x_i = mole fraction of *i*th component

x_l = mole fraction of low-boiling component

π = total pressure, lb./sq. in. abs.

ρ_c = critical molar density of mixture, g.-moles/cc.

ρ'_c = pseudocritical molar density of mixture, g.-moles/cc.

ρ_{cm} = critical molar density of pure methane, g.-moles/cc.

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Interrelation of Packing and Mixed Phase Flow Parameters with Liquid Residence Time Distribution

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Brine-air and kerosene-hydrogen systems were used for the mixed phase tests. No specific gas phase effects were detected. The measured variability, encompassing all three flow mechanisms, correlated well with particle Reynolds number for each system and decreased with increasing flow rate. However the variability component resulting solely from bulk liquid flow through the main bed channels was found to be relatively constant over a wide range of Reynolds number and independent of whether the bed was uniformly packed or contained large packing faults. The significance of these results to liquid-solids contacting efficiency is discussed .

The majority of previous publications which considered flow characteristics of packed beds have dealt with single-phase gas or liquid flow. In addition the bulk of these publications were based on theoretical models which used one of three approaches: piston flow, eddy diffusion, or void cell mixing (*1, 2, 3, 5, 6, 8*).

The use of tracer techniques is becoming increasingly popular for obtaining fluid dispersion and residence time distribution data in packed bed flow via transient response methods. The procedure generally involves the predetermined addition of a tracer stream to the entering liquid and time

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monitoring the tracer concentration in the bed effluent. Salt or dye tracers have been used (*4, 7, 10*) in the past with conductivity, colorimetric, or titrametric techniques for measuring the tracer outlet concentration. For example Schiesser and Lapidus (*10*) obtained flow distribution and residence time distribution data for water trickling through a packed bed and were able to separate the contributions of diffusion into the porous packing and flow in the interparticle voids by an analysis of transient response curves. The greater the sensitivity of the technique for measuring the tracer outlet concentration the better the chance to detect the flow mechanisms involved.

In the present investigation a highly sensitive radioactive tracer technique was used to obtain liquid residence time distributions for downflow operations primarily in 2-in. and 1-ft. diam. packed columns. Both gravity liquid and concurrent-cogravity liquid-gas flow were studied with porous and nonporous 1/8- and 1/16-in. cylindrical packings. Brine-air and kerosene-hydrogen systems were used for the mixed-phase tests. Pulse injection of appropriate radioactive tracers in the liquid stream was used to obtain the transient response of each system. The data were interpreted in terms of conventional dimensionless groups and statistical parameters of the residence time distribution, such as variability. Flow distribution data were obtained to supplement the residence time distribution measurements in the 1-ft. diam. column.

EXPERIMENTAL TECHNIQUES

In the small diameter (¾- and 2-in. I.D.) glass columns injection of a short duration pulse of tracer was accomplished with the aid of a hypodermic syringe placed so as to discharge into the entering liquid stream. In the larger 1- and 8-ft. diam. columns tracer injection was accomplished by temporarily diverting the main liquid flow into a bypass line which contained the tracer. In this case the entire operation was controlled from a panelboard. Solenoid valves were employed to control charging of the tracer from a reservoir as well as dispensing of the tracer into the main liquid stream. Impulse rather than step type of inputs were chosen because preliminary experiments had shown considerable difficulty in maintaining constant tracer concentration levels in the liquid. In addition the step function technique would have required unreasonably large amounts of expensive radioactive tracer material to provide the desired sensitivity.

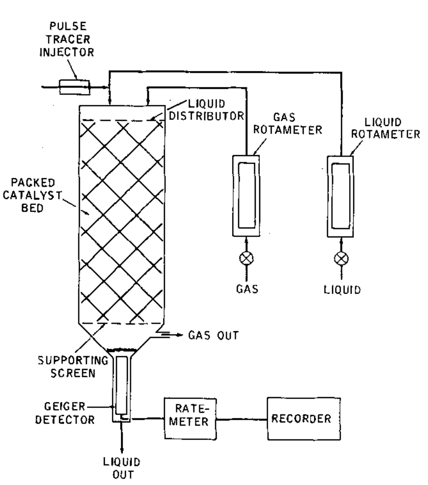

Fig. 1. Schematic diagram of experimental equipment.

Gas was disengaged directly below the packed section of the column and vented to the atmosphere. The liquid then flowed past a Geiger tube mounted in a vertical cylindrical section. Signals from the Geiger tube were amplified and sent to a ratemeter and then to a potentiometric chart recorder or a digital counter recorder. A schematic diagram of the experimental setup is shown in Figure 1.

The flow distribution tests were conducted with a forty-nine hole liquid distributor plate at the top of the 1-ft. column. Liquid was collected at the bottom of the packed section with a specially constructed member containing forty-nine equal area (2.3 sq.in.) cells. The packing material was charged to the columns with the aid of mechanical vibration and produced dense, uniformly packed beds having reproducible void volumes for a given packing size.

The systems that were specifically studied are summarized in Table 1. The majority of the experiments were carried out at ambient temperatures in the 2-in. I.D. × 2-ft. and 1-ft. I.D. × 11-ft. columns. However a few runs were made in a ¾-in. I.D. × 1-ft. unit to test the effect of column diameter. Both 1/16 and 1/8-in. diam. cylindrical porous and nonporous pellets varying in length from ⅛ to ¼ in. were used as packing. Liquid loading was studied over a wide range, 60 to 10,000 lb./hr. sq.ft., while gas rates were varied from 0 to 0.1 ft./sec. for the kerosene/hydrogen and calcium chloride brine/air systems.

Tracers

The basic advantage of a radioactive tracer over other tracer materials such as salts or dyes is the ease with which peak to background ratios in the range of 100:1 to 5,000:1 can be obtained. These high ratios allow a much more sensitive analysis of diffusive flow effects which occur in liquid-gas packed bed systems.

The radioactive tracer selected for residence time distribution studies must satisfy the following criteria. First it must be safe to handle and easy to dispose of. Therefore it must have a reasonably short half life and emission type and energy that make it suitable for laboratory use. Second it must be compatible with the liquid phase. Finally it should not be preferentially adsorbed on the surface of the packing. The following tracers were chosen for the present study based on the above criteria: carbon 12 in tagged octadecane and phosphorous 32 in tricresyl phosphate for the hydrocarbon systems, and rubidium-86 in rubidium chloride for the calcium chloride brine systems. The calcium chloride brine was chosen over pure water because rubidium plus absorbs on the packing surface when used in pure water. However addition of 25 wt. % calcuim chloride to the water produces a system where the concentration of rubidium plus is so small relative to calcium plus plus that little rubidium plus adsorption takes place. The same technique for minimizing tracer adsorption was used with the kerosene-tricresyl phosphate systems. Here the kerosene was spiked with tricresyl phosphate.

THEORY

The pulse tests directly provided a plot of effluent tracer concentration vs. time. A large number of statistical parameters can be calculated based on the moments of the distribution. However small experimental errors limit the usefulness of statistical parameters based on all moments above the second moment of the distribution.

If the assumption is made that the radioactive tracer behaved just like any other liquid molecule while in the packed bed, then the distribution also represents the liquid residence time distribution. The average liquid residence time can be calculated from suitable integration of the tracer effluent concentration vs. time, namely

$$\theta_{avg} = \frac{\int_{\theta = 0}^{\theta = \infty} \theta C d\theta}{\int_{\theta = 0}^{\theta = \infty} C d\theta} \qquad (1)$$

The per cent liquid holdup can be calculated from the average liquid residence time from

$$\%\ \text{liquid holdup} = \frac{\theta_{avg} \times Q_L}{V_T} \times 100 \qquad (2)$$

Another useful parameter of the distribution is defined as

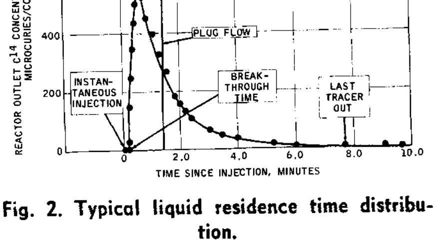

Fig. 2. Typical liquid residence time distribution.

Table 1. Summary of Residence Time Distribution Tests

Unit diam. × ht.	Packing	Liq.-gas system	Tracer	Liq. loading (lb./hr. sq. ft.)
3/4 in. × 1 ft.	1/16-in. porous and nonporous	CaCl_2 Brine/Air and Kerosene + TCP/H_2 Kerosene/H_2	Rb^{*}Cl TCP^{*} $\text{H}_{38}\text{C}_{18}^{*}$	100 to 1,200 75 to 750 60 to 120
2 in. × 1 ft. and 2 ft.	1/16-, 1/8-in. porous and nonporous	CaCl_2 Brine/Air† and Kerosene + TCP/H_2†	Rb^{*}Cl TCP^{*}	200 to 10,000 125 to 4,000
1 ft. × 4 ft. and 11 ft.	1/16-, 1/8-in. porous	CaCl_2 Brine/Air	Rb^{*}Cl	300 to 2,400
8 ft. × 13 ft.	1/16-, 1/8-in. porous	Kerosene/H_2	$\text{H}_{38}\text{C}_{18}^{*}$	400 to 900

† Single liquid phase tests also conducted.

$$1\%\ \text{breakthrough} = \frac{\text{time since injection for } 1\% \text{ of tracer to leave bed}}{\text{average liquid residence time}} \quad (3)$$

This will always be less than unity, but the closer it approaches unity the closer is the approach to plug flow.

The variability of the liquid residence time distribution is a particularly useful statistical parameter for characterizing the distribution of residence times. Variability is a measure of the nonuniformity or spread in residence time distribution and is defined as the standard deviation of residence times divided by the mean or average residence time. Thus

$$V = \frac{(\sigma^2)^{1/2}}{\theta_{avg}} \frac{\left[\left(\int_0^\infty \theta^2 C d\theta \Big/ \int_0^\infty C d\theta\right) - \left(\int_0^\infty \theta C d\theta \Big/ \int_0^\infty C d\theta\right)^2\right]^{1/2}}{\int_0^\infty \theta C d\theta \Big/ \int_0^\infty C d\theta} \quad (4)$$

In an idealized system zero variability would represent plug type of flow with no backmixing, while a variability of 1.0 would represent perfectly mixed flow. Figure 2 shows a typical liquid residence time distribution as well as one for plug type of flow.

Ideally the liquid residence time distribution should reflect disturbances of the impulse function which occur inside the packed bed itself. However physical limitations require the inclusion of extraneous lag volumes between the injection point at the top of the bed and the sampling point. Thus corrections must be applied to the data to account for the increased liquid residence time and increased variation in residence times from external equipment. The average residence time in the lag volumes must be subtracted from the overall measured average residence time to give the true value. This was done by determining the residence time distribution of the equipment less the packed bed before a series of runs on a given packed system were made. The σ^2 of the residence time distribution of the lag volume was then subtracted from the overall σ^2 in Equation (4) to give the variability of the liquid residence time distribution in the packed section of the bed alone. Of course it is preferable that all of the lag volumes be small relative to the bed volume. Therefore every effort to minimize lag effects was made in designing the experimental apparatus. The effect of the lag volume on variability was found to be small. For example for a run at 100 lb./hr. sq. ft. in the ¾ in. unit the θ for the lag volume was only 2 min., compared with 14 min. for the system including the packed bed. The correction for σ^2 was even smaller. For the lag volume σ^2 was 0.25, while for the entire packed bed system σ^2 was 21.16. Therefore there was negligible difference between the overall σ^2 (21.16) and the bed σ^2 (20.91).

RESULTS AND DISCUSSION

Effect of Bed Diameter

Since many of the residence time distribution tests were conducted in the 2 in. diam. unit, the question of column diameter affecting the liquid distributions obtained is of considerable importance. Therefore the variability obtained for the calcium chloride brine-air system flowing over ⅛-in. porous pellets was compared at equal liquid loadings for the ¾-in., 2-in. and 1-ft. diam. units. The variability was the same for each diameter unit at equivalent conditions, and it was concluded that no diameter effect existed.

The common design criterion for bed to particle diameter ratio has been 8:1 (*11*), although Schiesser and Lapidus (*10*) have detected radial variations in flow rates with ratios as high as 16:1. With the exception of the tests in the ¾-in. diam. unit all the data obtained in the present study were with bed/particle diameter ratios of 16 or greater.

Contributions of Flow Mechanisms to Variability

In flow through a packed bed of porous particles the measured variability includes contributions from both liquid flowing in the void channels between the particles and mass diffusion of tracer in the pores (*10*). It is important to distinguish between these hydrodynamic and diffusion effects

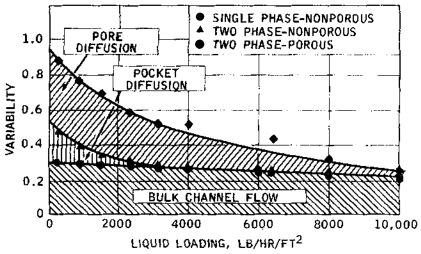

Fig. 3. Variability is composed of three additive factors.

Table 2. Experimentally Determined Tracer Diffusivities Compare Well with Literature Values

Tracer	Liquid	Conditions	Mol. diffusivity, sq. ft./hr. Literature	Experimental†
Rb^{*}Cl	CaCl_2	200 lb./hr. sq. ft. 1 atm., 70°F.	2×10^{-5}	2×10^{-5}
$\text{H}_{38}\text{C}_{18}^{*}$	Kerosene	400 lb./hr. sq. ft. 28 atm., 600°F.	5×10^{-5}	6×10^{-5}
TCP^{*}	Kerosene	125 lb./hr. sq. ft. 1 atm., 70°C.	5×10^{-6}	6×10^{-6}

† Values based on liquid velocities close to zero.

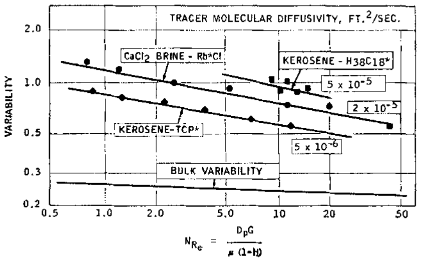

Fig. 4. Measured variability depends on tracer diffusivity.

when relating the significance of the tracer tests to gross liquid-solids contacting, namely the extent to which all the catalyst is covered with a moving liquid film.

Therefore tests were made in the 2-in. diam. column by means of the calcium chloride brine-air system to define the contribution of the various flow mechanisms to measured variability over a wide range of liquid loadings. These tests employed 2 ft. of 1/16- and 1/8-in. porous pellets varying in length from ⅛ to ¼ in. and nonporous pellets of the same dimensions. The variability due to bulk liquid flow was established by operating with nonporous packing under single liquid-phase flow utilizing a flooded bed where all the interparticle voids are filled with liquid. Tests with two-phase brine-air flow then established the effect of cocurrent gas flow on the liquid flow pattern. Finally two-phase flow with porous packing defined the effects of mass diffusion on variability. The two-phase tests were made at a constant gas flow rate of 0.1 ft./sec. to aid in varying the liquid holdup in the bed.

Measured variability was found to consist of three components for a mixed phase system with porous packings as shown in Figure 3. These components were:

1. Variability due to bulk flow through the bed channels which is constant at a baseline value of 0.20 to 0.25 over the entire 100 to 10,000 lb./hr.sq.ft. range of liquid loadings studied.
2. Variability due to diffusion of material in and out of stagnant pools of liquid in the bed. At high liquid rates, over 3,000 lbs./hr.sq.ft., these pools tend to disappear because of turbulence in the bed.
3. Variability due to pore diffusion which is large at low liquid rates, but whose effect is masked by the large bulk flow as liquid loading is increased. Variability from pore diffusion completely overrides variability from bulk liquid flow at low liquid loadings. Hence measured variabilities greater than 1.0, the limiting case for hydrodynamic flow, were observed.

Based on the above concepts measured variability per se should not be directly related to liquid-solids contacting because of the influences of diffusion of liquid from pores and stagnant liquid pockets, particularly at low liquid loadings. Instead gross liquid-solids contacting should be more closely allied with bulk liquid flow variability. Before bulk flow variability for conventional packed beds of porous pellets can be determined, methods for handling diffusive contributions to overall measured variability must be developed.

TABLE 3. VARIABILITY DOES NOT ACCOUNT FOR DIFFERENCES IN LIQUID DISTRIBUTION

Bed no.	I	II
Bed diam., ft.	1	
Bed ht., ft.	4	
Packing	1/16-in. porous	
Liquid loading, lb./hr. sq. ft. (brine)	600	
Gas velocity, ft./sec. (air)	0.2	
Octant flow/avg. bed flow		
Octant #1	1.69	0.92
#2	1.59	0.80
#3	0.93	0.95
#4	0.70	1.04
#5	0.78	1.12
#6	0.56	1.01
#7	0.62	1.06
#8	1.14	1.09
Variability		
Measured	0.83	0.82
Bulk liquid flow	0.30	0.28

Effect of Tracer Diffusivity

Variabilities determined by each of the three tracer systems employed were compared over a wide range of liquid flow rates to evaluate the dependency of measured variability on tracer molecular diffusivity. Measured variabilities were correlated with particle Reynolds number to allow unification of results from tests having different bed and liquid physical properties.

Results of this comparison showed that all of the variabilities obtained from a particular tracer system correlated well along a single line. Measured variability decreased as particle Reynolds number increased (Figure 4). At a given Reynolds number the measured variability decreased as tracer molecular diffusivity decreased. The case of a system with zero diffusivity is analogous to a single-phase nonporous bed where no contribution of diffusion to variability is made. Therefore in the limit, with zero diffusivity, measured variability is synonymous with bulk flow variability.

Values of molecular diffusivity for each tracer system used were determined from the tracer test data by the use of the Peclet number relationship between molecular diffusivity and the variability (*12*). After removing the contribution of the bulk flow variability from the measured values, at low liquid loadings, leaving only variability caused by diffusional transfer one may calculate the molecular diffusivity from

$$E = \frac{D_p v V_B^2}{(1-H)} \tag{5}$$

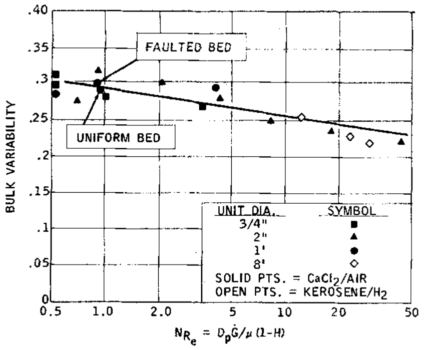

Fig. 5. Bulk liquid variability is insensitive to changes in variables.

These experimental values were found to agree well with molecular diffusivities calculated independently from equations available in the literature which relate diffusivity with other physical properties (*11*) as shown in Table 2. These results show that the use of radioactive tracers is a powerful technique for experimentally determining molecular diffusivities of liquids.

Significance of Residence Time Distribution Parameters to Liquid-Solids Contacting

The aim of a well-designed packed bed reactor is to attain the desired chemical reaction with a minimum of side reaction and without excess amounts of catalyst. In both single-phase and mixed-phase flow packed reactors the efficient use of catalyst depends on maximizing the per cent of catalyst in contact with a moving liquid film. The bulk liquid flow variability therefore should have more significance to liquid-solids contacting than the measured variability which is clouded by diffusional effects.

It may be reasoned that low values of the bulk liquid flow variability should indicate uniform liquid flow velocity with good probability of liquid-solids contacting. This is because high bulk liquid variabilities mean there were liquid streams with either or both extremely short or extremely long residence times in the reactor. Thus material that races through the reactor at several times the average velocity probably does so in a rivulet that hardly contacts any catalyst. The material that stayed in the reactor for several times the average residence time probably stays in a stagnant pool of liquid for a large proportion of that time and would have to depend on molecular diffusion to reach the catalyst surface.

A comparison of bulk liquid flow variabilities for a wide variety of bed

Table 4. Statistical Residence Time Distribution Parameters Do Not Vary Between Well Packed and Faulted Beds

Liquid loading, lb./hr. sq. ft.	Single phase Faulted Bulk var.	Single phase Faulted 1% break.	Single phase Well packed Bulk var.	Single phase Well packed 1% break.	Mixed phase Faulted Bulk var.	Mixed phase Faulted 1% break.	Mixed phase Well packed Bulk var.	Mixed phase Well packed 1% break.
400	0.19	0.75	0.20	0.75	0.21	0.78	0.23	0.79
4,800	0.16	0.82	0.19	0.78	0.19	0.80	0.20	0.80
10,000	0.15	0.79	0.16	0.82	0.16	0.78	0.18	0.78

Data on 2 in. × 24 in. bed of nonporous 1/16 in. pellets with 25% $CaCl_2$ brine feed.

and operating conditions was made after diffusive effects were subtracted out of the measured variabilities. As shown in Figure 5 no significant variation was found in bulk liquid flow variability over the entire range of Reynolds numbers for all the systems studied. These data illustrate the fact that bulk liquid flow variability is relatively insensitive to large changes in the contacting variables. Therefore the rather large changes of measured variability as a function of Reynolds number and system type noted in Figure 4 must be a result of diffusional effects.

In other residence time distribution studies Lapidus (7) concluded that liquid-solids contacting did not change appreciably with flow rate. If bulk liquid flow variability per se is a measure of liquid-solids contacting, the present results lead to the same conclusion. Further experiments involving simultaneous residence time distribution and flow distribution measurements were made to elucidate this point.

Tests made on 4-ft. beds of 1/16-in. porous pellets in the 1-ft. diam. column showed little difference in bulk liquid variability between beds showing drastically different flow distributions. An example of this is shown in Table 3 where the ratio of the flow in each radial octant of the cross-sectional area to average bed flow is given for two beds, only one of which has uniform flow patterns. Other tests were made in the 2-in. diam. column which was specifically designed to contain large packing faults in the form of open area. This open area represented up to 10% of the bed volume. Faults were also created by placing horizontal baffles to divert flow and create stagnant areas in the bed. As shown in Table 4 these tests showed no variation in variability or 1% breakthrough for a wide range of bed and operating conditions.

It may be concluded that liquid-solids contacting cannot be characterized purely from the bulk liquid flow variability determined from the liquid residence time distribution. The liquid may have a uniform velocity throughout the bed as indicated by a low variability but, because of channeling, may come in contact with only a part of the catalyst as shown by the flow distribution measurements. Unfortunately, although the flow distribution tests might give a better measure of liquid-solids contacting than the variability, flow distributions are difficult if not impossible to obtain in commercial units.

Other parameters of the residence time distribution are also not completely effective for determining quantitative differences in liquid-solids contacting during mixed-phase flow conditions. This ineffectiveness is a result of the fact that only average holdup is measured. Therefore for a holdup of 30% for example the liquid could be evenly distributed over all the packing surface or may represent large rivers flowing through the bed and contacting as little as 40% of the surface. From a qualitative standpoint increasing liquid loading in mixed-phase operations should improve liquid solids contacting since liquid holdup is increased (Figure 6). The increased liquid loading creates more turbulence in the bed thereby inducing local eddies which will minimize the number of stagnant liquid pools.

CONCLUSIONS

These studies have led to a greater understanding of the flow mechanisms occurring in two-phase porous packed bed systems. The spread in liquid residence time distributions as portrayed by variability has been shown to be a function of bulk liquid flow and diffusional flow mechanisms. Diffusional effects play a big role especially at low liquid flow rates. Although parameters of the residence time distribution such as variability and liquid holdup are not sufficient to quantitatively characterize liquid-solids contacting, some qualitative statements can be made. For example high liquid loadings have been shown to be desirable because of increased bed turbulence and liquid holdup. Analysis of the data obtained in this study by other techniques, such as transform mathematics, may provide better correlating groups than liquid holdup or variability. However these techniques fail to provide a realistic picture of the flow mechanisms occurring in the system.

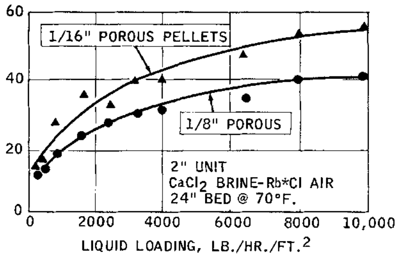

Fig. 6. Liquid holdup vs. liquid loading.

ACKNOWLEDGMENT

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NOTATION

C = effluent tracer concentration in liquid at any time
D = diffusivity, sq.ft./hr.
D_p = diameter of particle equivalent to diameter of sphere having same surface area as an avg. particle in the bed
E = molecular diffusivity, sq.ft./hr.
G = mass flow rate (liquid loading), lb./hr. sq.ft.
H = fractional liquid holdup
N_{Re} = particle Reynolds number = $\frac{D_pG}{\mu(1-H)}$
Q_L = volumetric liquid flow rate, cu. ft./hr.
v = liquid velocity based on column cross section, ft./hr.
V = overall variability
V_B = bulk liquid flow variability
V_T = total bed volume, cu. ft.
θ = time
θ_{avg} = average residence time of tracer molecules in the bed
σ = standard deviation
μ = viscosity

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