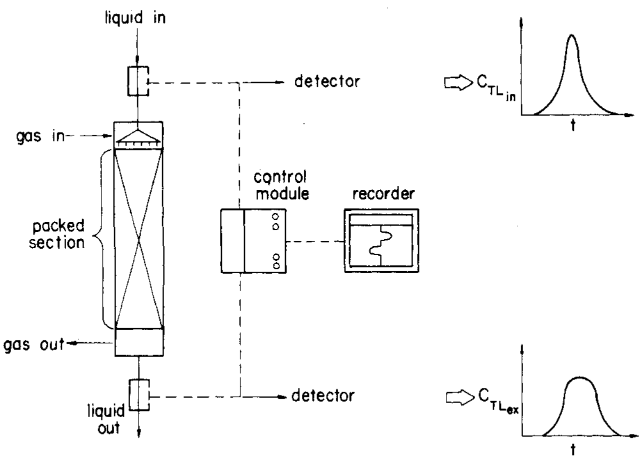

Fig. 2. Measurement of tracer concentrations.

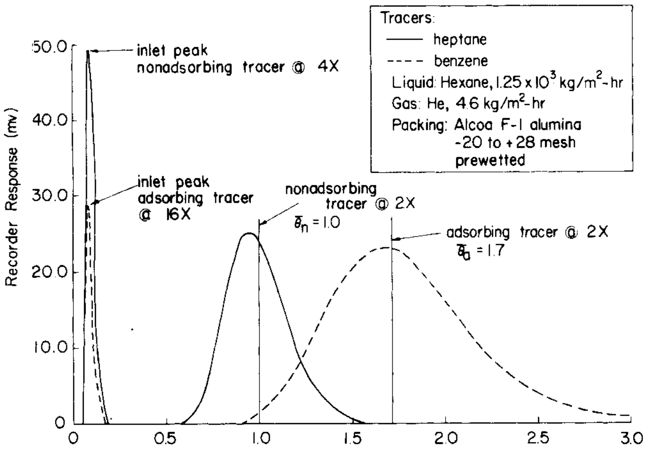

Fig. 3. Typical injection and response tracer curves.

dry, freshly activated aluminas. Within the accuracy of the data in this range of low concentrations, the isotherm is linear and adsorption is reversible. The adsorption equilibrium constants are indicated in the figures. Naphthalene was used as adsorbing tracer in runs with the nonporous packing for reasons discussed below.

All raw data from the experimental runs were processed by using an IBM 360-65 computer. A data reduction program was used routinely to convert data points of the RTD curves to the moments of the curve. The zeroth moment, or area under the RTD curve, was used to check the mass balance for tracer remaining in the liquid phase. The expressions used to calculate the first and second moment of the RTD curve are the same for both the adsorbing and the nonadsorbing tracer. The first moment or mean residence time can be calculated as

$$\bar{t} = \frac{\int_o^\infty tC_{TL\mathrm{ex}}(t)\,dt}{\int_o^\infty C_{TL\mathrm{ex}}(t)\,dt} - \frac{\int_o^\infty tC_{TL\mathrm{in}}(t)\,dt}{\int_o^\infty C_{TL\mathrm{in}}(t)\,dt} \tag{21}$$

Once $\bar{t}$'s are determined, the liquid holdup H_T and contacting efficiency η_c can be calculated by the previously given equations.

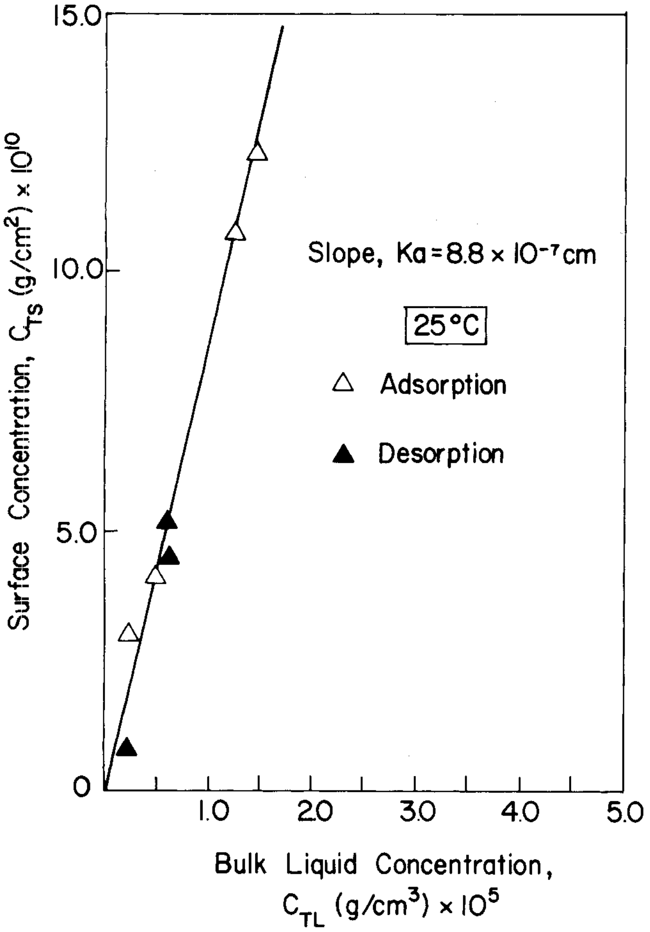

Fig. 4. Adsorption isotherm-benzene on Alcoa F-1 alumina from solution (solvent: *n*-hexane).

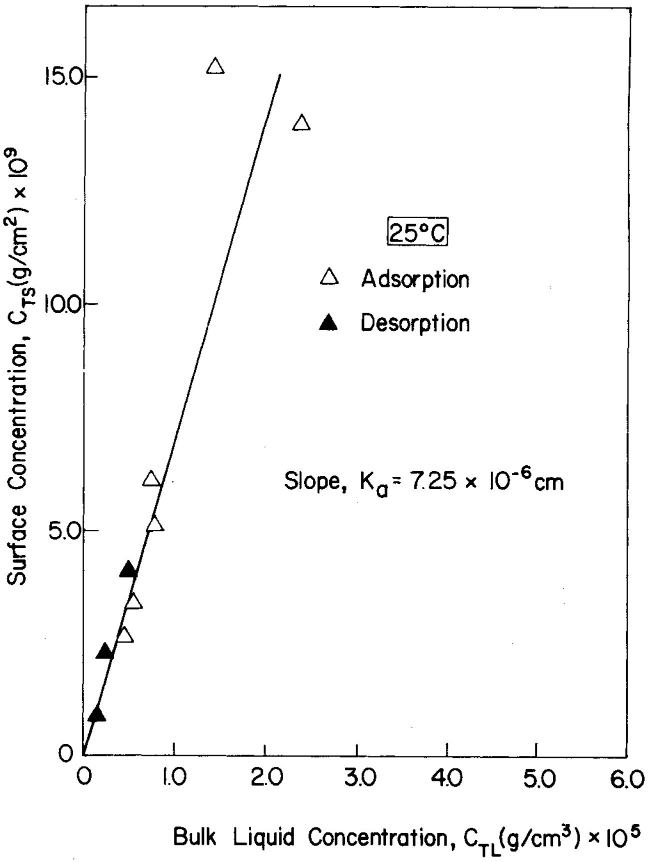

Fig. 5. Adsorption isotherm-benzene on Alcoa T-61/F-1 alumina from solution (solvent: *n*-hexane).

RESULTS AND DISCUSSION

Liquid Holdup

The comparison of tracer determined holdup to the volumetrically measured one is presented in Figure 6. The

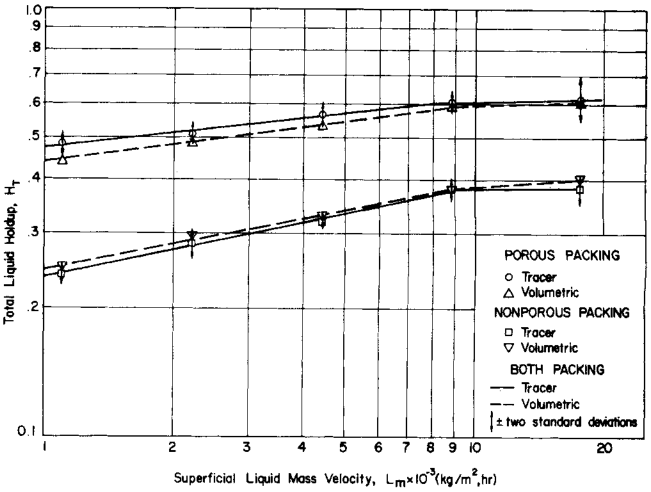

Fig. 6. Total and external (tracer-based and volumetric) liquid holdup as a function of liquid superficial mass veocity.

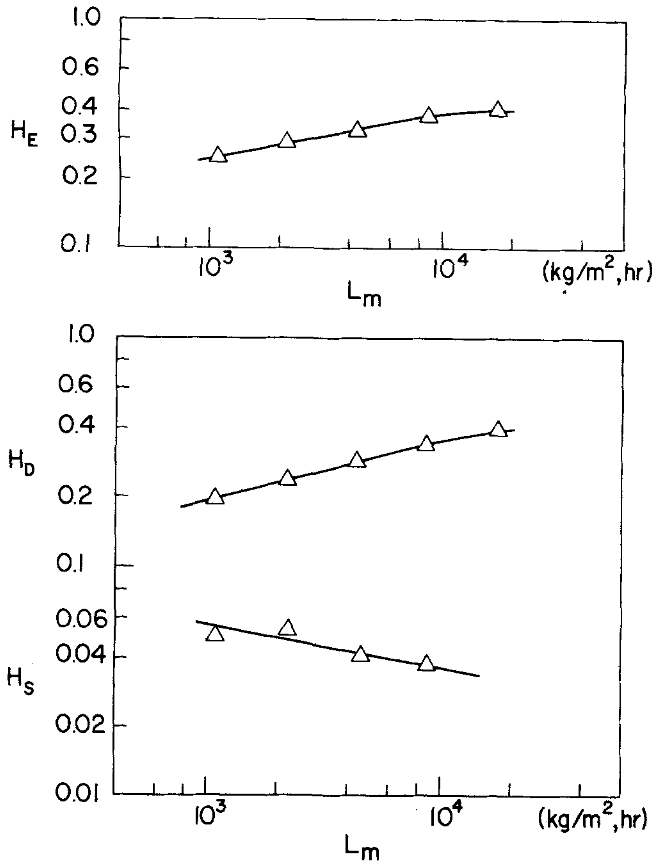

Fig. 7. External, dynamic, and static (volumetric) liquid holdup as a function of liquid superficial mass velocity.

tracer based average holdup data for nonporous packing are only about 4% lower than the volumetrically determined values at most flow rates, with a maximum difference of −7% at the highest flow rate of our study. On the other hand, the tracer determined average liquid holdups for porous packing are greater than the volumetric values by only about +6%, with the exception of +12% at the lowest liquid flow rate in the column. No definite bias in the data could be observed. The volumetric total holdup obtained on porous materials may actually be low if the required procedure of starting with a dry bed does not develop the same internal holdup levels which existed in the prewetted beds used for the tracer technique. A long period of time, about several hours or more, was indicated by Shulman et al. (1955) as being necessary to achieve relatively constant holdup starting with a dry bed of larger nonporous packing. Even larger times are necessary for beds of porous particles. A comparison with literature data demonstrates that the reproducibility of holdup data in our laboratory was very good. The differences between holdup calculated by using Equation (6), which is based on the assumption of no vaporization, and that obtained by using Equation (26), which is based on the assumption that complete vaporization equilibrium is achieved, were less than 1%.

Holdup for nonporous particles, also by using the volumetrically determined static holdup, is plotted as a function of liquid mass velocity in Figure 7. Total holdup was found to be proportional to $L_m^{0.20}$ over most of the flow range. Holdup appeared to level off for flow rates around 10^4 kg/m^2 hr (2.8 kg/m^{2}s). Dynamic holdup, plotted in the same figure for comparison, showed a greater dependence on flow rate; that is, it was proportional to $L_m^{0.26}$. For laminar flow over spheres, dynamic holdup is predicted to be proportional to $L_m^{1/3}$ by theory (Davidson et al., 1959). Static holdup was found to decrease with increasing liquid velocity in agreement with the observations of Gelbe (1968). Static holdup, measured after liquid flow was reduced to zero, was found to have a relatively constant value of 0.05. Liquid holdup appeared to be independent of gas flow rate, which was varied from 2×10^{-4} to 2×10^{-3} kg/m^{2}s. This lack of dependence of liquid holdup on gas flow rate was also found by Hochman and Effron (1969), Ross (1965), Robinson (1975), and Sater and Levenspiel (1972).

Holdup measured for the porous packing has also been plotted vs. liquid mass velocity in Figure 8. Total holdup for the porous material showed a slightly lower dependence on flow rate ($L_m^{0.15}$) compared to the total holdup for nonporous material H_E as is shown in the same figure. This is due to the fact that the internal holdup component obtained by the subtraction ($H_T - H_E$), as suggested by Lapidus (1957), demonstrated only a very weak dependence on liquid flow rate, indicating that the pores of the material used in this study are filled by capillarity. The comparison of holdup data obtained in this study to data of others and to available holdup correlations is presented elsewhere (Schwartz et al., 1976).

Contacting Efficiency

The values of contacting efficiency for nonporous packing (fraction of external area that is wetted) and for porous packing (fraction of total BET area that is wetted) are presented in Figure 9 as functions of liquid mass velocity and particle Reynolds number. The range of values obtained as a result of a randomized 5 × 2 factorial experiment design with three replicates is indicated. Heptane and naphthalene were used as nonadsorbing and

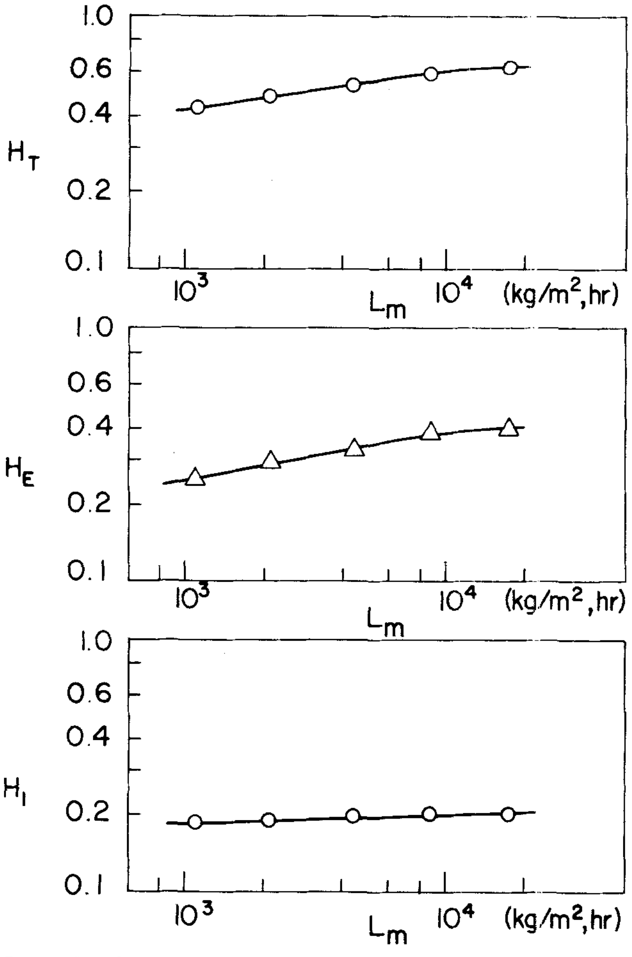

Fig. 8. Total, external, and internal (volumetric) liquid holdup as a function of liquid superficial mass velocity.

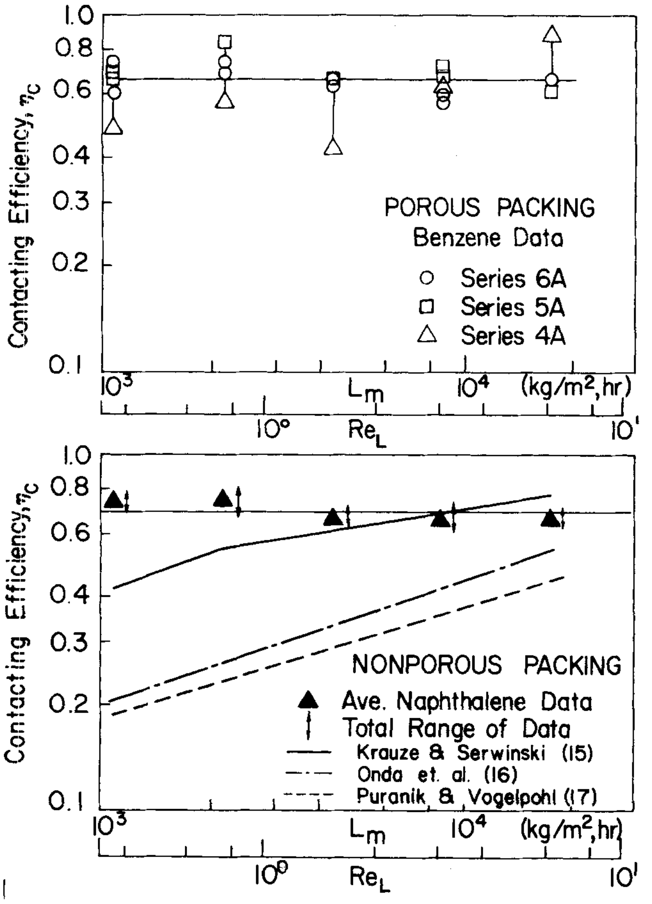

Fig. 9. Contacting efficiency of porous and relatively nonporous alumina.

adsorbing tracer, respectively, for nonporous packing and heptane and benezene with the porous one. No vaporization correction was necessary for naphthalene, and the maximum correction for heptane, as discussed earlier, amounts to 1%. The vaporization correction for benzene is potentially large, since the maximum equilibrium amount vaporized ranged from 29% at the lowest flow rate to 1% at the highest. However, the values of contacting efficiency which are based on complete vaporization were only 1 to 6% higher (depending on flow rate) than the ones calculated on the assumption of no vaporization. Variation in η_c values due to vaporization cannot be used to explain the apparent random variation in calculated contacting efficiency which occurs at all flow rates.

Contacting efficiency based on external area of the nonporous particles appears to be uniform for this particular system at the conditions of our study presented in Table 2. The statistical F test indicates no significant variation of contacting efficiency with flow rate. The line of best fit of all the data is a horizontal line at about 65% contacting efficiency. This level of external contacting is close to the values predicted by the correlation of Krauze and Serwinski (1971). The other available wetted area correlations of Puranik and Vogelpohl (1974) and Onda et al. (1967), which are also presented in Figure 9, do not fit the data of this study at all. Similarly, an overall value of 66% over the whole range of liquid flow rate studied characterizes the contacting efficiency, that is, the fraction of the catalyst BET total area that is wetted, on porous packing. This high level of contacting might have been expected, since the bed had been prewetted prior to the tracer runs. It is important to point out that the same level of contacting efficiency was obtained whether the calculation was based on Equation (7), that is, on total BET area and a properly evaluated K_a value from static adsorption experiments, or on Equation (10) which compared the total benzene (or naphthalene) available areas in trickle flow and a liquid filled column.

TABLE 2. RANGE OF VARIABLES AND PHYSICAL PROPERTIES OF THIS STUDY

$0.39 < Re_L < 6.20$
$2.9 \times 10^{-6} < We_L < 7.5 \times 10^{-4}$
$5.8 \times 10^{-5} < Fr_L < 1.5 \times 10^{-2}$
$\sigma_L/\sigma_c = 0.66$
$T = 25°C$
$1.0 \times 10^3 < L_m < 1.8 \times 10^4$ kg/m² hr
$0.40 < G_m < 4.10$ kg/m² hr
$\sigma_L = 18.2$ dyne/cm
$\mu_L = 0.315$ cp
$\rho_L = 0.656$ g/cm³
$\overline{d}_p = 0.06$ cm

Another estimate of contacting efficiency of a porous material is fractional pore filling. This can be calculated from holdup data by using Equation (5) based on the assumption of Lapidus (1957) that external holdup at given operating conditions is the same for porous and nonporous packing of the same size. The fraction of total pore volume filled with liquids can be characterized by a constant average value of 0.78, based on tracer determined holdup, and 0.66, based on volumetrically measured holdups. This constancy of holdup over a range of flow rates is in agreement with the observations of Lapidus (1957) and Schiesser and Lapidus (1961). The better agreement between η_c and F_i based on volumetric measurements is only coincidental. As seen from Figure 6, the volumetrically determined holdups almost always lie within two standard deviations from the average values determined by the tracer technique. Volumetric data were obtained on the same bed, while tracer data were collected on a number of repacked beds. There is also reason to believe that external holdup on porous and nonporous particles is not the same, being larger on the former, which will lead to an overestimate of F_i if holdup subtraction is used.

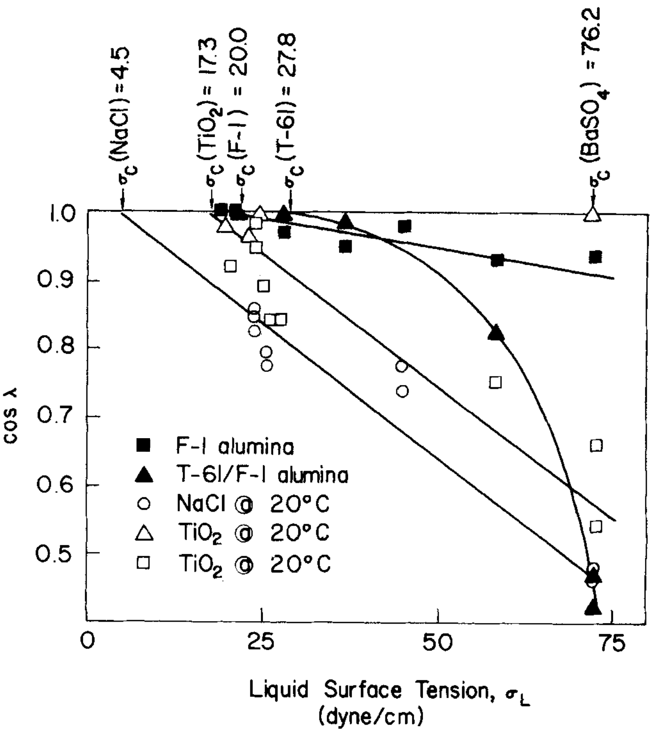

Fig. 10. Cosine of the contact angle as a function of liquid surface tension.

The apparent discrepancy between the observations that holdup increases with flow rate for both porous and nonporous packing while contacting efficiency remains constant can possibly be explained as follows. When liquid flow rate increases, contacting patterns, which were established in the bed initially, do not change (Satterfield, 1975), and increasing holdup only causes an increasing depth of liquid film passing over the solid packing. This would apply to our study only if reactor scale incomplete contacting is the cause of the observed contacting efficiency and not particle scale incomplete contacting. The contact angle measurements (Schwartz, 1975) presented in Figure 10 demonstrate that hexane with surface tension of $\sigma_L = 18.2$ dyne/cm should spread readily over both porous F-1 alumina ($\sigma_c = 20.0$ dyne/cm) and nonporous T-61/F-1 alumina ($\sigma_c = 27.8$ dyne/cm). It is doubtful that hexane would establish rivulets only partially wetting the small particles used ($\overline{d_p} = 0.06$ cm). If this were the case, such rivulets would tend to spread, thus contacting more area upon increased flow. Data demonstrate that the fraction of total voidage that is liquid filled increases at approximately the same rate for both packings, indicating that the increased holdup is mainly due to increased thickness of liquid films in the bed and close to the wall in the regions where the particles were already completely wetted externally and internally. This would indicate reactor scale incomplete contacting and existence of poorly wetted regions in the bed. The approximately same value of contacting efficiency in porous beds (based on total internal catalyst area) and nonporous beds (based on external area) seems to point towards the same conclusion.

ACCURACY AND PRECISION OF THE TRACER TECHNIQUE

The two tracer techniques applied to the helium-hexane-alumina system yield high levels of holdup and contacting efficiency but with some scatter of the values for liquid-solid contacting efficiency η_c. These results raise the question of whether this variation can be attributed to experimental error or whether the variation in contacting efficiency is in reality due to the randomness of the physical processes occurring in the bed with two-phase flow. The tracer experiment is, without doubt, a statistical process.

The accuracy of the contacting efficiency data depends on the accuracy of the holdup data which are used in the calculation. The tracer based holdup measurements agreed in general with the volumetric ones within 10% for the porous and 5% for the nonporous packing. The volumetric data presented are results of single runs, while tracer data are averages of repeated experiments on repacked beds. The volumetric data are within two standard deviations of the tracer determined means. In the worst possible case, an overestimate of 10% in holdup for porous packing and underestimate of 5% for the nonporous one lead to an error of 25% in internal holdup and fraction of a liquid filled internal voidage F_i. However, an error of 10% in holdup results in errors of less than 10% in contacting efficiency η_c, due to the fact that in general $\bar{t}_T < \bar{t}_T^* - \bar{t}_T$. The method of analyzing the tracer data has been shown not to be a source of inaccuracy (Schwartz, 1975).

The observed variance in the data must now be addressed. The repeated measurements of $\bar{t}$ for a given tracer within a run, where the trickle-bed column was verified to be operating at steady state (that is, constant readings of variables, such as flow rates, pressure drop, etc., constant liquid level in the separator, and flat base line of the refractometer output, etc.) could give as little as zero variation or at the most a ±10% range about the average at high flow rates. The great majority of the repeated measurements varied in value only about 2% of the average. The larger variation reported in this study as indicated in Figure 9 occurred when replicates of the experiment were performed on repacked beds. Variations in bed density, bed porosity, and total amount of packing upon repacking did not exceed 2%. The stimulus pulse data were very reproducible, with the maximum range of ±0.01 minute about the average, which is, at most, ±2% of the response mean time at low flow and ±4% at high flow. Liquid flow rates never varied by more than 1%, while gas flow rate was maintained within 2% of the target value. Any variations in the physical properties of the materials used, with the exception of adsorption potential as described below, were minimized by blending. No run was made until the refractometer achieved a steady base line, with less than 1% short term noise or long term drift which confirmed that the liquid flow rate, pressure drop, and temperature were constant. The mean residence times were calculated properly by dividing the calculated first moment of the tracer curve with the area under the curve. The only two remaining sources of error are the correction for tracer vaporization and the possible variation of the adsorption equilibrium constant K_a in time or upon repacking.

The correction to the mean residence time for tracer vaporization was addressed in the previous section and shown to be less than 6%.

Variation in the adsorption equilibrium constant would considerably affect the values of contacting efficiency as obtained from replicates of the experiments. That such variation may occur was first observed when extremely low values of contacting efficiency were obtained by using benzene as tracer on nonporous T61/F1 packing. For the repeated experiments on the same bed, the 95% confidence intervals for $\bar{t}_T^*$ of benzene varied about the average value at each flow rate from 2 to 4%. However, the low values indicated unrealistically low contacting, in contradiction with holdup measurements, which pointed to a possible deviation from a statically measured adsorption coefficient as large as a factor of 6. In order to check these results, single-phase runs were performed on the same but completely flooded bed at the same liquid flow rates with no flow of gas. Holdup agreed well with the bed porosity, while the adsorption constant K_a, calculated from Equation (7), yielded an average value of 5.3×10^{-7} cm with only moderate variation around the mean. This dynamically determined value is an order of magnitude lower than the statically determined value of 7.25×10^{-6} cm, and the two values should be the same, independent of the method (Buffham, 1972).

This decrease in the adsorption coefficient is most probably due to the deactivation of the adsorption sites by the strong, preferential adsorption of water. A possible source of moisture for water adsorption is the dry packing procedure used to load the column. To check this, adsorption isotherm measurements of benzene were made on alumina which had been exposed to air for ½ hr which is the approximate time needed to weigh the packing and fill the column. The data obtained on various batches of such air exposed packing show a decrease in adsorption compared to dry, activated packing, but with considerable scatter in the results. More controlled studies on porous alumina (Snyder, 1968) showed a decrease in the effective $K_{a_{\mathrm{eff}}}$, based on volume of liquid required for chromatographic separation of several compounds eluted by pentane, by as much as an order of magnitude with the addition of only 4 wt% water. The importance of protecting the packing from water deactivation is obvious from these results. However, the dry method of packing with intermittent vibration produced by far the most reproducible bed densities and was retained. The deactivated state of the bed upon packing was taken into account in this work by evaluating the K_a for the new state of packing. The net result of the lower K_a values was that benzene mean residence times were very close to the values obtained with heptane in the case of nonporous packing. This led to the selection of naphthalene for adsorbable tracer, as its K_a value even on deactivated alumina is an order of magnitude higher ($K_a = 4 \times 10^{-6}$ cm).

In summary, the most significant source of variation in the values of contacting efficiency appears to be caused by changes in the adsorption characteristics due to different and uncontrolled degrees of water deactivation of the alumina which occurred when the column had to be repacked. An error analysis for η_c confirms this. Slow cumulative deactivation by the presence of water traces in the liquid and gas phase was possible. This indicates that in the case of slowly deactivating packing, Equation (10), which does not require an explicit value for K_a, should be used. Its validity was confirmed in this study, as well as the general validity of the tracer method.

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation for financial support (Grant No. GK-38554). The contribution of George Roberts, Engelhard Industries, in initiating this research is sincerely appreciated. The preparation and donation of alumina used in this work by the Aluminum Company of America is gratefully acknowledged.

NOTATION

A_T = total catalyst surface area, cm^2
A_w = total catalyst area contacted by liquid, cm^2
a = specific catalyst area wetted by liquid = A_W/H_TV, cm^{-1}
C_o = tracer concentration in the input stream, g cm^{-3}
C_{TL} = concentration of tracer in the liquid phase, g cm^{-3}
C_{TL}^* = concentration of adsorbable tracer in the liquid phase, g cm^{-3}
C_{TV} = concentration of tracer in the vapor phase, g cm^{-3}
C_{TS} = concentration of tracer on the solid, g cm^{-2}
d_p = particle diameter, cm
E = exit age distribution, s^{-1}
F = cumulative exit age distribution, dimensionless
F_i = fractional pore fillup with liquid, cm^3 liquid/cm^3 particle pore volume, dimensionless
H_D = dynamic liquid holdup, cm^3 liquid/cm^3 empty reactor, dimensionless
H_E = liquid holdup external to packing, cm^3 external liquid/cm^3 empty reactor, dimensionless
H_I = liquid holdup in the interior of porous packing particles cm^3 liquid within particles/cm^3 empty reactor, dimensionless
H_s = static external liquid holdup, cm^3 stagnant liquid external to packing/cm^3 empty reactor, dimensionless
H_T = total liquid holdup, cm^3 liquid/cm^3 empty reactor, dimensionless
h_T = total vapor holdup, cm^3 vapor/cm^3 empty reactor, dimensionless
K_a = equilibrium distribution coefficient for tracer between catalyst and liquid, cm
$K_{a_{\text{eff}}}$ = linear isotherm equivalent retention volume (volume of solvent required to move center of chromatographic sample to end of bed), cm^3/g adsorbent
K_{VL} = vapor-liquid equilibrium constant defined by Equation (16), dimensionless
k = liquid-solid adsorption rate constant, cm s^{-1}
L_m = liquid mass superficial velocity, g cm^{-2}s^{-1}
$M_T{}^i$ = mass of tracer injected in impulse injection, g
P = pressure in the bed, kg cm^{-2}
Q_L = volumetric liquid flow rate, cm^3 s^{-1}
Q_V = volumetric gas flow rate, cm^3 s^{-1}
R = universal gas constant, kg cm mole^{-1} °K
R_T = rate of tracer transport from liquid to gas phase, g/cm^3
Re_L = liquid particle Reynolds number, $= \rho_L d_p U_{SL}/\mu_L$, dimensionless
S_T = rate of tracer transport from liquid to solid, g/s cm^2
s = Laplace transform variable, dimensionless
T = temperature, °K
t = time, s
$\overline{t_L}$ = mean residence time of the liquid phase, s
$\overline{t_T}$ = mean residence time of a nonadsorbing tracer in the liquid phase, s
$\overline{t_T}^*$ = mean residence time of an adsorbing tracer in the liquid phase, s
U_{SL} = liquid superficial velocity, cm^{-1}
U_{SV} = gas superficial velocity, cm s^{-1}
V = total volume of the empty reactor, cm^3
x = axial coordinate along the reactor, cm

Greek Letters

ϵ = porosity of the packed, bed, cm^3 interparticle voidage/cm^3 empty reactor, dimensionless
η_c = contacting efficiency based on total catalyst area, dimensionless
η_{CE} = contacting efficiency based on external catalyst area, dimensionless
θ = dimensionless time, $= t/\overline{t}$, dimensionless
θ_p = particle porosity, cm^3 intraparticle voidage/cm^3 particle volume, dimensionless
λ = contact angle, radians
μ_o = zero$^{\text{th}}$ moment of the tracer concentration curve defined by Equation (17), g cm^{-3} s
μ_1 = first moment of the tracer concentration curve defined by Equation (18), g cm^{-3} s^2
μ_L = viscosity of the liquid phase, poises
σ_c = critical surface tension of solid defined as the liquid surface tension at which cosine of the contact angle, λ, equals one, dyne cm^{-1}
σ_L = surface tension of liquid, dyne cm^{-1}

Subscripts

e = vaporizable tracer
ex = at the exit of the bed
in = at the entrance of the bed
LF = liquid filled bed
nonporous = nonporous packing
porous = porous packing

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Supplementary material has been deposited as Document No. 02852 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Ave. South, New York, NY 10016 and may be obtained for $3.00 for microfiche or $5.00 for photocopies.

Manuscript received March 1, 1976; revision received May 25 and accepted May 27, 1976.

Selective Hydrogenation and Mass Transfer in a Fixed-Bed Catalytic Reactor with Gas-Liquid Concurrent Upflow

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Reaction rates of selective hydrogenation of phenylacetylene (PA) and styrene were studied in a packed-bed reactor with concurrent gas and liquid upflow. The surface reaction rates were expressed by the reaction between adsorbed PA or styrene and dissociated hydrogen atoms competing for the same active sites. The contributions of mass transfer rate were determined, and better selectivity conditions were discussed.

SCOPE

Since concurrent operation is not limited by flooding, gas-liquid reactions requiring a solid catalyst are generally carried out in a gas-liquid upward concurrent flow in industrial applications. During development work on a reactor to convert PA to styrene in a mixture of styrene and xylene with hydrogen in the presence of a supported

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