COMMUNICATIONS TO THE EDITOR

Equivalence of Pulse and Step Residence Time Measurements in a Trickle-Phase Bed

LEONARD B. ROTHFELD and J. L. RALPH
Shell Development Company, Emeryville, California

This communication describes experiments performed to ascertain the equivalence of pulse and step input liquid residence time data in cocurrent, downward, gas-liquid flow through packed beds (trickle-phase beds). Contrary to results in the literature, we find that data taken by the different methods are equivalent.

The distribution of residence times in a piece of process equipment may be measured by injecting a pulse of tracer into the inlet stream and measuring the downstream concentration as a function of time. Alternately, a step change in inlet tracer concentration may be introduced, and the effluent analyzed to follow the approach to the new steady state. According to Laplace transform theory, the time integral of the pulse data should be equivalent to the step data if the system is linear (*5*); that is

$$\left[1-\frac{\int_0^t c\,dt}{\int_0^\infty c\,dt}\right]_{\text{pulse}} = \left[\frac{c - c_2}{c_1 - c_2}\right]_{\substack{\text{step}\\ \text{decrease}}} = \left[1-\frac{c - c_1}{c_2 - c_1}\right]_{\substack{\text{step}\\ \text{increase}}}$$

where c_1 and c_2 are the inlet tracer concentrations before and after the step change, respectively.

Contrary to the theory, Lapidus (*2*) and Schiesser and Lapidus (*3*) report large differences between data obtained by the three methods in a trickle-phase bed of porous particles, particularly in the tail of the distribution (that part which represents removal of the last 10% of tracer from the bed). With sodium chloride as tracer in tap water flowing at 74.5 ft./hr. superficial velocity through a 4-ft. long, 4-in. diam. bed of ¼-in. porous alumina spheres, these authors find the tail of the step-elution (concentration decrease) curve delayed relative to that of the step-saturation (concentration increase) curve, which, in turn, falls later than the tail of the integrated-pulse curve. The discrepancy between the elution and pulse data amounts to a factor of 4 on the time scale of their graphs at c/c_0 of 0.01. Inasmuch as they obtain identical results at different concentration levels, Schiesser and Lapidus conclude that nonlinear effects are absent.

In a series of step tracer experiments in trickle-phase beds under many different conditions Hofmann (*1*) finds no difference between elution and saturation; he reports no pulse measurements. Since the experimental results of Schiesser and Lapidus raise doubts about the interpretation of residence time data, a repetition of their experiment seems worthwhile.

Although the primary objective of this work is to test the equivalence of pulse and step residence time measurements, an important related question concerns the relation between the mean residence time and the total holdup in experiments with the air-water system. It is customary to assume that

$$\bar{t} = \frac{hV}{Q} \qquad (1)$$

With this relation, Schiesser and Lapidus calculate the "apparent percentage of internal voids filled with liquid" as the ratio of h_i calculated from $\bar{t}$ to the value of h_i for all internal voids filled. In this way they find the apparent percentage filled to be 78.8% from elution data, 46.2% from saturation, and 27.8% from the pulse run.

Superficially, one might expect the mean residence time to reflect only that portion of the internal holdup which is in particles contacted by flowing liquid. But if the liquid is sufficiently nonvolatile to undergo capillary condensation in the pores, liquid will fill and remain in the interior of all particles. Since all of the particle interiors are interconnected and thus accessible to the external streams, the holdup calculated from the mean residence time should include all of the internal void volume, and the mean residence time should be independent of the method of measurement. Of course, the column must be operated long

Table 1. Properties of Catalyst

Nominal diameter	1/16 in.
Nominal length	1/4 in.
Pore volume	0.63 cc./g.
Internal void fraction	0.384 cc./cc. bed
Residual holdup	0.053 cc. H_2O/cc. bed
External void fraction (dry)	0.422 cc./cc. bed
Bulk density	0.61 g./cc. bed

Table 2. Experimental Results

Run no.	75	74	82	73A	83
Type of input	Pulse	Step elution	Step saturation	Pulse	Step elution
Superficial velocity					
Water, ft./hr.	38.2	39.5	38.2	2.28	2.41
Air, ft./sec.	1.52	1.52	1.52	1.52	1.52
Liquid distribution*	0.12	0.18	0.13	0.23	0.23
Mean residence time, min.	4.2	3.8	4.1	60	60
Holdup†					
Internal	0.384	0.384	0.384	0.384	0.384
Residual	0.053	0.053	0.053	0.053	0.053
Free-draining	0.121	0.118	0.118	0.042	0.054
Total	0.558	0.555	0.555	0.479	0.491
From $\bar{t}$	0.685	0.610	0.651	0.581	0.574
Difference	0.127	0.055	0.096	0.102	0.083

* Liquid distribution refers to standard deviation among flows from five equal-area collectors, divided by mean flow.

† Internal holdup refers to internal void volume/bed volume.
Free-draining holdup refers to liquid collected during 10-min. draining period after shutdown.
Residual holdup refers to liquid remaining outside particles after draining.

Mr. Rothfeld is with Shell Oil Company, Houston Research Laboratory, Deer Park, Texas.

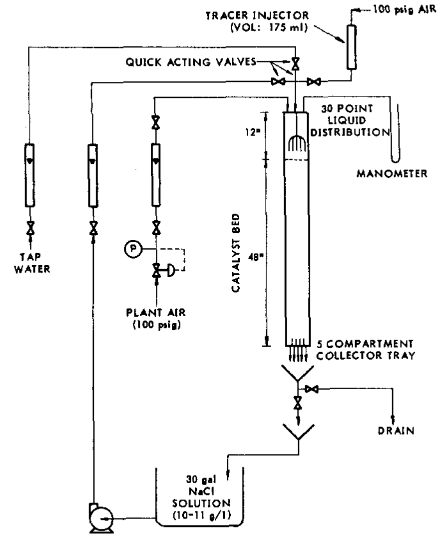

Fig. 1. Schematic diagram of experimental apparatus.

enough to fill the particles before the residence time run is started.

EXPERIMENTAL APPARATUS AND TECHNIQUE

The experimental equipment and procedure are essentially the same as those of Schiesser and Lapidus with two important exceptions. Instead of the 1/4-in. porous alumina spheres used by Schiesser and Lapidus, the present experiments employ a commercial alumina-based extruded catalyst, the properties of which are given in Table 1. The bed is packed dry and is 4 in. in diam. and 4 ft. long in agreement with Schiesser and Lapidus. Liquid superficial velocity is about 39 and 2.3 ft./hr.; the data of Schiesser and Lapidus are at 74.5 ft./hr.

Figure 1 shows the column and attached equipment for the metering of air and tap water, the injection of a pulse of tracer solution, and the recirculation of a tracer solution. The incoming liquid was distributed to the top of the bed through a 30-point tubular distributor. The outlet liquid was removed through a compartmented collector tray of five compartments which could be sampled separately or collectively.

Prior to each run, liquid flow of the initial concentration level was maintained through the bed for several hours to insure that the liquid in the pores is the same as the feed liquid. Liquid and air flow rates were then set and allowed to line out for 20 to 30 min. before admitting the tracer at zero time.

For the pulse experiments an injection of 100 ml. of sodium chloride tracer solution (ca. 270 g./l.) was made beginning at zero time. Duration of the injection was 2 to 10 sec. depending on the flow rate used. During the injection period the water flow was shut off. Grab samples of the effluent liquid were taken over the duration of the run. The inlet liquid was sampled periodically to follow any change in its concentration. The run was continued until the outlet concentration approximated the inlet concentration. Equivalent salt con-

(*Continued on page 855*)

INFORMATION RETRIEVAL[*]

Mass transfer and contactor efficiency in a stirred liquid-liquid reactor, Engel, A. J., and O. A. Hougen, **A.I.Ch.E. Journal, 9,** No. 6, p. 724 (November, 1963).

Key Words: Mixing-9, Agitation-9, Stirring-9, Reactor-10, Reactor Design-9, Mass Transfer-9, Liquid-Liquid Systems-8, Contactor Efficiency-7, Particle Size-8, Kinetics-7, Catalysis-6, Correlations-8, Isoamyl Acetate-1, Water-1, Acetic Acid-2, Isoamyl Alcohol-2, Ion Exchange Resin-4, Aqueous Solution-5.

Abstract: A correlation of mass transfer data in a stirred batch reactor has been made for the hydrolysis of liquid isoamyl acetate dispersed in a large volume of excess water, where the reaction was catalyzed by acidic cation exchange-resin particles kept in suspension by stirring. It was found that the operating parameters affected the overall reaction rate only when the size of catalyst particles was less than about 100 μ. This reaction system may prove of general value in establishing the contactor efficiency of stirred reactors in liquid-liquid systems catalyzed by solids.

A theoretical and experimental investigation of the effects of horizontal barriers in thermal diffusion columns, Fleming, J. R., and J. E. Powers, **A.I.Ch.E. Journal 9,** No. 6, p. 730 (November, 1963).

Key Words: Ethanol-1, Ethyl Alcohol-1, Water-1, Mixtures-1, Barriers-6, Temperature-6, Concentration-7, Separation-8, Purification-8, Theory-9, Experiment-9, Column-10, Thermogravitational-10, Thermal Diffusion-10, Transient-10, Steady State-10, Batch-10, Flow-10, Throughput-10, Model-10, Transform-10, Binary-, Horizontal-, Number of-, Diameter-, Difference of -, Mathematical-, Laplace-.

Abstract: The influence of horizontal barriers on the separation of binary mixtures in thermogravitational thermal diffusion columns was investigated theoretically and experimentally. A mathematical model was developed with the assumption that the barriers divide the column into a number of smaller columns with interconnecting end feeds and also slightly reduce the thermogravitational flow. The mathematical results are in agreement with experimental data obtained under transient and steady state batch as well as steady state flow operating conditions. Parameters varied (with an ethanol-water system) were number of barriers (0 to 50), temperature difference (2 values), and barrier diameter (2 values).

Maximum and minimum bounds on freezing-melting rates with time-dependent boundary conditions, Hamill, T. D., and S. G. Bankoff, **A.I.Ch.E. Journal, 9,** No. 6, p. 741 (November, 1963).

Key Words: Melting-9, Freezing-9, Heat Transfer-9, Wall Heat Flux-6, Wall Temperature-6, Melt Thickness-7, Thickness of Solidified Material-7, Integral Equation-10, Similarity Transformation-10.

Abstract: The problem considered is the freezing or melting of a semi-infinite slab initially at the phase transition temperature subjected to an arbitrary, although monotonic, wall temperature or wall heat flux. Upper and lower bounds are established after the differential equation and associated boundary conditions are converted into integral equation form. Comparisons are made with several exact solutions.

Nuclear radiation-induced cracking of n-hexadecane, Guernsey, Edwin O., Henry Shaw, and William E. Smith, **A.I.Ch.E. Journal, 9,** No. 6, p. 744 (November, 1963).

Key Words: n-hexadecane-1, Irradiation Products-2, Nuclear Radiation-4, Temperature-6, Radiation Dose-6, Dose Rate-6, Radiation Yields-7, Product Distribution-7, Radiation-Induced Cracking-8, Product Analyses-8, Gamma Heating-9, Radiation Process Design-9, Beam Tube Reaction Vessel-10.

Abstract: N-hexadecane has been irradiated with mixed radiation from a nuclear reactor. Radiation conversions in vapor phase exposures, expressed as molecules of n-hexadecane converted per 100 ev. of energy absorbed (G values) were 200 to 1200 at 750°F. Products were similar to those obtained in thermal cracking. However there were significant increases in hydrogen yields and reductions in yields of very light hydrocarbons.

In liquid phase irradiations at 750°F. conversions of n-hexadecane up to 15 wt. % were obtained. Nearly half of this conversion was attributed to the direct utilization of radiation. G values were 30 to 60. The total product distribution, resulting from both radiation and thermal conversions, could be changed by variation of cracking temperature and/or radiation dose.

(*Continued on page 855*)

---

[*] For details on the use of these key words and the A.I.Ch.E. Information Retrieval Program, see **Chem. Eng. Progr.,** 57, No. 5, p. 55 (May, 1961), No. 6, p. 73 (June, 1961); **58,** No. 7, p. 9 (July, 1962).

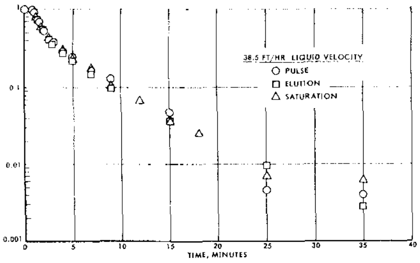

Fig. 2. Experimental residence time data.

centration of the tap water varied from 0.02 to 0.08 g./l.

In the step elution experiments a sodium chloride solution (10 to 11 g./l) was recirculated for the initial tracer level. At zero time the liquid flow was switched to once-through tap water. Grab samples of the inlet and outlet streams were taken as in the pulse runs.

In the step saturation experiments the initial tracer level was established with flowing tap water. At zero time the flow was switched to the 10 to 11 g./l. sodium chloride solution. Samples were obtained as in the other runs.

The sodium chloride concentration of the samples was determined from conductance measurements on a conductivity bridge with conductivity cells of 1.0 and 10. cell constant to cover the range 0.02 to 12 g./l.

RESULTS

The residence time data are shown in Figures 2 and 3 where the ordinates are c/c_0 for step elution, $1 - c/c_0$ for step saturation, and

$$1 - \frac{\int_0^t c\,dt}{\int_0^\infty c\,dt}$$

for the integrated pulse. For each run, the data obtained by the various methods are essentially the same. Mean residence times (Table 2) for each run also agree.

The total holdup calculated from the mean residence time consistently exceeds that obtained by adding the internal, residual, and free-draining holdups. The discrepancy is independent of the method of residence time measurement and the flow rate, and the mean difference between the fractional holdups is 0.09.

DISCUSSION

The data not only confirm the equivalence of pulse and step residence

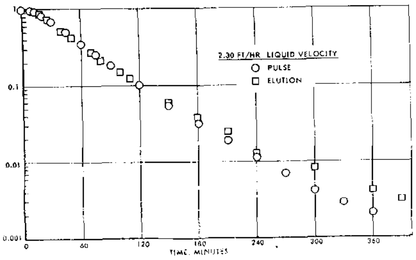

Fig. 3. Experimental residence time data.

INFORMATION RETRIEVAL

(*Continued from page 853*)

Direct analogy between mass and heat transfer to beds of spheres, Sen Gupta, Ashis, and George Thodos, **A.I.Ch.E. Journal, 9,** No. 6, p. 751 (November, 1963).

Key Words: Mass Transfer-9, Heat Transfer-9, Analogy-9, Packed Beds-5, Distended Beds-5, Gases-5, Drying-8, Mass Transfer Coefficients-7, Heat Transfer Coefficients-7, Void Fraction-10, Water Evaporation-9, Adiabatic Process-10, Celite Catalyst Carriers-4, Spheres-5.

Abstract: A one-to-one correspondence between mass and heat transfer in the flow of gases through packed and distended beds of spheres has been verified experimentally. This was made possible by designing the experiment and the experimental unit to operate under strictly convective conditions by eliminating radiative and conductive contributions, by maintaining low mass transfer rates, and by using the appropriate driving potential across the gas film, Δp^*. The resulting generalized relationship for both mass and heat transfer can be expressed in terms of ϵ, the void fraction of the bed, and j, the transfer factor, as follows: $\epsilon j = 2.06/N_{Re}^{0.575}$

A selectivity factor in vapor-phase hydrocarbon oxidation catalysis, Callahan, J. L., and R. K. Grasselli, **A.I.Ch.E. Journal, 9,** No. 6, p. 755 (November, 1963).

Key Words: A. Catalysis-8, Heterogeneous-8, Oxidation-8, 9, Hydrocarbon-1, 6, 8, Selectivity-9, Theory-9, Surface Topology-7, Monte Carlo Statistics-10, Catalytic Sites-7, 9, Surface Coverage-7, Oxidation State-6, Metal-Oxides-4, 6, 7, 8, Bond-Energy (Inorg.)-7, 9. B. Copper Oxide-4, 7, Silicon Carbide-4, Hydrocarbons-1, 6, Propylene-1, 6, Oxygen-1, 6, Hydrogen-1, 6, Carbon Monoxide-2, 3, Carbon Dioxide-2, 3, Water-2, 3, Acrolein-2, Helium-5, Gas Chromatography-10, Slug Microreactor-10.

Abstract: A novel hypothesis capable of explaining selectivity in vapor phase heterogeneous oxidation catalysis and supporting experimental data are described. Product selectivity for the oxidation of propylene is related to the degree of coverage and distribution of oxygen atoms of the catalyst surface. The randomness of gaseous reactant molecular collisions with the catalyst surface permits the construction of surface models with Monte Carlo methods used for various degrees of coverage. By assigning molecular stoichiometry to permitted reactions, the reaction selectivity is computed for each model. Differences in catalyst and process requirements between processes operating in overall oxidizing or reducing atmospheres are discussed.

Unsteady state absorption of carbon dioxide by dilute sodium hydroxide solutions, Rehm T. R., A. J. Moll, and A. L. Babb, **A.I.Ch.E. Journal, 9,** No. 6, p. 760 (November, 1963).

Key Words: A. Gas absorption-8, Carbon Dioxide-1, Sodium Hydroxide-1, Sodium Bicarbonate-2, Water-5, Contact Time-6, Absorption Rate-7, Laminar Jet-10. B. Partial Differential Equations-1, Contact Time-6, Concentrations-7, Absorption Rate-7, Gas Absorption-8, Mathematical Model-9, IBM-709-10, Numerical Solution-10.

Abstract: Carbon dioxide is absorbed into laminar jets of sodium hydroxide solutions. Rate equations based on a two-reaction second-order model are solved numerically. Agreement of 5% is obtained between numerical and experimental results.

Measurements of turbulent flow development in tubes and annuli with square or rounded entrances, Olson, R. M., and E. M. Sparrow, **A.I.Ch.E. Journal, 9,** No. 6, p. 766 (November, 1963).

Key Words: Fluid Flow-8, Pressure Drop-7, Annuli-5, Tube-5, Entrance Length-7, Friction Factor-7, Laminar Turbulent Transition-8, Reynolds Number-6, Inlet Shape-6, Measurements-10.

Abstract: Pressures were measured in the entrance and fully developed region of annuli and a tube with square and rounded entrances using water in the Reynolds number range from 16,000 to 70,000. Entrance lengths for the annuli were about 20 to 25 hydraulic diameters based on pressure gradient. This agrees with results for tubes and parallel-plate channels, but differs from prior results for annuli. Separation and high losses for the square entrances and boundary-layer transition and low losses for the rounded entrances were observed. Fully developed friction factors were calculated and compared with theory.

(*Continued on page 860*)

time measurements but also show that the mean residence time for sodium chloride tracer is about 9% greater than that for completely filled internal voids. These high mean residence times suggest the possibility of adsorption of tracer on the surface of the catalyst. Adsorption raises the apparent internal holdup by a volume of solution equivalent to the mass of tracer adsorbed at equilibrium. Thus, if the adsorption is small enough to be described by a linear isotherm

$$m_a = K_a c$$

The apparent holdup due to adsorption, h_a, is

$$h_a = \frac{m_a \rho_B}{c} = \rho_B K_a$$

With $h_a = 0.09$ and $\rho_B = 0.61$ g./cc.

$$K_a = 0.15 \frac{\text{mg./g.}}{\text{g./l.}}$$

In these experiments, c is about 10 g./l. and m_a is about 1.5 mg./g. This amounts to less than 1/20 of a monolayer if we assume that the surface area is 300 sq. meter/g. and the surface concentration of a monolayer is at least one molecule per 100Å.^{2} Hence, the assumption of a linear isotherm is probably valid.

In order to measure the adsorption equilibrium constant independently, 100-g. samples of dried catalyst were immersed in 250 ml. of about 10 g./l. sodium chloride solution in a sealed bottle and allowed to stand for several days without agitation. Samples of the solution were then analyzed by electrical conductivity and by Mohr's method for chloride. Water slowly leaches salts out of the catalysts; therefore, additional 100-g. samples were immersed in 250 ml. of distilled water which was analyzed by the same methods after an equal time period. Equilibrium is approached slowly because of the lack of agitation. The results of these tests are

Duration of test, days	4	12	25
Mass adsorbed, mg./g.	0.7	0.95	0.8
Final sodium chloride conc. g./l.	11.50	10.10	11.45
Adsorption constant, K_a	0.061	0.094	0.070
Apparent holdup, h_a	0.037	0.057	0.043

These data indicate that equilibrium is probably reached in less than 4 days.

From the results of the three tests, the mean value of the apparent holdup due to adsorption is 0.045. Since the holdup calculated from the mean residence time exceeds the measured total

(*Continued on page 859*)

(*Continued from page 856*)

holdup by 0.09, an additional holdup of 0.045 remains unaccounted for. Perhaps additional terms should be added to the right-hand side of Equation (1). van der Laan (5) shows theoretically that terms dependent on the Peclet number may appear for certain boundary conditions in models of single-phase flow through packed beds.

In any case, the above experiments show that the residence time distribution does not depend on the type of input, and that the holdup calculated from the mean residence time is at least as great as the measured total holdup which is calculated by assuming that all internal voids are filled with liquid.

CONCLUSIONS

In trickle-phase flow under the conditions of the present experiment, residence time distributions measured by pulse, step saturation, and step elution are essentially the same. For all runs, the total holdup calculated from the mean residence time exceeds the sum of the internal, residual, and free-draining holdups by about 0.09. About half of the excess holdup can be attributed to adsorption of sodium chloride tracer. These results substantiate the validity of the pulse technique for measurement of residence time distributions in trickle phase beds.

NOTATION

c = concentration in the liquid phase
c_1 = inlet tracer concentration before step change
c_2 = inlet tracer concentration after step change
c_0 = concentration of step change corrected for background
h = total fractional holdup = $h_i + h_o$
h_a = holdup due to adsorption
h_i = holdup due to pores in particle interior
h_o = holdup external to particles (residual plus free draining)
K_a = adsorption constant
m_a = mass of tracer absorbed per unit mass of catalyst
Q = volumetric liquid flow rate
t = time after pulse injection or step change
$\bar{t}$ = mean residence time
V = volume of bed
ρ_B = mass of catalyst per unit volume of bed

LITERATURE CITED

1. Hofmann, H. P., Ph.D. thesis, Darmstadt Tech. Hochschule (1954).
2. Lapidus, Leon, *Ind. Eng. Chem.*, 49, 1000 (1957).
3. Schiesser, W. E., and Leon Lapidus, *A.I.Ch.E. Journal*, 7, 163 (1961).
4. van der Laan, E. T., *Chem. Eng. Sci.*, 7, 187 (1958)
5. Wylie, C. R., Jr., "Advanced Engineering Mathematics," p. 196, McGraw-Hill, New York (1951).