TABLE 3. RADII r OF SEVERAL MOLECULES ESTIMATED FROM $r = n^{-1/3}$. n IS THE NUMBER DENSITY OF THE MOLECULES IN A PURE SATURATED LIQUID STATE AT A LOW VAPOR PRESSURE.

		From Ref. 1	From Eq. (3)	From Ref. 1	From Eq. (4)
	$r(nm)$	p	p	$A \times 10^{10}$	$A \times 10^{10}$
Ar	0.181	0.44_9	0.450	2.17	2.14
CH_4	0.189	0.47_2	0.480	1.59	1.50
Kr	0.200	0.49_9	0.517	1.12	0.969
Xe	0.207	0.56_3	0.539	0.550	0.750
CCl_4	0.272	0.71_7	0.688	0.112	0.1309
$(CH_3)_4Sn$	0.307	0.73_2	0.743	0.0895	0.0694
$(C_2H_3)_4Sn$	0.345	0.77_7	0.790	0.0498	0.0404
$(C_3H_7)_4Sn$	0.380	0.81_7	0.825	0.0297	0.0269
$(C_4H_9)_4S$	0.410	0.84_9	0.849	0.0207	0.0201
$(C_{12}H_{25})_4Sn$	0.565	0.94_2	0.936	0.00571	0.00732

with a coefficient of determination 0.9921. Values of p predicted from Eq. (3) are given in the fourth column of Table 3. The agreement of fitted and observed p is quite good, the fitted values generally being within a percent or two of observed values—in the worst case, CCl_4, fitted and observed p are within 5%. We also analyzed the data by dividing the solvent into two groups, one, the compact molecules benzene, cyclohexane, carbon tetrachloride and tetrabutyltin, and the second, the other solvents given in Table 1. In general, the least squares fit using two solvent groups was only a little or no better than using only one group.

As mentioned, with Eqs. (2) and (3), Eq. (1) provides a correlation between solvent viscosity and solute diffusivity with no undetermined parameters. Combining Eq. (3) with Eq. (2), we obtain

$$10^{10}A = 0.0005036 \exp (1.5124\ nm/r) \qquad (4)$$

Predictions of Eq. (4) are compared with observed values of A in Table 3. The average absolute percent difference between Eq. (4) and observed values is about 13%. The worst case is tetradodecyltin for which the predicted A is 28% too high.

With Eqs. (3) and (4), Eq. (1) becomes a powerful predictive tool. For a given solute whose diffusivity is desired in a given solvent, we need only the solvent viscosity and the density n of the liquid solute at a low vapor pressure. Then estimating $r = n^{-1/3}$, computing p from Eq. (3) and A from Eq. (4), we estimate D from Eq. (1). On the basis of the comparisons made in Table 3, the estimated D is expected to be within (often well within) about 25% of the actual value.

The accuracy of Eq. (1) over such a wide range of conditions begs for a simple theoretical basis, as does the dependence of p and A on molecular size. We presently have no such theory, but we believe Eq. (1), with Eqs. (3) and (4), constitutes an important empiricism for engineering estimates of diffusivity.

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NOTATION

A = solute dependent constant in Eqs. (1), (2), and (4)
D = tracer diffusivity
n = solvent number density
p = solute dependent constant in Eqs. (1), (2), and (3)
r = solute radius
T = absolute temperature

Greek Letters

η = solvent viscosity
ρ_m = solvent mass density

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Two-Phase Pressure Drop in Cocurrent Downflow in Packed Beds: Air-Silicone Oil Systems

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Since the advent of hydrogen processing technology to crack and desulfurize-denitrify petroleum fractions in trickle bed reactors, these units have become ubiquitous in the refinery complexes of the world. The design and successful operation of trickle bed reactors depends on both an adequate knowledge of the heterogeneous catalytic reactions taking place and the fluid mechanical behavior of the gas-liquid-solid system. Accurate prediction of two-phase pressure drop in packed bed reactors is necessary, not only for specification and sizing and major equipment, but also as a subjective means of insuring an adequate liquid distribution within the bed, by designing for operation at, or in excess of, some predetermined value. In addition, a reasonable estimate of pressure drop as a catalyst run progresses is necessary to insure adequate compressor and pump capacity.

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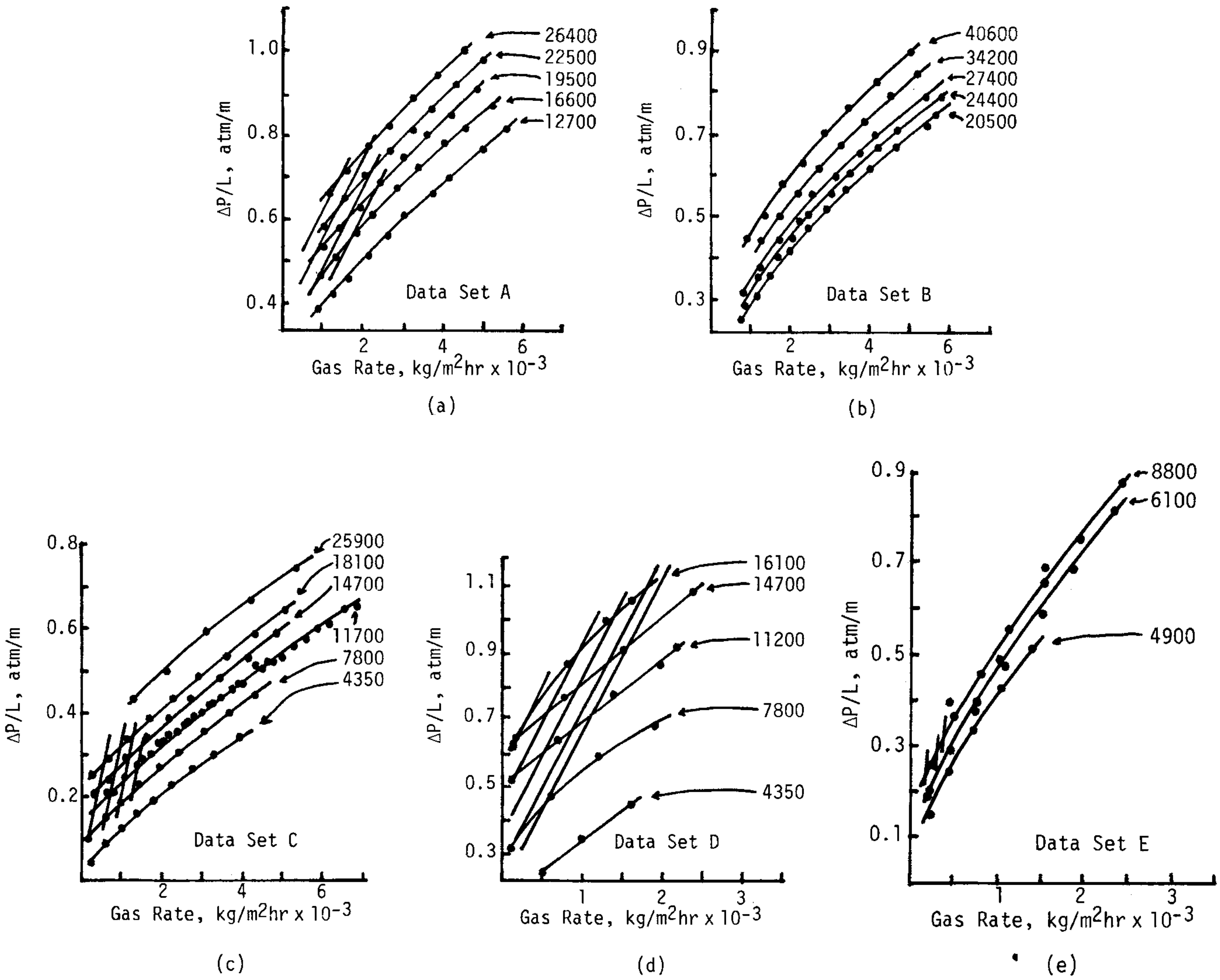

Figure 1. Effect of gas and liquid flow rate on two-phase pressure drop for air-silicone oil. Curves are for constant liquid rate in units of kg/m² hr. Metric conversion: 1 atm = 101.325 kPa.

Almost all of the two-phase pressure drop studies in the literature have been done using air and water as the test fluids. Also, the packings have tended to be relatively large (3-25mm effective particle diameter). To varying extents, all the correlations are empirical, so the direct use of air-water based correlations to hydrogen-heavy hydrocarbon systems without some checking seems unwise. This article presents new data for two-phase pressure drops taken using liquids specifically chosen as analogs of the relatively heavy petroleum and kerogen fractions of particular interest in today's world.

EXPERIMENTAL PROGRAM

To replicate liquid phase physical properties as closely as possible, without the attendant hazards of using hydrocarbons, the experimental liquids were Dow-Corning DC200 series silicone fluids. The fluids used had measured viscosities ranging from 1.5 to 8 centipoise, densities of 0.9 to 0.92 gm/cc, and a surface tension (compared to air) of 18 to 20 dynes/cm. In the experiments, the gas phase was air.

All the data reported were taken using a test bed 55 mm ID and 1.5 m long. A number of different packings were used to allow comparison of results among different packing sizes and geometries.

A special chimney distributor insured an even initial liquid distribution in the bed. The final distribution could be measured by a special 25 mm ID annular pipe extending up into the bed. Under a wide variety of flow conditions with different packings, the fraction of liquid passing through this central core compared favorably with the ratio of the area available to flow inside and outside the sampling core.

The experimental procedure was relatively simple. The column would be stabilized at the gas and liquid flowrate, and the manometer and rotameter readings recorded. The raw data are then reduced by computer. The gas and liquid flow rate are chosen so that the data could be analyzed in a block manner with comparisons either along lines of constant liquid flowrate or constant gas flowrate.

TWO-PHASE PRESSURE DROP DATA

The two-phase pressure drop data are shown in Figure 1(a-e). The crosshatch regions in the figures show where pressure pulsations were noted in the column. This region corresponds to the pulsing flow regime noted by others (Larkins et.al 1961, Beimesch and Kessler 1971). Pressure drops reported in the pulsing region are the average of the extremes noted. The amplitude of the pressure pulsations seldom exceeded ± 10 mm Hg.

The pressure drop data show a fairly linear dependence on gas rate for a given liquid rate, particularly at the highest gas and liquid rates. The increase in pressure drop with increasing

TABLE 1. COMPARISON OF TWO-PHASE PRESSURE CROP CORRELATIONS

Data Set	Packing and Liquid	Larkins Equation Average Absolute Error, %	Larkins Equation Mean Error, %	This Work Average Absolute Error, %	This Work Mean Error, %
A	1.6 mm Sphere 4.7 cp Liquid	21.5	−21.5	8.8	5.0
B	1.6 mm Sphere 1.5 cp Liquid	38.4	−38.4	17.3	−16.3
C	2.9 mm Sphere 4.7 cp Liquid	25.6	−14.8	15.9	−11.9
D	0.8 mm Extrudate 4.7 cp Liquid	39.7	−39.7	28.8	2.6
E	0.8 mm Extrudate 1.5 cp Liquid	13.0	6.6	13.7	1.2
	Overall	24.6	−17.5	15.9	−4.5

liquid rate and with increasing liquid viscosity is very self-consistent. The flow regime transitions appeared to have little effect on the pressure drops. Many of the pressure drop curves were taken by a series of increasing gas rates, followed by a series of decreasing gas rates to look for hysteresis. At no time were any hysteresis effects noted. This appears to be in contrast with the results presented recently by Kan and Greenfield (1978).

TWO-PHASE PRESSURE DROP CORRELATION

The two-phase pressure drop correlation which is most commonly used in the industry is the correlation of Larkins et al. (1961). This expression

$$\log_{10}\left[\left(\frac{\Delta P}{Z}\right)_{\text{two-phase}} \Big/ \left(\left(\frac{\Delta P}{Z}\right)_{\text{liq}} + \left(\frac{\Delta P}{Z}\right)_{\text{gas}}\right)\right] = \frac{0.416}{(\log_{10}\chi)^2 + 0.666} \qquad (1)$$

where $\chi = [(\Delta P/Z)_l/(\Delta P/Z)_g]^{1/2}$, is an empirical mixing rule to calculate the two-phase pressure drop from the single phase gas and liquid pressure drops. The Ergun (1952) equation is used to calculate both of the single phase pressure drops. As first shown by Larkins (1959) the two-phase pressure drop may be given by

$$\left(\frac{\Delta P}{Z}\right)_{\text{two-phase}} = \left(\frac{\Delta P}{Z}\right)_{\text{gas}} (\beta_{\text{gas}})^{-x} \qquad (2)$$

where $\beta_{\text{gas}} = 1-\beta_{nc}$. In Larkins' development, β_{gas} is a function of the two-phase pressure drop and a somewhat circular relationship is developed. However, Clements (1978) has developed a theoretical model which gives

$$\beta_{\text{gas}} \propto \frac{RE_g We_g}{Re_l} \qquad (3)$$

This result suggests that Equation 2 may then be written as

$$\left(\frac{P}{Z}\right)_{\text{two-phase}} \Big/ \left(\frac{P}{Z}\right)_{\text{gas}} \propto \left(\frac{Re_g We_g}{Re_l}\right)^{-x} \qquad (4)$$

If we take the data presented here, we can obtain the expression

$$\left(\frac{P}{Z}\right)_{\text{two-phase}} \Big/ \left(\frac{P}{Z}\right)_{\text{gas}} = 190\,\mu_l D_p \left(\frac{\epsilon}{1-\epsilon}\right)^3 \left(\frac{Re_g We_g}{Re_l}\right)^{-1/3} \qquad (5)$$

Here $D_p(\epsilon/1-\epsilon)^3$ accounts for variable bed properties and, of course, μ accounts for differences in liquid viscosity. The constant, 190, is for D_p[ft], and μ_L[lb$_m$ft hr]. The exponent −1/3 is a rounded off result of a linear least squares curve fit and is also indicated by other purely hydrodynamic considerations. The data available are insufficient to tell if the exponent, x, is truly constant, or if it depends on other parameters.

The experimental data reported here are compared with Larkins equation and with Equation (5) in Table 1. Equation (5) should be directly usable for hydrogen hydrocarbon systems, because of the similarity of physical properties to the substances on which the equation is based. Applicability to a wider set of gas-liquid-solid systems must be established.

SUMMARY OF RESULTS

1. Original experimental data for two-phase pressure drop at conditions approximating commercially interesting points are presented.
2. The Larkins equation does not completely correlate the two-phase pressure drop data from this work, but the theoretically based Equation (5) can effectively predict pressure drops for catalyst-heavy hydrocarbon systems. The Larkins equation gave an average absolute error of 25% with a mean error of 18%, while Equation (5) gave an average absolute error of 16% and a mean error of 5%. Use of Equation (5) with other liquids should be substantiated with further experimental data.

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NOTATION

D_p = effective particle diameter, cm
g = acceleration of gravity, cm/sec^2
G = superficial gas flow rate, gm/cm^{2}sec
Ga = Galileo number $D_p{}^3 g\rho^2/\mu^2$
L = superficial liquid flow rate, gm/cm^{2}sec
$\Delta P/Z$ = pressure drop per unit length, atm/m
Re = Reynolds number, D_pG/μ_G, D_pL/μ_L
U_L, U_G = velocity of liquid and gas, respectively, cm/sec
We = Weber number, $U_G{}^2 D_p \mu_{Gc}/\sigma$

Greek Letters

β_{nc} = dynamic holdup, (cm^3 of liquid)/(cm^3 of bed)
∂_L, ∂_G = predicted single-phase pressure drops for gas and liquid, respectively, atm/cm
μ_L, μ_G = liquid and gas phase viscosity, cp
ρ_L, ρ_G = liquid and gas phase density, gm/cc
χ = $[(\Delta P/L)_l/(\Delta P/L)_g]^{1/2}$
σ = surface tension, dyne/cm

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Dynamic Liquid Holdup in Two-Phase Downflow in Packed Beds: Air-Silicone Oil System

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There are three purely fluid mechanical aspects to the design and operation of two-phase, cocurrent packed bed catalytic reactors. These are the overall pressure drop through the bed, the fluid flow regime, and the dynamic liquid holdup. In this note, new data are presented for the dynamic liquid holdup in systems which were chosen to be closely analogous to fairly heavy petroleum fractions found in various hydrotreating reactors.

The dynamic liquid holdup, as used here, is that fraction of the total voidage of the packed bed occupied by readily drainable liquid. This excludes liquid trapped in the catalyst pore volume and the thin liquid film, which tends to adhere to the catalyst surface after complete drainage.

The importance of the dynamic liquid holdup in effective operation of hydroprocessing reactors is well documented (Mears 1974, Ross 1965, Goto and Smith 1975). The amount of liquid held in the interstices of the catalyst bed affects the chemical reaction rate and the average liquid residence time. In planning shutdown procedures, it is important to know how much liquid is held in the bed in order to estimate drainage times.

EXPERIMENTAL PROGRAM

To replicate hydrocarbon liquid phase properties as closely as possible, without the attendant hazards of using hydrocarbons, the experimental liquids used were Dow-Corning DC 200 series silicone fluids. These fluids had measured viscosities of 3.2 and 8.2 centipoise, densities of 0.9 to 0.92 gm/cc, and a surface tension (compared to air) of 18 to 20 dynes/cm. Air was the gas phase in most experiments, but R12 (dichlorodifluoromethane) was used in a few tests to investigate gas viscosity and density effects on holdup.

All of the data were taken in a glass test column 55 mm ID and 1.5 m long. The several packing-fluid-gas systems studied are shown in Table 1. All of the packings were commercial catalysts. The experimental procedure was relatively simple. The column would be allowed to stabilize at a desired combination of liquid and gas flow rates. The liquid and gas flow rates were chosen so that the data could be analyzed in a block, with comparisons either along lines of constant liquid or constant gas flow rate. The liquid holdup measurements were taken by simply cutting off the liquid flow and collecting the liquid as it drained out. The liquid was collected in timed fractions for a period of 30 min. When the timed data are plotted as in Figure 1, the initial volume of liquid can be obtained by extrapolation to zero time.

TABLE 1. PACKING-LIQUID-GAS SYSTEMS.

Packing Size	Void Fraction	Liquid	Gas
1.04 mm extrudate	0.361	3.2 cp silicone	Air
1.04 mm extrudate	0.361	3.2 cp silicone	R12
1.04 mm extrudate	0.361	8.2 cp silicone	Air
1.39 mm extrudate	0.330	3.2 cp silicone	Air
3.35 mm extrudate	0.320	3.2 cp silicone	Air

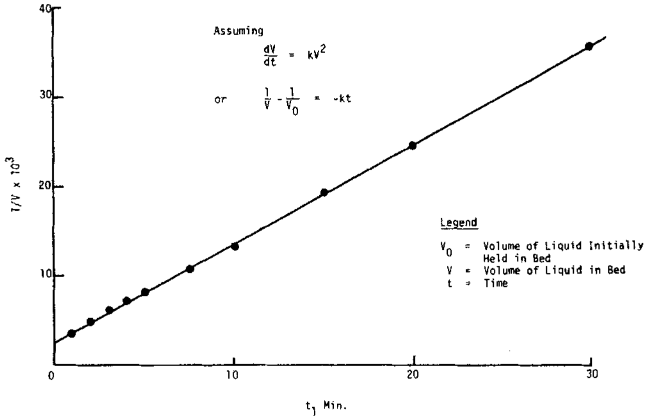

Figure 1. 1/*V* versus *t*.

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