Surface Effects in a Pulsed, Packed Column

M. L. JACKSON, K. L. HOLMAN, and D. B. GROVE

University of Idaho, Moscow, Idaho

Mass transfer rates and flooding limits are basic to the use of packed columns for liquid-liquid extraction. The input of pulsing energy increases transfer rates and promotes counterflow of the two phases. The wetting characteristics of the packing influence performance.

The toluene-benzoic acid-water system was used to observe the performance of a 2-in. diam. column containing ceramic (hydrophilic) rings, polyethylene (hydrophobic) rings, or a sieve-plate cartridge. The packed columns showed lower flooding limits than the plate column, but polyethylene packing gave highest transfer rates and capacities. The pulsing energy input was much lower for the plastic packing to effect a higher transfer rate.

Flooding limits for the pulsed, packed columns were lower than for packed columns which were not pulsed. Columns packed with rings so that the ratio of diameter to packing size was 4:1 gave higher flooding limits and better performance than a ratio of 8:1. The use of the two types of packing in alternating bands resulted in a performance intermediate between that of each packing employed separately, and no advantage was indicated in reference to flooding limits or transfer rates.

Liquid-liquid extraction columns have been found particularly effective for the recovery of uranium from fission products. The input of pulsing energy increases the rate of mass transfer and permits a reduction in the height of the column required and in capital investment.

In a sieve-plate column the dispersed and continuous phases pass through holes in the plates and result in intimate contact between the phases. The pulsing action is necessary for satisfactory counterflow of the phases which may not otherwise occur. The pulsed, plate column has been investigated in detail (*13* among many) in reference to its performance and flooding characteristics.

The packed column offers a simpler type of construction, especially for larger diameters. The proper use of pulsed, packed columns requires information about flooding limits and transfer rates. Wetting characteristics of the packing surfaces are of special significance in liquid-liquid systems. The work reported below was conducted to observe the effect of surface wetting characteristics on performance and to compare a packed column with a plate column for the same system and operating conditions.

SURFACE EFFECTS

Little information appears in the literature concerning the performance and flooding characteristics of pulsed, packed columns. Qualitative behavior can be inferred; if the continuous phase wets the packing, the dispersed phase will move through the column as small droplets; if the dispersed phase wets the packing, it will move up the column as a film on the packing surface. In the latter case holdup of the dispersed phase will increase, and flooding will probably tend to occur at lower flow rates. However interfacial surface may increase in the packed section, and higher transfer rates may result.

The transfer mechanism in the dispersed phase may also be modified by the nature of the solid surface. Circulation in droplets is an important factor in the rate observed (*14*). If the dispersed phase wets the packing, circulation may be increased through tendency of the droplet to rise while in contact with the solid on one side. Danckwerts (*4*) proposed the surface renewal theory, an extension of the penetration theory of Higbie, as being more description of the mechanism of mass transfer for the flow of liquids over packing. The mechanism for this case was postulated as being one of unsteady state diffusion to elements of liquid constantly being renewed at the interface. It was proposed specifically for the case of gas absorption but has equal significance for liquid-liquid systems in packed columns.

Garner (*6*) cites a quantitative method for the determination of the wetting characteristics of various solid surfaces. Contact angles of drops of either toluene or water, in the presence of the other, were measured. These angles corresponded to cases where the water was receding and advancing. The difference in the cosines of the two angles is a measure of the hydrophilic or hydrophobic nature of the surface and some values of interest are summarized in Table 1. The negative and positive values have relative significance, and it is seen that polyethylene is less hydrophilic than unglazed porcelain.

This data was used by Garner (*5*) to show that the performance of a plate extraction column (not pulsed) was influenced significantly by the wetting characteristics of the plate material. Buchanan (*3*) found that the rates of formation and sizes of drops were influenced by the wetting characteristics of orifice plates.

Sobotik and Himmelblau (*15*) studied the effect of plate wetting characteristics in a pulsed, sieve-plate column. The use of stainless steel or polyethylene plates gave about the same rates when the acetic acid was transferred from the water phase to the continuous ketone phase. However substantially higher rates were observed for acid transfer from the continuous ketone phase to water for polyethylene plates. An alternating plate arrangement gave results intermediate between the performance of all polyethylene or all stainless steel plate columns.

Morello and Beckman (*11*) considered that $(H_t)_W$ was zero for a toluene-diethylamine-water system in a column packed with small glass beads. This paper uses calculation procedures similar to those employed in the present work.

Ballard and Piret (*2*) observed the flow mechanism in a liquid-liquid packed column (not pulsed) and found this to depend upon whether the dispersed or the continuous phase preferentially wet the packing. Also flooding limits were correlated for unglazed porcelain ring packing.

EXPERIMENTAL PROCEDURES

The pulsed extraction column shown schematically in Figure 1 indicates the devices used for measurement of flow rates and for level control. The column consisted of a 2-ft section of 2-in. standard Pyrex glass pipe fitted with a glass tee at

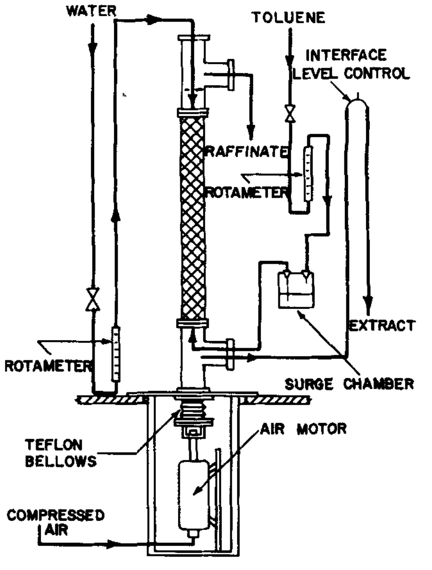

Fig. 1. Diagram of pulsed extraction column.

D. B. Grove is with United Technology Corporation, Sunnyvale, California.

either end as a disengaging section. Pulsing was provided by a unique arrangement with a bellows (a 2-in. expansion joint) and a reciprocating air motor. The stroke and frequency of the latter was easily controlled and was believed to provide a pulse approximating a sine curve. This arrangement, in addition to being relatively inexpensive, eliminated the hazard of an electric motor in the presence of solvent vapors. The possibility of cavitation was avoided by connecting the bellows directly to the bottom of the column. Operation of the unit was found to be simple and dependable, and this method of pulsing was used for ⅜- and ½-in. packing and for a sieve-plate arrangement. Although the bulk of the data was obtained with this pulsing unit, the results cited for ¼-in. packing were obtained by means of a modified Wallace-Tiernan chemical feeder. This unit provided a pulse which was sawtoothed in profile.

Plates for the column were designed for optimum performance as suggested by Sege (*13*). They represented a compromise between flow capacity and transfer rate. The plates were of 2-in. spacing with ⅛-in. holes and 23% free area (fifty-two holes on equilateral triangles). The plates were 1/32 in. in thickness, and the plate cartridge for the 2-ft. section of column contained twelve plates.

Packing material for the 2-ft. transfer section consisted of Raschig-type of rings in ¼- to ½-in. sizes. Two material types were selected which had different wetting characteristics as given in Table 1; these were unglazed ceramic rings and polyethylene tubing cut with length equal to the diameter. The ceramic rings were dumped in the column which had previously been filled with water. The plastic rings were added to the empty column and held in place by screens because of their buoyancy. The plastic rings appeared to be unaffected by the toluene even after considerable use.

Condensed steam was employed to provide water of suitable purity, and the toluene and benzoic acid were of reagent grade.

No distribution devices were found to be necessary to introduce the two liquids into the column, and the toluene was maintained as the dispersed phase. It was believed that end effects were small in comparison with the transfer occurring in the main section of the column. Samples of the exit streams were taken after about 1 hr., and steady state operation was assumed when samples remained constant for all runs (C_{T1} = 0.0113 ± 0.0002 lb. moles/cu. ft) and the flow rate of this phase was likewise kept constant (V_T = 0.074 cu. ft./hr.). Water, without acid, was fed to the column and the transfer was from the toluene to the water phase. The rate of flow of the water phase was varied over a considerable range (0.05 to 0.95 cu. ft./hr.), in most cases until flooding of the column occurred.

TABLE 1. HYDROPHILIC CHARACTER OF PACKING AND PLATE MATERIALS (*6*)

Material	Relative value
Glass	—1.66
Porcelain, glazed	—0.88
Mild steel, rusted	—0.77
Porcelain, unglazed	0.85
Mild steel, clean	1.31
Polyethylene	1.85
Teflon	1.92

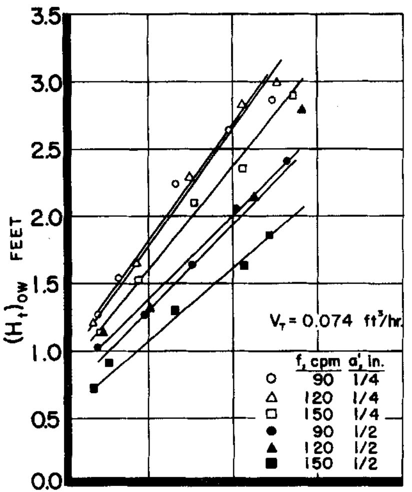

Fig. 2. Performance of a pulsed sieve-plate column.

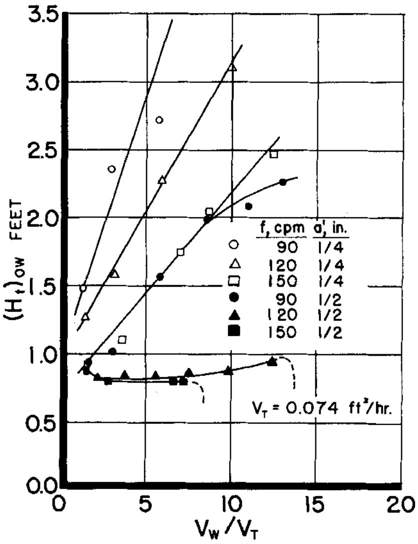

Fig. 3. Performance of a pulsed packed column with ½-in. ceramic rings.

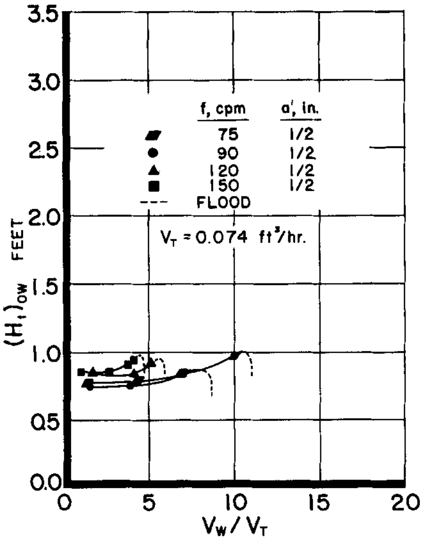

Fig. 4. Performance of a pulsed packed column with ½-in. polyethylene rings.

For the ¼-in. rings the inlet acid concentration was the same, but the toluene flow rate was lower at 0.023 cu ft./hr.

Equilibrium data for the toluene-benzoic acid-water system has been reported by several investigators (*1, 9, 10, 12*). These were not in agreement, and check analyses were made at several temperatures for the two phases which had been brought to equilibrium. The resulting values agreed with those reported by Li and Newton (*9*), and the data of these investigators was used for the calculations. The equilibrium data of Appel and Elgin (*1*), when used for mass transfer calculations, in some cases gave negative values of heights transfer units at zero flow rates.

MASS TRANSFER CALCULATIONS

The equations used for making mass transfer calculations, and for interpreting the results, are summarized below:

Operating line:

$$C_W = (V_T/V_W)\,C_T - (V_T/V_W)\,C_{T2} \quad (1)$$

Equilibrium line:

$$C_W^* = m\,C_T \quad (2)$$

From rates:

$$dC_W/(C_W^* - C_W) = (K_W/V_W)\,dA \quad (3)$$

Define:

$$Z = (N_t)_{OW}\,(H_t)_{OW} \quad (4)$$

$$(H_t)_{OW} = V_W/(K_W\,a) \quad (5)$$

Approximately:

$$(N_t)_{OW} = (C_{W1} - C_{W2})/(C_W^* - C_W)_{\text{log mean}} \quad (6)$$

Approximately:

$$(H_t)_{OW} = (H_t)_W + (H_t)_T\,m\,(V_W/V_T) \quad (7)$$

The operating line is given by Equation (1) and has a constant slope (V_T/V_W) because the toluene and water phases were immiscible and volumes were essentially unaffected by solute transfer. Terminal compositions establish the operating line. In many cases the equilibrium line could be approximated by a straight line over the range of compositions observed as by Equation (2), thereby permitting the use of a log mean driving force. Equation (3) was integrated graphically where the use of a straight line for the equilibrium line was not feasible.

The height of a transfer unit $(H_t)_{OW}$ has the significance indicated by Equation (5) and was calculated from Equation (4) for a 2-ft. column height and the calculated number of transfer units. The number of overall transfer units $(N_t)_{OW}$ was obtained by the use of Equation (6) in most cases.

Equation (7) is valid only for the situation where the equilibrium line is straight. It should apply approximately, but not literally, to most cases in the present investigation. If the fluid mechanics are such that the coefficients of mass transfer are constant, then a plot of the overall height of a transfer unit $(H_t)_{OW}$ vs. the ratio of liquid flow rates (V_W/V_T) will be a straight line. The intercept on the ordinate indicates the value of $(H_t)_W$ and the slope may be used to calculate $(H_t)_T$. The use of either the two-film or surface-renewal theories of mass transfer leads to equations of similar form, and the above film values are proper.

EXPERIMENTAL RESULTS

The original experimental data are available (7, 8). The energy input to effect transfer by the pulse is at least roughly proportional to the product of the frequency and amplitude (f by a'). Relative pulsing energies used are indicated in Table 2. Results are best presented as plots in the form suggested by Equation (7).

Figure 2 indicates the performance obtained for the pulsed, sieve-plate column. Approximately straight lines were obtained which indicated the validity of Equation (7) for this arrangement. The individual film values decreased with increased pulsing action as indicated by the lower intercepts and slopes. The six pulsing energy levels show an orderly decrease in the overall height of a transfer unit and a corresponding increase in transfer rates. The maximum flow ratios given represent approximate maximums in column operation because there is a tendency toward emulsification and carry-over of fine droplets of the dispersed phase. The performance of the plate column has most significance in relation to the performance of the packed sections.

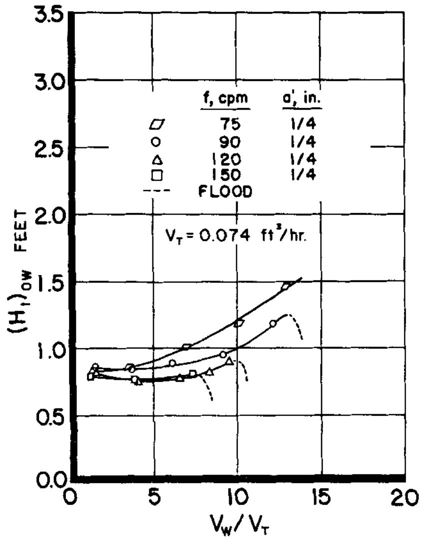

Fig. 5. Performance of a pulsed packed column with ½-in. polyethylene rings.

TABLE 2. RELATIVE PULSING ENERGIES USED IN THIS INVESTIGATION

f, pulse frequency, cycles/min.	a', amplitude, in.	f by a'
1/4-in. packing		
60	1/4	15
60	5/16	19
60	13/32	25
1/2-in. packing		
75	1/4	19
90	1/4	22
120	1/4	30
150	1/4	38
75	1/2	38
90	1/2	45
120	1/2	60
150	1/2	75

ONE HALF-INCH PACKING

Results for a packed column with ½-in. ceramic rings are given in Figure 3. As the pulsing energy increased, the overall height of a transfer unit decreased with an obvious abrupt change in behavior. The latter was apparently caused by approaching emulsification and some change in holdup within the packing. Although good transfer was obtained at the higher energy levels of pulsing, flooding occurred at lower flow rates than for the sieve-plate column.

Figure 4 shows that low values of $(H_t)_{OW}$ were obtained for ½-in. polyethylene packing at high pulsing energies, but that flooding occurred so early as to render the column relatively ineffective. However, as indicated in Figure 5, good performance was obtained without flooding at lower values of the frequency-amplitude product. The curved lines obtained in some cases are possibly the result of variable circulation rates in the dispersed droplets.

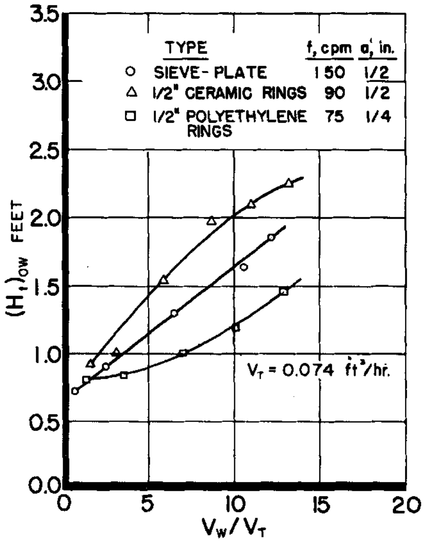

Fig. 6. Performance of pulsed sieve plate and packed columns.

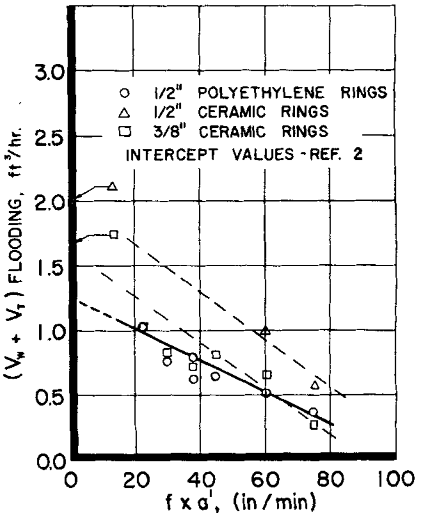

Fig. 7. Flooding rates of pulsed, packed columns.

The best performance data, consistent with usable operating conditions, was selected for each type of column with the results given in Figure 6. The polyethylene packing gave heights of the transfer unit which were about 25% lower than those for the sieve-plate column, with ceramic packing the least effective. It is quite significant that the pulse energy input with polyethylene packing was one-fourth that of the sieve-plate column. The transfer rates were also somewhat better for plastic rings.

Approximate flooding limits were observed and are given in Figure 7. Flooding limits were observed to decrease almost linearly with increasing pulse energy (f by a'). The dotted lines in Figure 7 are estimated for the ceramic rings of two sizes. The values at zero pulsing energy were taken from the literature (2) and appear to be consistent with the flooding characteristics observed for pulsed, packed columns. The use of polyethylene packing leads to lower flooding limits than for the ceramic type.

ONE QUARTER-INCH PACKING

Results for ¼-in. packing were obtained preliminary to the work with ½-in. packing (7). The pulse was of a rather extreme sawtooth type and was used because of the convenience of available equipment. The surface area presented by the smaller packing is relatively much greater.

Figure 8 gives the results with the small ceramic rings. Contrary to the results cited above the height of a transfer unit increased with increasing pulse energy. This effect possibly was the result of low holdup of the dispersed phase. Figure 9 indicates the performance observed with polyethylene packing where $(H_t)_{OW}$ decreases with increasing pulse energy. Transfer rates are seen to be definitely much

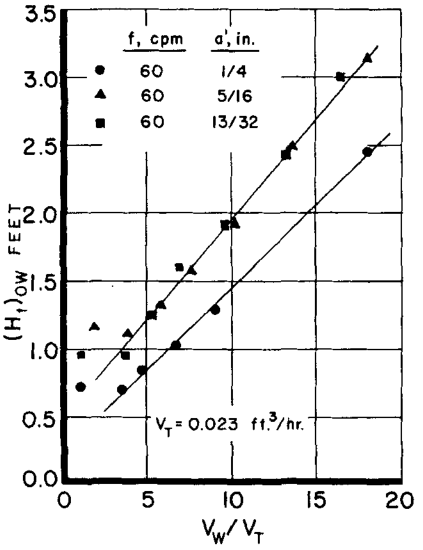

Fig. 8. Performance of a pulsed packed column with ¼-in. ceramic rings.

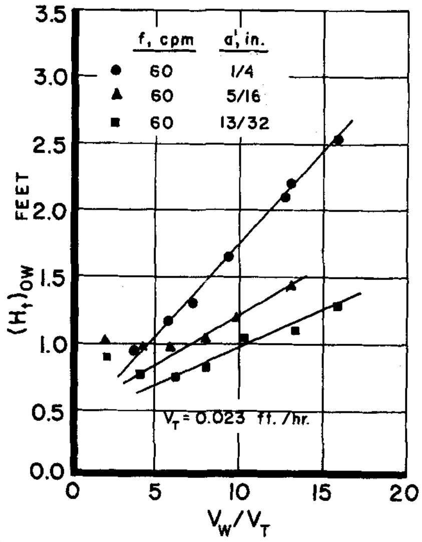

Fig. 9. Performance of a pulsed packed column with ¼-in. polyethylene rings.

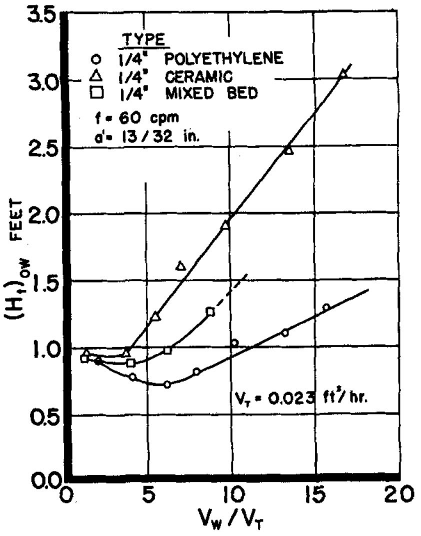

Fig. 10. Performance of pulsed packed and mixed bed columns.

better for the plastic packing. The sawtoothed pulse was reversed for a series of runs and little change in rate resulted. From this limited information it was tentatively concluded that the pulse shape had little effect on column performance.

Only limited information was obtained on flooding although the column obviously flooded more readily than with the larger packing. With ¼-in. polyethylene packing for (f by a') = 45 the column flooded at a combined flow rate of $(V_T + V_W) = 0.23$ cu. ft./hr. The corresponding flooding condition for ½-in. packing would permit a combined flow rate three times greater than this value.

Because plate columns of the zebra type (alternating bands of plates having different wetting characteristics) permit higher flooding limits a packed column with alternating bands of the two packing types was investigated. Figure 10 shows the results obtained with ¼-in. packing in 2-in. bands. Contrary to results with plate columns the flooding limit was drastically reduced and performance was intermediate between that for a column packed with either type of material. Mixed packing, distributed in a random fashion rather than in alternating bands, might show better flooding limits while retaining good transfer characteristics. The use of larger packing might also lead to better performance of mixed beds.

SUMMARY AND CONCLUSIONS

A pulsed, packed column showed a performance equal to or exceeding that of a pulsed, sieve-plate column for the water-benzoic acid-toluene system. The packed column is limited by lower flooding limits but may exhibit higher capacities because of better transfer performance.

The wetting characteristics of the packing surface can have a pronounced effect on performance. An unglazed ceramic packing wet by water gave higher flooding limits than a polyethylene packing wet by toluene. However transfer rates were substantially higher for polyethylene packing. A ratio of column diameter to packing size of 4:1 was found more satisfactory than a ratio of 8:1 because of higher flooding limits.

A significantly lower pulse energy input was possible for the plastic packing wet by the organic phase. The energy requirement was only one-fourth that for a sieve-plate column which used the same system.

The simplicity of the packed column for large diameters, and the advantage of low energy input and higher transfer rates in some cases, indicates that pulsed, packed columns should be considered for processing applications with liquid-liquid systems. An economic evaluation would dictate a final selection.

NOTATION

a = interfacial surface area, sq. ft./cu. ft. of packed volume
a' = pulse amplitude, in.
A = interfacial transfer area, sq. ft.
C_T = concentration of benzoic acid in toluene, lb. moles/cu. ft.
C_W = concentration of benzoic acid in water, lb. moles/cu. ft.; C_W^* — in equilibrium with C_T
f = pulse frequency, cycles/min.
H_t = height of a transfer unit, ft.
K_W = overall mass transfer coefficient based on water phase, lb. moles/(hr.) (sq. ft.) (unit ΔC)
m = slope of equilibrium-solubility curve, dimensionless
N_t = number of transfer units, dimensionless
V = volumetric rate of flow, cu. ft./hr.
Z = height of transfer section, ft.

Subscripts

1 = terminal condition, bottom of the column
2 = terminal condition, top of the column
O = overall
T = toluene or toluene film
W = water or water film

LITERATURE CITED

1. Appel, F. J., and J. C. Elgin, *Ind. Eng. Chem.*, **29**, 450 (1937).
2. Ballard, J. H., and E. L. Piret, *ibid.*, **42**, 1088 (1950).
3. Buchanan, R. H., *Australian J. Appl. Sci.*, **3**, 233 (1952).
4. Danckwerts, P. V., *Ind. Eng. Chem.*, **43**, 1460 (1951).
5. Garner, F. H., S. R. M. Ellis, and J. W. Hill, *Trans. Inst. Chem. Engrs. (London)*, **34**, 223 (1956).
6. Garner, F. H., et al., *A.I.Ch.E. Journal*, **1**, 185 (1955).
7. Grove, D. B., M.S. Ch.E. thesis, Univ. Idaho, Moscow, Idaho (1960).
8. Holman, K. L., M.S. Ch.E. thesis, Univ. Idaho, Moscow, Idaho (1961).
9. Li, W. H., and W. M. Newton, *A.I.Ch.E. Journal*, **3**, 56 (1957).
10. Mayfield, F. D., and W. L. Church, Jr., *Ind. Eng. Chem.*, **44**, 2253 (1952).
11. Morello, V. S., and R. B. Beckman, *ibid.*, **42**, 1078 (1950).
12. Row, S. B., J. H. Koffolt, and J. R. Withrow, *Trans. Am. Inst. Chem. Engrs.*, **37**, 559 (1941).
13. Sege, G., and F. M. Woodfield, *Chem. Eng. Progr.*, **50**, 396 (1954).
14. Skelland, A. H. P., and F. H. Garner, *Ind. Eng. Chem.*, **46**, 1255 (1954).
15. Sobotik, R. H., and D. M. Himmelblau, *A.I.Ch.E. Journal*, **6**, 619 (1960).

Manuscript received July 11, 1961; revision received April 9, 1962; paper accepted April 12, 1962; paper presented at A.I.Ch.E. New York meeting.