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A LIQUID EXTRACTION COLUMN WITH RECIPROCATED WIRE MESH PACKING

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In a new type of pulsating, liquid extractor, pulsating energy is added to the countercurrently flowing liquid streams by a stainless steel wire mesh packing which is reciprocated vertically in a 3-inch i.d. extraction column. The mass transfer performance and flooding characteristics are studied as a function of the frequency and amplitude of reciprocation, the total solvent and feed throughputs, and choice of phase dispersion. The benzene-HAc-H_2O and MIBK-HAc-H_2O systems were used. Extraction data for the benzene system were correlated in terms of a dimensionless pulse velocity group. Operating throughputs are significantly higher than those achieved with other designs of mechanically aided extractors, while maintaining high rates of extraction.

Many techniques have been proposed for enhancing the efficiency of liquid extractors. The input of pulsating energy is one common technique for obtaining high rates of mass transfer in extractors. The cyclic acceleration and deacceleration of the two liquid phases resulting from the pulsations generally leads to high interfacial area renewal rates, high relative velocities between dispersed and continuous phases, and an increase in the interfacial area per unit volume—all of which increase the rate of extraction.

The principles of adding pulsating, mechanical energy to an extraction column by reciprocating motion originated with van Dijck (1935), who proposed two methods: Pulsating the liquids as they flow through stationary perforated plates, and vertically reciprocating the perforated plates while the liquids flow through the extraction column. The first technique (and many variations of it) has been extensively utilized (Olney and Miller, 1963; Treybal, 1963c). The second method has received relatively modest attention until recently (Elenkov *et al.*, 1966; Fenske and

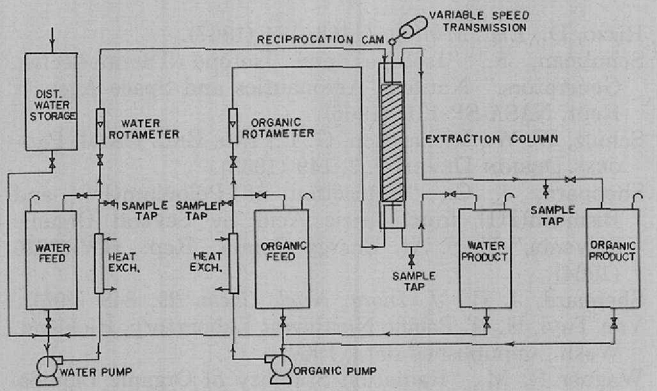

Figure 1. Schematic diagram of extractor system

Long, 1955; Gelperin *et al.*, 1965; Issac and DeWitte, 1958; Karr, 1959; Landau *et al.*, 1964; Long and Fenske, 1961; Maksimenko *et al.*, 1966; Prochazka *et al.*, 1965); however, these recent investigations have all involved the use of reciprocating perforated plates.

This article describes the performance of a new type of pulsating liquid countercurrent extractor designed by Carr (1963), which is somewhat analogous to the second pulsation method described by van Dijck (1935). The unique feature of this extractor is that the pulsation energy is imparted to the two countercurrently flowing liquid streams by a wire mesh packing which is reciprocated vertically in the column at selected frequencies and amplitudes. The mass transfer performance and flooding characteristics (maximum throughputs) of this column are studied as a function of the pertinent variables: frequency of reciprocation; amplitude of reciprocation; combined stream throughput (the absolute sum of the two liquid stream flow rates); choice of phase dispersion; and, in some cases, direction of mass transfer. The study is concerned primarily with a relatively high interfacial tension system (benzene–acetic acid–water), although a relatively low interfacial tension system (methyl isobutyl ketone–acetic acid–water) is also studied. The effect of using packing of different shapes and porosity and different wetting characteristics was not investigated.

Experimental Work

Apparatus. Figure 1 is a schematic diagram of the countercurrent extraction column system. The feed and product tanks were 55-gallon drums. City tap water was distilled and stored in a 55-gallon drum for use in the experiments. The feeds were pumped to the column by centrifugal pumps. Flow rates were controlled by needle valves at the inlet of the column and measured by calibrated rotameters. Sample taps for concentration measurements of both liquid streams were located near the inlet and outlet of the column. The feed temperature control system consisted of double-pipe countercurrent heat exchangers in the feed tank recirculation lines and a constant temperature bath, complete with pumps and heaters.

The column consisted of a 3-foot length of 3-inch i.d. borosilicate glass pipe. The packed height of 23 inches contained stainless steel wire mesh wound around an axial shaft. The packing was held at the top and bottom by four small pins radiating from the axial shaft. The void volume of the wire mesh packing was determined to be about 95 volume %. The wire mesh was supplied by the Packed Column Corp., and the mesh wire was 0.011 inch in diameter.

The packing was vibrated by vertically reciprocating the axial shaft which entered the column through a Teflon bushing. A cam-shaft follower was fitted at the top end of the shaft, and circular cams to produce the desired displacement amplitudes were eccentrically mounted on the output shaft of a $\frac{1}{4}$-h.p. electric motor with a variable speed transmission (Figure 2). The amplitude of displacement, *A*, is defined as the linear movement of the packing between extreme positions. Three eccentric cams were utilized, providing total displacements of $\frac{3}{32}$, $\frac{1}{8}$, and $\frac{3}{16}$ inch. The reciprocation frequency, *F*, was adjusted by means of the variable speed transmission (0 to 1100 r.p.m.), which was calibrated using a tachometer.

The position of the principal interface level in the column was controlled by needle valves on the exit side of the column; the interface was kept at a level about 3 inches above or below the column packing, depending upon which phase was dispersed. Both liquid phases were distributed over the packing cross-sectional area by distributors (described below); and actual operation of the column, with the principal interface at either the top or bottom of the column, determined which phase was dispersed. The liquid distributors were constructed from $\frac{3}{8}$-inch stainless steel tubing, welded into a $2\frac{1}{4}$-inch circle. Thirty 0.0520-inch diameter holes were drilled in the face of the distributor circle at various angles to provide an even distribution of liquid over the packing cross section. The top and bottom distributors were located approximately $\frac{1}{4}$ inch from the packing. The exiting streams left the column through one $\frac{3}{8}$-inch opening at the top and bottom of the column.

All materials in contact with the liquid extraction system were stainless steel, Teflon, or borosilicate glass (with the exception of nylon sight glasses used for the storage drums in the MIBK experiments). Thus, major sources of contaminating surface-active agents were eliminated.

Materials and Physical Data. Reagent grade glacial acetic acid was used as the solute. For the benzene–acetic acid–

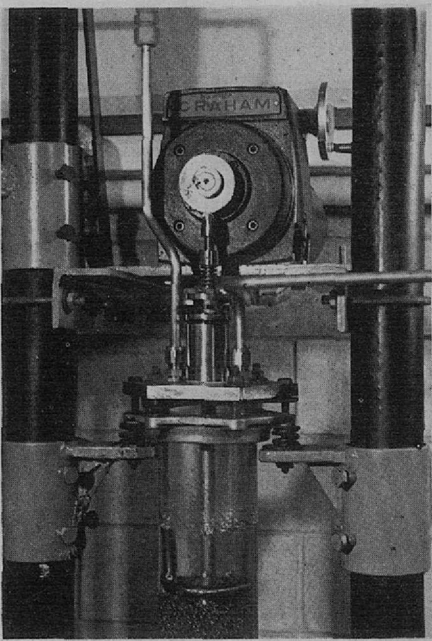

Figure 2. Detailed view of top of extraction column

water ternary system, reagent grade benzene was used; for the MIBK–acetic acid–water system technical grade methyl isobutyl ketone (MIBK) was used. The experiments using benzene as the extract solvent were conducted at 24.5° ± 2.0° C.; those using MIBK as the extract solvent, 28.0° ± 1.0° C. The approximate values of the interfacial tensions and density differences for these systems are: benzene-water, $\sigma \approx 35$ dynes per cm. and $\Delta\rho \approx 0.13$ gram per ml.; MIBK-water, $\sigma \approx 8$ dynes per cm. and $\Delta\rho \approx 0.20$ gram per ml.

The concentration of acetic acid in the liquid streams was determined by titration with standardized sodium hydroxide solutions, using phenolphthalein as the end point indicator. When titrating the organic phase samples, a large excess of distilled water was added to the sample, and the mixture vigorously agitated during the titration. Preliminary extraction tests indicated that steady-state exit concentrations were attained after about 4 column volumes of liquid were in contact; consequently, samples of the exit and input streams were taken after at least this volume of fluid had passed through the column.

The benzene-water system was investigated with acetic acid transfer from the water phase to the benzene phase; experiments were performed with both the benzene and water dispersed. The acetic acid concentration (weight per cent) in all runs was approximately 6.0 and 0.04% in the inlet water and benzene phases, respectively. The MIBK-water system was investigated with acetic acid transfer both from the water phase ($\approx$3.0% HAc) to the MIBK phase ($\approx$0.5% HAc) and from the MIBK phase ($\approx$1.5% HAc) to the water phase ($\approx$0% HAc), and with both the MIBK phase and water phase dispersed.

Equilibrium data for the benzene–acetic acid–water system at 25° C. have been reported (Brown and Bury, 1923; Tudose, 1962). Equilibrium data obtained in this laboratory agreed well with literature values at acetic acid concentrations in water of 3.5 weight % or less; however, at aqueous acetic acid concentrations of about 6.0 weight %, the laboratory values of the equilibrium acid concentration in benzene were about 10% less than those reported in the literature (Figure 27, Özsoy, 1966). The equilibrium data obtained in this laboratory were used in this work. The data were nonlinear and were fitted by least-squares by the following second-order curve ($0 < x \leqq 0.0735$):

$$y = 0.287x^2 + 0.0174x - 9.07\ (10^{-7}) \qquad (1)$$

In the range of operation ($x \approx 0.06$), the solute favors the aqueous phase at about a 30 to 1 ratio; thus, the resistance to mass transfer is mainly in the benzene phase. The over-all HTU calculated in this work is, therefore, almost equal to the individual HTU for the benzene phase.

The equilibrium distribution data for the MIBK–acetic acid–water system are represented by the following linear relation:

$$y = 0.637x \qquad (2)$$

over the entire range of concentrations studied ($0.004 \leqq x \leqq 0.035$). These data are in excellent agreement with the data of Scheibel and Karr (1950). The total resistance to mass transfer is probably about equally distributed between the MIBK and aqueous phase.

A comment concerning the reasons for the choice of the two ternary systems used in this work is necessary. One of the systems was MIBK–acetic acid–water, used by a large number of workers. Thus the experimental results for this (reciprocated packing) column could be compared with previous laboratory investigations of other columns. However, as pointed out by Scheibel (1950), Treybal (1964), and other workers, extraction with this system is relatively easy (giving higher stage efficiencies or lower HTU's and HETS's)—implying that the performance of a previously untested column with this system may appear unrealistically good. This ease of extraction is probably related to at least three factors: The acetic acid favors the ketone almost as much as the water; the low interfacial tension of this system probably enhances surface renewal; and the viscosities are relatively low. Thus the comparisons of the results for this system must be tempered by the above observations.

The second system used was benzene–acetic acid–water. This system has not been used by as many workers as the MIBK system, but it has the virtue of being relatively difficult to extract. In the benzene–acetic acid–water system, the solute favors the aqueous phase over the organic phase at approximately a 30 to 1 ratio; thus acetic acid is not readily transferred to the benzene phase. Also, the relatively high interfacial tension may not tend to enhance surface renewal in the column.

Experimental Procedure

Detailed information concerning experimentation with the benzene–acetic acid–water and the MIBK–acetic acid–water systems is given by Özsoy (1966) and Konkle (1964), respectively. The details of column operation for both cases are nearly identical; however, the procedure and results for the benzene system are stressed in this report, in part because the benzene experiments were planned for analysis by statistical methods. The major differences in the operating procedure between the benzene and MIBK experiments are:

A 2 to 1 ratio of benzene to water but a 1 to 1 ratio of MIBK to water volumetric flow rates was used.

Using benzene, experiments were performed with solute transfer only from the aqueous to organic phase, with both phases dispersed.

Using MIBK, experiments were performed with solute transfer from the aqueous to organic phase and vice versa, with both phases dispersed.

For both groups of experiments (benzene and MIBK) the effect of transfer into and out of the dispersed phase was investigated. To reduce the total number of runs, transfer only from the aqueous to the organic phase was studied for the benzene experiments. The 2 to 1 ratio of flow rates for the benzene phase was chosen because it was desired to extract an appreciable amount of acetic acid by the benzene for accurate concentration measurement (tending to rule out ratios of the order of 1 to 1 or less). Ratios much higher than 2 to 1 were very difficult to study because of unsuitability of the particular rotameters used in this work at high flow rates.

The mass transfer performance of the reciprocated packed column was evaluated as a function of: amplitude of packing displacement, A; frequency of reciprocation of the packing, F; total throughput, V_T (the sum of the solvent and feed stream flow rates); and choice of dispersed phase, P. Using the benzene system, all possible combinations of three levels of each variable (A, F, and V_T) were investigated with either the aqueous or benzene phase dispersed. [For a full-factorial experiment design, these levels of the variables require 54 ($= 3 \times 3 \times 3 \times 2$)

runs. The duplication of one out of every three runs augmented the number of runs by 18, to bring the total to 72 runs. These 72 experiments were randomly sequenced and divided into three blocks of 24 runs each. Three blocks were used to detect (by statistical analysis) any potential buildup of surface-active agents with time in the system. Six runs with no mechanical agitation were added to each of the three blocks to increase the total number of experiments to 90. The purpose of the latter 18 runs (with the column performing as a normal packed column) was to determine the absolute enhancement of extraction due to the input of vibration energy.]

Before the extraction performance of the column was investigated, it was necessary to determine the operating regions of the column—that is, flooding or maximum throughput characteristics were investigated at various levels of amplitude and frequency of packing vibration.

Flow Characteristics (Flooding)

All flooding studies were conducted in the presence of mass transfer. Concentrations closely approximated those used for the extraction studies performed later in this work.

Benzene System. In preliminary throughput experiments with packing reciprocation frequencies over 800 cycles per minute, an emulsion of benzene in water was observed for all amplitudes of packing displacement (3/32, 1/8, and 3/16 inch) when the total throughput was over 85.5 cu. feet per hour sq. feet. At high total throughputs (≧171 cu. feet per hour sq. feet) with the application of high frequencies (580 and 750 cycles per minute) and amplitudes (1/8 and 3/16 inch), there was very slight entrainment of minute droplets of the aqueous phase in the benzene, regardless of which phase was dispersed.

For no energy input at low flow rates (below 85.5 cu. feet per hour sq. feet total throughput), channeling was very pronounced. The two phases could be seen to pass each other without dispersion to any significant degree. At low flow rates, channeling was more pronounced with the aqueous phase dispersed than with the benzene phase dispersed. This phenomenon can be partially explained by the Marongoni effect (Dunn *et al.*, 1965; Groothius and Zuiderweg, 1960). Since mass transfer is out of the water droplets, there is a greater tendency for these droplets to coalesce, leading perhaps to more channeling with water dispersed. The packing used in this work appeared to be preferentially wetted by the aqueous phase; and when the dispersed phase preferentially wets the packing, channeling and coalescence (on packing) are known to be enhanced (Treybal, 1963b). As flow rates increased, channeling decreased considerably, but never ceased completely.

The flooding rates (maximum, total flow) were determined by increasing the flow rates of the two phases (while maintaining the 2 to 1 benzene-water volumetric flow ratio which was used in the extraction runs) until flooding occurred. During the flooding tests, mass transfer of acetic acid was from the aqueous to the organic phase—the direction used later in the extraction studies. Upon the basis of the above preliminary throughput experiments the following levels of reciprocation frequency were studied: 0, 370, 580 and 750 cycles per minute. The available displacement amplitudes of 3/32, 1/8, and 3/16 inch were used. Tests were performed with both the benzene and aqueous phases dispersed. These combinations of variables resulted in a total of 20 experiments to determine the maximum throughputs, $(V_T)_F$.

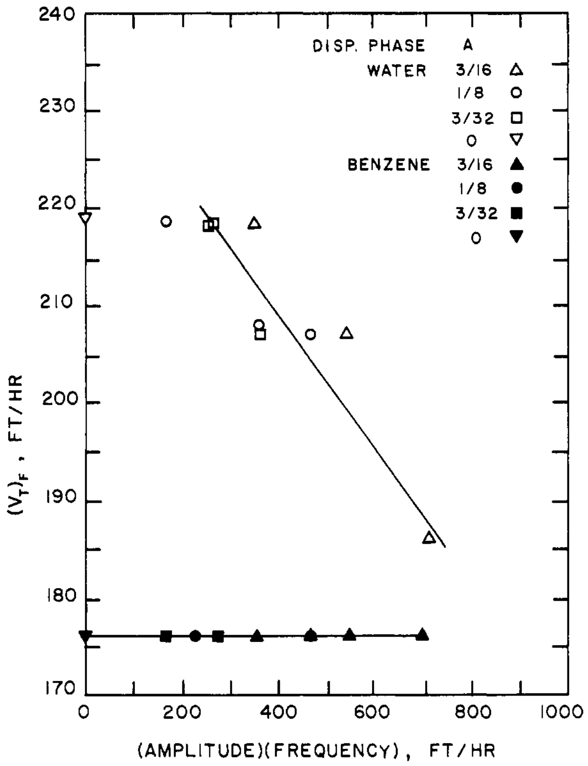

Figure 3. Effect of amplitude and frequency on flooding rate for benzene–acetic acid–water system

The results of the flooding tests for the benzene system are presented in Figure 3 as a function of the relative intensity of reciprocation—i.e., the product of *A* and *F*.

With the organic phase dispersed, a flooding rate of about 176 cu. feet per hour sq. feet was observed for all combinations of frequency and amplitude. With the aqueous phase dispersed, the flooding rates were observed to decrease with increasing energy input from 218 to 186 cu. feet per hour sq. feet.

The observation of lower flooding rates with the benzene phase dispersed may be attributed to the direction of mass transfer. Mass transfer out of the droplets usually induces coalescence of the dispersed phase, whereas mass transfer into the droplets usually inhibits coalescence and tends to keep the droplets in a finely dispersed form which increases the possibility of flooding.

With benzene dispersed as the flow rates were increased, the impingement of benzene jets emerging from the dispersion nozzles on the packing caused emulsification of the benzene, and the column flooded. With the aqueous phase dispersed (at flow rates where benzene had started emulsifying), water also appeared to flood because of emulsification; however, after passing through about 2 inches in the packing, the emulsion coalesced into larger droplets, which could find their way through the packing without flooding (thus leading to slightly higher flooding throughputs than for the experiments with benzene dispersed).

Although there were no quantitative measurements of the dispersed phase holdup in the column, the holdup increased with increasing amplitude and frequency.

MIBK System. The flooding rates observed for the MIBK–acetic acid–water system were about 100% higher

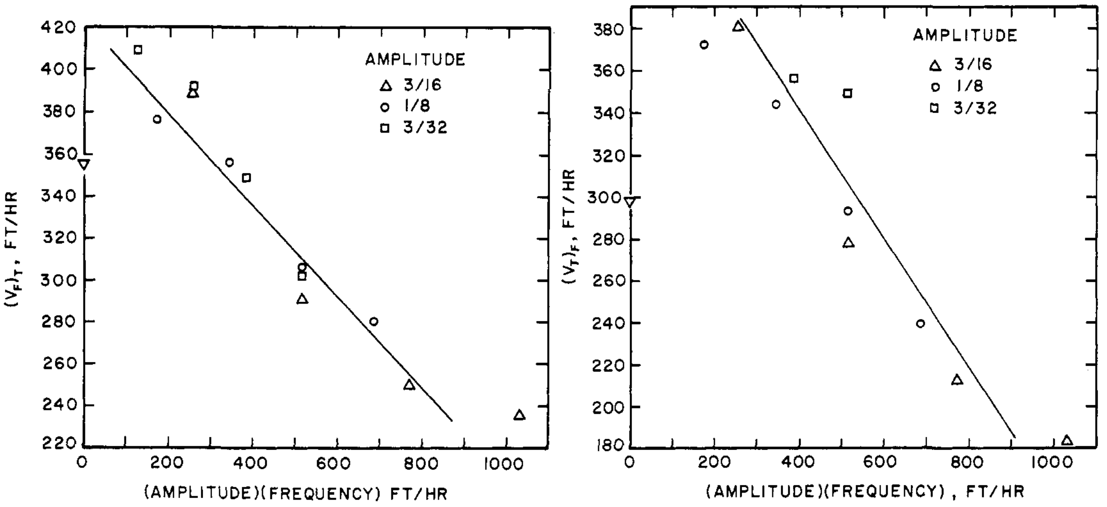

Figure 4. Effect of amplitude and frequency on flooding rate for MIBK–acetic acid–water system

Left. MIBK dispersed, transfer into dispersed

Right. Water dispersed, transfer into dispersed

than for the benzene–acetic acid–water system. Flooding experiments were performed for the MIBK system under four conditions: MIBK dispersed, transfer into the dispersed phase; MIBK dispersed, transfer out of the dispersed phase; water dispersed, transfer into the dispersed phase; and water dispersed, transfer out of the dispersed phase. With no agitation, flooding rates were (for the above four cases) 352, 326, 298, and 370 cu. feet per hour sq. feet, respectively. The highest flooding rate observed when the packing was reciprocated was 408 cu. feet per hour sq. feet for the first condition, at an amplitude of 3/32 inch and a frequency of 275 cycles per minute. The lowest flooding rate observed with agitation was 154 cu. feet per hour sq. feet for the second case, at an amplitude of 3/16 inch and a frequency of 1100 cycles per minute. The flooding results for the first and third cases are presented in Figure 4 as a function of the relative intensity of reciprocation, *AF*.

In general, for both ternary systems studied, the maximum total flow $(V_o + V_W)_F$ decreases as the reciprocation intensity (AF) increases, although in some situations the maximum throughput remains constant with reciprocation intensity (benzene dispersed in water, transfer into droplets) or even passes through a maximum before decreasing (MIBK dispersed, transfer into droplets).

Extraction Performance

Performance Criteria. The height of an over-all transfer unit, HTU_o, based on the organic phase was primarily used as the mass transfer performance index. The HTU_o was calculated from the following expression, which is a modification of Equations 8.13 and 8.26 of Treybal (1963a):

$$HTU_o = \frac{H(E-1)}{\ln\left[\frac{(1-E)\,(y_2 - mx_1 - k)}{y_1 - mx_1 - k} + E\right]} \qquad (3)$$

The HTU_o is referred to later as $(HTU_o)_d$ or $(HTU_o)_c$, depending on whether the organic phase is the dispersed or continuous phase. The use of the above relation is based upon the assumptions that the slope of the equilibrium curve is constant over the range of operation—i.e., the equilibrium curve can be represented by $y = mx + k$; axial mixing in the column is negligible; and the flow rates remain essentially constant through the column.

[Since the concentration difference between the aqueous phase inlet and exit streams was small (less than 0.4 weight %), the HTU_o values obtained using the two limiting values of the slope, m, were at most 3% different from each other. For the results reported in this work, the slope of the equilibrium curve was evaluated at the arithmetic average of the two ends of the operating line—i.e., at $\bar{x} = (x_1 + x_2)/2$—for each individual extraction run. In general, the straight line tangent to the equilibrium curve has a finite, non-zero intercept, k—this is considered in Equation 3. If one were to neglect the constant k for the benzene experiments, the calculations would erroneously lead to significantly higher HTU_o values.

The second and third assumptions are equivalent to assuming a linear operating relation. Visual observations of channeling in the column along the walls and around the axial shaft suggest that the second assumption may be poor. The third assumption is well justified, since the quantity of acetic acid extracted by the organic phase from the aqueous phase is small.]

In addition to representing the column mass transfer performance in terms of the HTU_o, an over-all efficiency of extraction, η, was used for the benzene system, where η was defined as the ratio of the actual extraction that has taken place $(y_2 - y_1)$ to the extraction that would have been realized had the two phases at the raffinate input end of the extractor approached equilibrium $(y^* - y_1)$:

$$\eta = \frac{y_2 - y_1}{y^* - y_1}\,100 \qquad (4)$$

An index which has been used to compare the liquid-handling capacity and efficiency of liquid extractors simultaneously is the quantity

$$I = \frac{V_o + V_w}{HETS} = \frac{V_T}{HETS} \qquad (5)$$

for which a large numerical value is desirable (Landau *et al.*; Treybal, 1964). The index, I, is called the volumetric

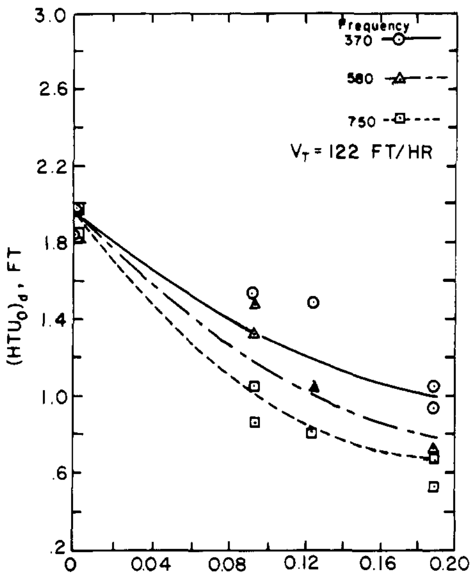

Figure 5. Effect of amplitude of packing displacement on column performance with benzene dispersed

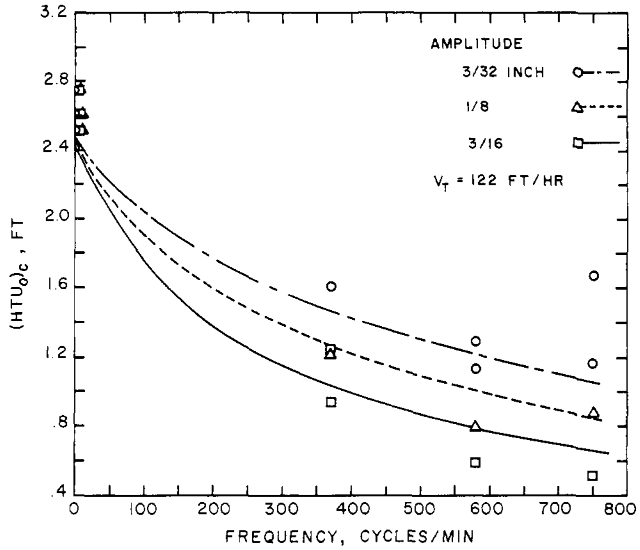

Figure 6. Effect of reciprocation frequency on column performance with water dispersed

Benzene system

efficiency. In this work, the height equivalent to a theoretical stage (HETS) was calculated using the following relation (Treybal, 1963d), assuming linear operating and equilibrium relations:

$$\text{HETS} = (\text{HTU}_o)\frac{\ln E}{E - 1} \quad (6)$$

where

$$E = m\,\frac{V_o\rho_o}{V_w\rho_w} \quad (7)$$

As pointed out by Treybal (1964), care must be taken that only liquid-liquid systems of "comparable difficulty of extraction" be considered when assessing the size of this index. The liquid-handling capacity of the columns being compared with this index should also be considered.

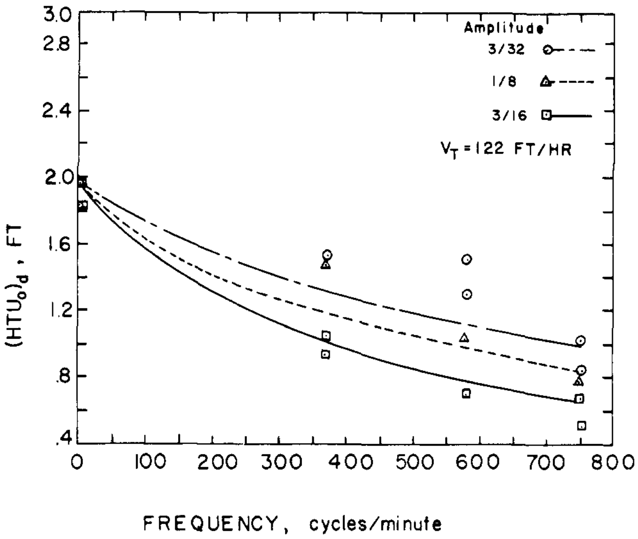

Figure 7. Effect of reciprocation frequency on column performance with benzene dispersed

Benzene system

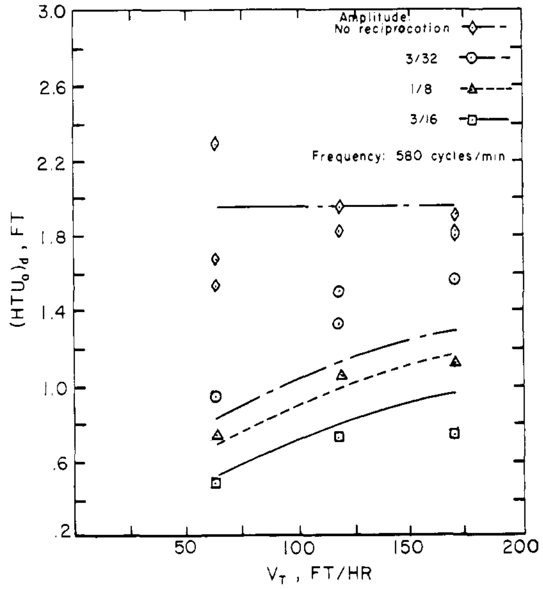

Figure 8. Effect of total throughput on column performance with benzene dispersed

Benzene system

The height equivalent to a theoretical stage (HETS) is used later in this work rather than the HTU when comparing mass transfer performance of different contactors.

Variables and Range. The extraction performance of the new column developed in this work was studied as a function of the total throughput (V_T), amplitude of packing displacement (A), frequency of packing reciprocation (F), and choice of dispersed phase. As a result of the flooding studies, the following levels of the variables were studied for the benzene–acetic acid–water system:

V_T = 65.2, 122, 175 cubic feet per hour sq. feet; (flooding)

F = 0, 370, 580, 750 cycles per minute

A = 0, $^3/_{32}$, $^1/_8$, $^3/_{16}$ inch

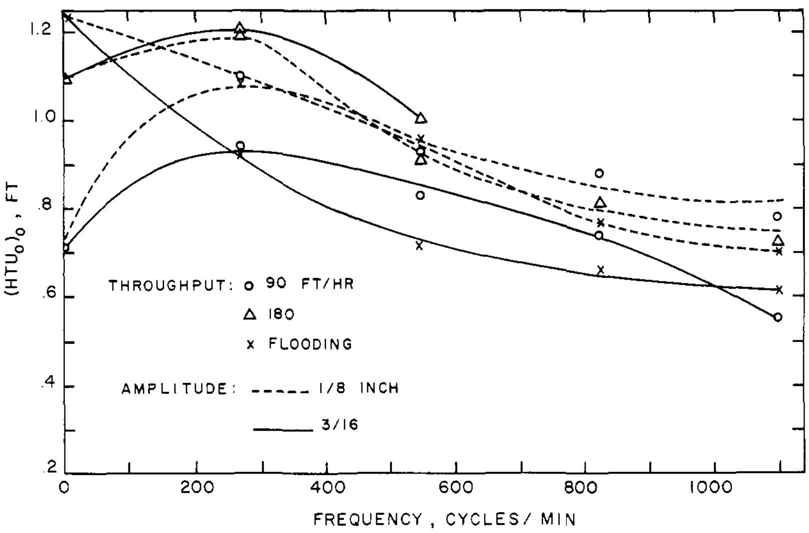

Figure 9. Effect of reciprocation frequency on column performance with transfer from MIBK to water phase, MIBK dispersed

MIBK system

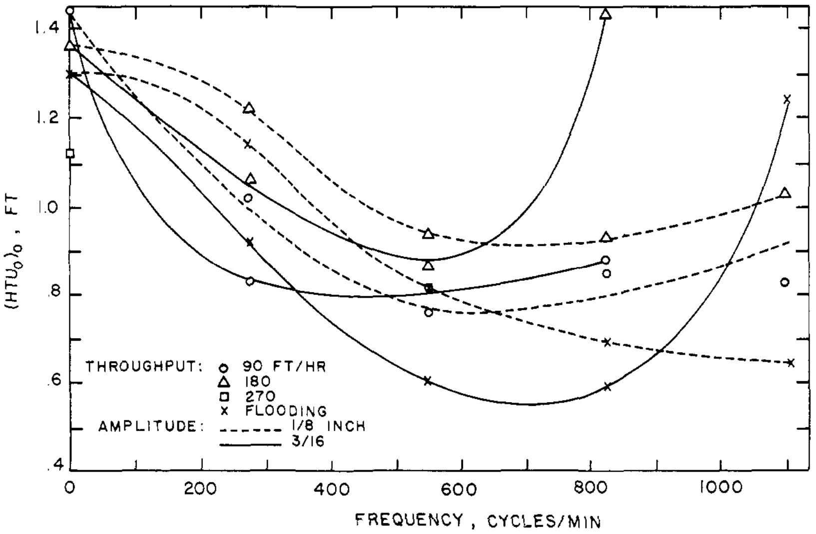

Figure 10. Effect of reciprocation frequency on column performance with transfer from water phase to MIBK phase, MIBK dispersed

MIBK system

The experimentation was performed using the factorial design described earlier. Illustrative data for the benzene system are given in Figures 5 to 8. The curves on these figures represent correlations of the data developed later in this work.

Only very selected results for the MIBK system are given here (Figures 9 and 10). The curves on these figures do not represent correlations of the data. Konkle gives further details concerning the MIBK-acetic acid-water system (1964). The following range of variables were studied for the MIBK system:

V_T = 90, 180, 270 cu. feet per hour sq. feet; (flooding)

F = 0, 285, 555, 825, 1100 cycles per minute

A = 0, $^3/_{32}$, $^1/_8$, $^3/_{16}$ inch

Effect of Variables. An analysis of variance of the three blocks of experiments for the benzene system indicated no apparent change in the system with time—e.g., accumulation of surface-active impurities.

An analysis of variance of the benzene experiments at the 95% confidence level indicated no significant difference in mass transfer performance arising from the choice of phase dispersion when the packing is reciprocated. Examination of Figures 6 and 7 tends to confirm this observation. There are at least two compensating effects which tend to reduce the difference that might arise as a result of phase dispersion in the benzene experiments.

[In an attempt to explain this, consider the volumetric mass transfer coefficient, Ka. Let us denote the coefficient as K_ca_c and K_da_d for the case of water dispersed and benzene dispersed, respectively. Consider the situation for a fixed intensity of reciprocation (high enough to prevent significant channeling) and constant organic and aqueous phase flow rates. Also, suppose one assumes the droplets in the packed column are so small that droplet internal circulation is negligible. In the case of water dispersed, most of the resistance to mass transfer is in the continuous phase (as a result of the equilibrium distribution), where it can be reduced by the intense mixing in the continuous phase due to the reciprocated packing. When benzene is dispersed, the continuous phase resistance is already low; the majority of the resistance is inside the droplets, and continuous phase turbulence probably has a negligible effect in reducing the total resistance to mass transfer. Thus, probably $K_c > K_d$.

The probable effect of choice of phase dispersion on a will now be considered. When droplet coalescence is inhibited, it is expected that the vibrating action of the packing will lead to smaller droplets—i.e., greater a values—the opposite is expected when coalescence is enhanced. When water is dispersed, coalescence of the droplets is induced for two reasons: Solute transfer is out of the droplets (enhancing droplet-droplet coalescence); and the packing is preferentially wetted by the dispersed water phase (probably allowing some droplets to stick temporarily to the packing and coalesce into large droplets before being thrown off the packing by the vibrating action). When benzene is dispersed, coalescence of the droplets is inhibited, since solute transfer is into the droplets and benzene does not preferentially wet the packing. Thus, probably one can except $a_c < a_d$.

Summarizing,

$$K_c > K_d$$

$$a_c < a_d$$

Thus the directional effects of the inequalities are such that one might expect that

$$K_c a_c \approx K_d a_d$$

provided the extent of the inequalities are approximately "balanced" in the opposing directions. In terms of the nomenclature for the height of a transfer unit introduced above, one might expect that

$$(\mathrm{HTU}_o)_c \approx (\mathrm{HTU}_o)_d$$

When there is no energy input (and thus little reduction of resistance in the continuous phase), the value of HTU_o ($= V_o/Ka$) for water dispersed is slightly higher than for benzene dispersed, which would tend to agree with the above reasoning.]

For a given total throughput, when either the frequency or amplitude is increased, lower HTU values are generally obtained (Figures 5, 6, and 7). This suggests, as expected, that the addition of mechanical energy enhances turbulence in the continuous phase, increases surface renewal, increases the interfacial area per unit column volume, and as observed visually through the column walls increases the dispersed phase holdup. The lowest height of a transfer unit observed was 0.47 foot when water was dispersed at a total throughput of 65.2 cu. feet per hour sq. feet, frequency of 750 cycles per minute, and amplitude of $\frac{3}{16}$ inch. When benzene was dispersed, the lowest HTU value observed was 0.48 foot at a total throughput at 65.2 cu. feet per hour sq. feet, amplitude of $\frac{3}{16}$ inch, and frequencies of 580 and 750 cycles per minute.

An increase in total throughput, for given values of amplitude and frequency, results in an increase in the HTU_o (Figure 8). This might be explained by noting that HTU_o equals V_o/Ka. Since a constant flow ratio (V_o/V_w) of 2 to 1 is used in the benzene experiments, an increase in total throughput, V_T, results in an increase in V_o and V_w. Apparently the increase in Ka resulting from the increased flow rates, V_o and V_w, is not enough to compensate for the increase in V_o in the expression for the HTU_o. An increase in axial mixing with increase in V_T might also contribute to a slow increase in K.

Similar trends were noted for the MIBK-acetic acid-water system, although the HTU_o values for the no-reciprocation runs were significantly smaller for the MIBK system than for the benzene system. However, in some MIBK experiments, minimums were observed in the HTU_o *vs.* frequency curves as frequency was increased. It was possible to operate at frequencies up to 1100 cycles per minute and total throughputs up to 362 cu. feet per hour sq. feet with the MIBK system, as compared with lower values for the benzene experiments. The lowest HTU observed was 0.45 foot when water was dispersed and transfer was to the continuous phase at a total throughput of 180 cu. feet per hour sq. feet, frequency of 1100 cycles per minute, and amplitude of $\frac{3}{32}$ inch. For transfer to the dispersed phase, $(\mathrm{HTU})_{\mathrm{min}}$ was 0.26 foot at V_T = 180 cu. feet per hour sq. feet, F = 825 cycles per minute, and $A = \frac{3}{32}$ inch. The lowest HTU observed was 0.55 foot when MIBK was dispersed and transfer was to the continuous phase at V_T = 90 cu. feet per hour sq. feet, F = 1100 cycles per minute, and $A = \frac{3}{16}$ inch. For transfer to the dispersed phase, the lowest HTU observed was 0.60 foot at V_T = 247 cu. feet per hour sq. feet (flooding), F = 825 cycles per minute, and $A = \frac{3}{32}$ inch.

To give some idea of how the column performance with benzene and MIBK systems compare, consider the following results at 90.5 cu. feet per hour sq. feet at approximately equal relative reciprocation intensities, for water dispersed and for transfer out of the droplets:

Benzene. (AF) = 109 inches per minute, F = 580 cycles per minute, $A = \frac{3}{16}$ inch. The HTU_o decreased to 0.60 foot from 2.4 feet (at zero reciprocation frequency)

MIBK. (AF) = 103 inches per minute, F = 825 cycles per minute, $A = \frac{1}{8}$ inch. The HTU_o decreased to 0.58 foot from 1.12 feet (at zero reciprocation frequency).

The ratio of organic to water volumetric flow rates of the benzene and MIBK systems is 2 to 1 and 1 to 1, respectively.

The extraction efficiency, η, defined by Equation 4 was plotted as a function of reciprocation intensity, AF. Because of space considerations, only the figure for benzene dispersed in water is given here (Figure 11). For clarity, the data for total throughputs of 122 cu. feet per hour sq. feet are omitted from the figure. As expected, the extraction efficiency increases as reciprocation intensity increases. The trend when water is dispersed is very similar, except that the values of η are about 52% at AF = zero and approach 97% at AF = 140 inches per minute. These results are expected to be dependent upon the particular input solute concentrations used in this study.

Another technique for describing the enhancement in extraction performance (Long and Fenske, 1961) is to plot $[(H/\mathrm{HTU}) - (H/\mathrm{HTU})_{AF=0}]$ *vs.* AF (see Figure 12 for the data for benzene dispersed). A log-log plot (not shown here) of the same data tends to suggest the following approximate relation

$$[H/\mathrm{HTU}) - (H/\mathrm{HTU})_{AF=0}] \propto [AF]^{1.4}$$

although this form of a relation does not appear to agree

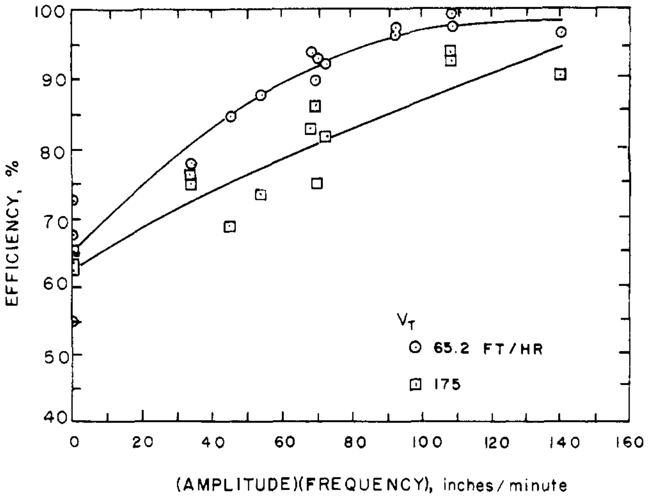

Figure 11. Relative effect of intensity of reciprocation on efficiency with benzene dispersed

very closely with the trends shown in Figure 12 as AF increases.

Experimental Correlations of Benzene Data. The experimental mass transfer data (HTU's) for the benzene–acetic acid–water system were empirically correlated by the least-squares technique.

$$\mathrm{HTU}_o = \phi\ (A,\ F,\ V_o,\ V_u,\ \text{choice of phase dispersion}) \quad (8)$$

for the given extraction column and physical system. Since a 2 to 1 ratio of V_o to V_u was maintained in this study, Equation 8 is reduced to

$$\mathrm{HTU}_o = \phi\ (A,\ F,\ V_T) \quad (9)$$

where $V_T = (V_o + V_u)$.

Initially, several modifications of the following dimensional form were employed:

$$\mathrm{HTU}_o = b_1 + b_a A + B_3 A^2 + b_4 F + b_5 F^2 + b_6 V_T + b_7 (V_T)^2 \quad (10)$$

with the following relations recommended for benzene and water dispersed, respectively:

$$(\mathrm{HTU}_o)_d = 1.54 - 16.3\ A^2 - 0.0010\ F + 0.00280\ V_T \quad (11)$$

$$(\mathrm{HTU}_o)_c = 1.95 - 23.2\ A^2 - 0.00170\ F + 0.00455\ V_T \quad (12)$$

Equations 11 and 12 represent the data with an average absolute percentage deviation (AAPD) of 11 and 15%, respectively.

The data were also correlated by the following dimensional forms for benzene and water dispersed, respectively.

$$(\mathrm{HTU}_o)_d = 1.48 - 0.0064\ F(A^{0.74}) + 0.00274\ V_T \quad (13)$$

$$(\mathrm{HTU}_o)_c = 1.86 - 0.0076\ F(A^{0.60}) + 0.00443\ V_T \quad (14)$$

with AAPD s of 14 and 19%, respectively.

Finally, dimensional analysis suggests the following relations between dimensionless groups:

$$\frac{H}{\mathrm{HTU}_o} = \phi\left[\frac{AF}{V_T}\right] \quad (15)$$

where H, the height of packing, is included even though it was not varied in this work. The dimensionless group (AF/V_T) is similar to the pulse velocity group used by Krasuk and Smith (1964) in an interesting study of mass transfer from solid particles (the stationary packing) in a pulsed column of usual design. The dimensionless group H/HTU_o is the number of transfer units.

Two functional forms were assumed for Equation 15. The first functional form was applied only to the data with pulsating energy input, and the results are given as follows for benzene and water dispersed, respectively:

$$\frac{H}{(\mathrm{HTU}_o)_d} = 1.1\left(\frac{AF}{V_T}\right)^{0.55} \quad (16)$$

In Equations 16 to 19, the units of A and F are feet and cycles per hour, respectively.

$$\frac{H}{(\mathrm{HTU}_o)_c} = 0.94\ \left(\frac{AF}{V_T}\right)^{0.65} \quad (17)$$

with AAPD's of 12 and 15%, respectively.

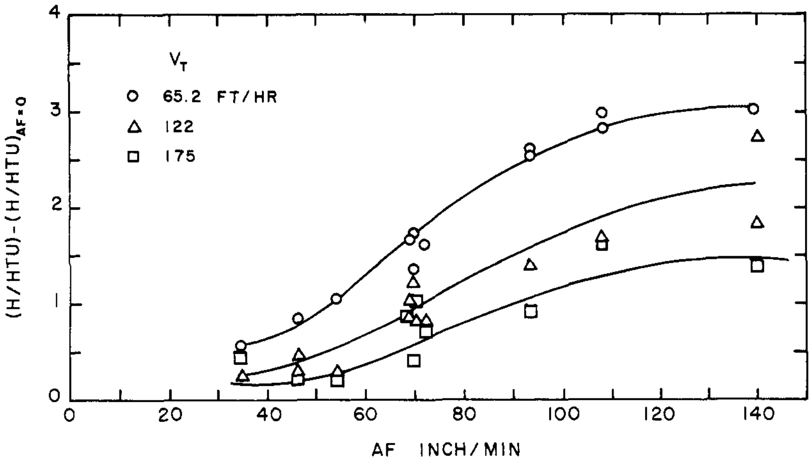

Figure 12. Enhancement of column performance due to reciprocation

Benzene dispersed. Benzene system

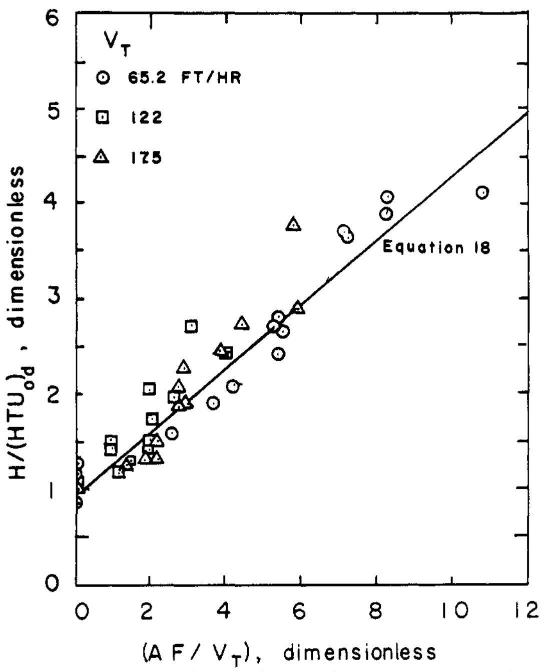

Figure 13. Number of transfer units (H/HTU) as a function of pulse velocity group (AF/V_T)

Benzene dispersed. Benzene system

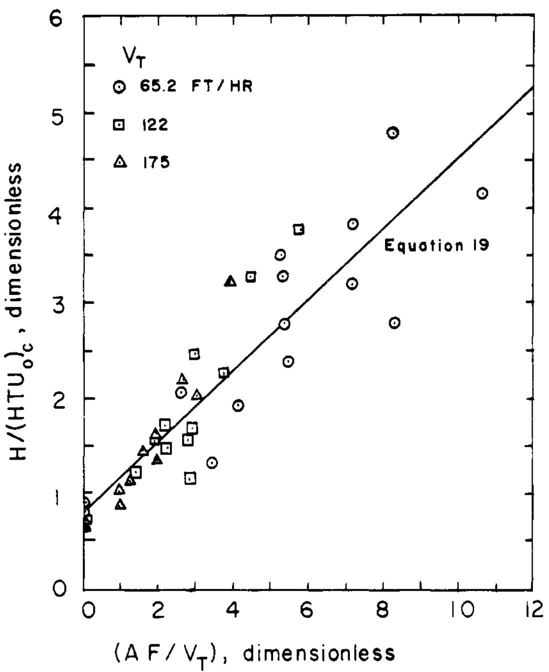

Figure 14. Number of transfer units (H/HTU) as a function of pulse velocity group (AF/V_T)

Water dispersed. Benzene system

The following functional forms were applied to the data for both pulsating and nonpulsating energy input, and the results are given as follows for benzene and water dispersed, respectively:

$$\frac{H}{(\text{HTU}_o)_d} = 0.98 + 0.33 \left(\frac{AF}{V_T}\right) \tag{18}$$

$$\frac{H}{(\text{HTU}_o)_c} = 0.78 + 0.37 \left(\frac{AF}{V_T}\right) \tag{19}$$

with AAPD's of 11 and 14%, respectively. The above relations (Equations 18 and 19) are recommended for preliminary design purposes in view of their simplicity, relative accuracy, and ability to describe nonpulsating runs; these two equations are plotted on the appropriate figures of experimental data for the benzene system previously included in this report (Figures 5 to 8).

The extraction data for the benzene system are also presented in dimensionless form in Figures 13 and 14.

Comparisons with Other Columns

The performance of the reciprocated wire mesh extraction column developed in this work is compared with the performance of a number of other extractors in Tables I and II for the MIBK-HAc-H_2O and benzene-HAc-H_2O systems.

MIBK. For comparison, the calculated over-all HTU's were converted to HETS's, as most of the designs of mechanically aided columns were continuous stagewise equipment rather than continuous differential contactors. In some instances, performance data were obtained at considerably higher acetic acid concentrations than that used in this work.

With the exception of the case of transfer into the dispersed phase, other types of equipment offer generally lower HETS values than those obtained with the reciprocated wire mesh contactor developed in this work. For transfer into the dispersed phase (either water or MIBK), the lowest HETS for this work occurred at high throughputs, resulting in significantly higher volumetric efficiencies (V_T/HETS) than those available with other extractors reported in the literature (Table I). Depending upon the choice of phase dispersion or direction of transfer, the values of the volumetric efficiency for this extractor at the lowest HETS were about 1.5 to 4 times larger than those reported for the closest competitor. This excellent performance is primarily a result of the very high throughputs possible with this column.

The flooding flow rates attained with the column developed in this work are, in general, much greater than for other columns. With water dispersed (depending on the direction of transfer), the flooding rate was about 10 to 20% greater than the controlled cycling sieve plate contactor (which appears to have the highest flooding rate for the MIBK system reported, prior to the development of this column). Flooding performance for the case with MIBK dispersed is even better from a competitive standpoint—V_T being almost a factor of 5 times greater than that for the Oldshue-Rushton (1952) extractor, which has the next best flooding performance. Under flooding conditions, the volumetric efficiencies for this column are significantly greater than for all other extractors, with the possible exception of the extractor of Karr (1959).

Benzene. The reciprocated wire mesh extractor has a higher volumetric efficiency (V_T/HETS) when evaluated at the lowest HETS value than all other contactors described in Table II. The values of the volumetric efficiency calculated at the lowest HETS for this extractor are about 2.5 times larger than those for the rotating disk-blade contactor of Tudose (1962). The pulsed-packed column (Potnis *et al.*, 1959) and in one case the disk-blade contactor (Tudose, 1962) have lower HETS's than those obtained in this work; however, the operable flow rates in the reciprocated wire mesh contactor are about five times greater than those reported for the pulsed-packed column at the minimum HETS values and nearly

Table I. Comparison of This Work with Reported Performance of Mechanically Aided Extractors Utilizing MIBK–Acetic Acid–Water System

				Performance at Onset of Flooding			Performance at Lowest HETS		
Type of Column	*Column Diam., Inches*	*Dispersed Phase*	*Direction of Transfer*	$(V_T)_F$, *cu. ft./(hr., sq. ft.)*	*HETS, ft.*	$(V_T)_F$/*HETS, hr.*$^{-1}$	V_T, *cu. ft./(hr. sq. ft.)*	*HETS, ft.*	(V_T)/*HETS, hr.*$^{-1}$
Rotating disc									
(Reman and Olney, 1955)	8.0	H_2O		138	0.53	262	131	0.36	364
Turbine agitator, horizontal baffles									
(Scheibel, 1956)	11.5	H_2O					61.2	0.25	245
Alternate agitated and packed sections									
(Scheibel and Karr, 1950)	11.5	H_2O	d→c	79.5	0.67	119		0.77	
Controlled-cycling sieve plate									
(Szabo *et al.*, 1964)	2.0	H_2O		304	1.17	260		0.54	
Reciprocating plate	3.0	H_2O	d→c	246	0.63	390	80.2	0.43	187
(Karr, 1959)			d←c	228	0.65	351	73.1	0.36	203
Reciprocating wire mesh packing	3.0	H_2O	d→c	382	1.55	247	183	0.62	295
(This work)			d←c	380	0.97	392	183	0.37	495
Turbine agitators in baffled compartments	6.0	MIBK	d→c	66.8	0.46	146	38.2	0.31	123
(Oldshue and Rushton, 1952)			d←c						
Pulsed packed									
(Chantry *et al.*, 1955)	1.57	MIBK	d←c	19.9	0.43	47			
Pulsed sieve-tray									
(Chantry *et al.*, 1955)	1.57	MIBK	d←c	35.6	0.77	46	19.2	0.33	58
Pulsed spray									
(Billerbeck *et al.*, 1956)	1.5	MIBK	d←c	123	1.21	102	105	0.92	114
Reciprocating wire mesh packing	3.0	MIBK	d→c	310[a]	1.72	180	259	0.96	270
(This work)			d←c	407	1.58	258	349	0.82	426

[a] *No mechanical agitation.*

Table II. Comparison of This Work with Reported Performance of Mechanically Aided Extractors Utilizing Benzene–Acetic Acid–Water System

				Performance at Lowest HETS				
Type of Extractor	*Extractor Diam., Inches*	*Dispersed Phase*	*Direction of Transfer*	V_T, *ft.*^{3}/*hr. ft.*^{2}	*HTU, ft.*	*HETS, ft.*	V_T/*HETS, hr.*$^{-1}$	*Comments*
Spray column								
(Sherwood *et al.*, 1939)	3.55	C_6H_6	d←c	90	3.0	11.3	8.0	
Packed column								
(Sherwood *et al.*, 1939)	3.55	C_6H_6	d←c	30	2.0	7.55	4.0	[a]
			d←c	90	2.4	9.04	10.0	[b]
		C_6H_6	d←c	52	2.9	9.9	5.2	[c]
		H_2O	d→c	40	3.4	14.1	2.8	[d]
			d→c	60	5.2	16.3	3.7	[e]
Pulsed-packed								
(Potnis *et al.*, 1959)	1.25	C_6H_6	d←c	12.5	0.41	1.08	11.6	
Rotating disk with blades								
(Tudose, 1962)	2.84	C_6H_6	d←c	26.6	0.62	1.84	14.5	
			d→c	21.5	0.36	1.02	21.0	
Reciprocated wire mesh packing								
(this work)	3.0	C_6H_6	d←c	65	0.48	1.27	52.1	
		H_2O	d→c	65	0.47	1.24	52.3	

[a] *Run 3, ½-inch carbon rings.* [b] *Run 32, 1-inch carbon rings.* [c] *Flooding.* [d] *Run 16, ½-inch carbon rings, $V_u/V_o = 3$.* [e] *Run 18, ½-inch carbon rings, $V_u/V_o = 1$.*

three times greater than for the column designed by Tudose (1962). The spray and packed columns (Sherwood *et al.*, 1939) have flow rates comparable to those attained in the column described in this work (at the minimum HETS value), but the minimum HETS's are at least six times greater than those for the reciprocated wire mesh extractor.

Using the benzene system, the largest values of the volumetric efficiency (V_T/HETS) attained with this extractor of nonflooding conditions were 110 hours^{-1} for water dispersed (at V_T = 178 cu. feet per hour sq. feet, A = 3/16 inch, F = 750 cycles per minute, and HETS = 1.61 feet) and 93.2 hours^{-1} for benzene dispersed (V_T = 178 cu. feet per hour sq. feet, A = 3/16 inch, F = 580 cycles per minute, and HETS = 1.91 feet). This may be compared with values of the volumetric efficiency for this extractor of about 52 hours^{-1} at the lowest HETS values of about 1.24 feet. The largest values of V_T/HETS for this column appear to be about four times larger than reported values for other contactors using the benzene–acetic acid–water system.

Unfortunately, flooding data for the columns described in the literature (using the benzene system) are almost nonexistant. Flooding rates observed for the packed columns (Sherwood *et al.*, 1939) were approximately 100 cu. feet per hour sq. feet, about one half the flooding throughputs observed for the reciprocated wire mesh contactor developed in this work.

Under incipient flooding conditions, the largest values of V_T/HETS attained with this extractor were 182 hours^{-1} for water dispersed (at V_T = 179, HETS = 1.05 feet, AF = 705 feet per hour). These values of V_T/HETS appear to be about eight times larger than reported values for other contactors using the benzene–acetic acid–water system.

Other Systems. Extreme care should be taken when comparing the performance of various types of contactors using different extraction systems. However, the following results for "difficult to extract" systems are of interest. Treybal (1964) designed a mechanically agitated extractor and reports the following performance using the kerosine-butylamine-water system: at V_T/HETS = 147 hours^{-1}, V_T = 74.8 cu. feet per hour sq. feet, and HETS = 0.51 foot. Karr (1959) using a reciprocating plate contactor and the *o*-xylene–acetic acid–water system reports the following: V_T/HETS = 142 hours^{-1} at a value of V_T = 107 cu. feet per hour sq. feet and HETS = 0.76 foot.

Summary

An extractor with reciprocated wire mesh packing was developed. Its performance was analyzed using the MIBK–acetic acid–water and the benzene–acetic acid–water systems. The effect of such variables as reciprocation frequency and amplitude, total throughput, phase dispersion, and direction of mass transfer were studied. It was possible to correlate the number of transfer units satisfactorily for the benzene systems with a linear function of the pulse velocity group (AF/V_T).

The liquid handling capacity of this extractor is much greater than that reported for other extractors using these liquid extraction systems. At flooding conditions, the total throughput is 1.3 to 3 times higher than the closest competitor using the MIBK system and 1.4 to 6 times greater when measured at the conditions which give the lowest HETS.

The mass transfer performance of this contactor in terms of the lowest HETS observed is not as good as for several other contactors; however, in practice this may be compensated for by the ability to achieve very high flow rates.

For both extraction systems, the volumetric efficiencies (V_T/HETS) observed are much higher, in general, than those reported for all other extractors. In some cases, volumetric efficiencies under nonflooding conditions are four times higher than the performance of the nearest competing extractor, using either of these two extraction systems.

Nomenclature

a = interfacial area per unit of contactor volume, cu. feet per sq. feet
A = reciprocation amplitude, inches (unless stated otherwise)
b_n = empirical constants in Equation 10, n = 1 to 7
E = extraction factor defined by Equation 6
F = reciprocation frequency, cycles per minute (unless stated otherwise)
H = contactor height, feet
HETS = height equivalent to a theoretical stage, feet
HTU_o = over-all height of a transfer unit, feet
k = constant in equilibrium curve, weight fraction
K = over-all mass transfer coefficient, feet per hour
m = constant in equilibrium curve, dimensionless
P = choice of dispersed phase
V = superficial volumetric flow rate, cu. feet per hour sq. feet
V_T = total volumetric flow rate (= $V_o + V_w$), cu. feet per hour sq. feet
x = weight fraction of solute in aqueous phase, dimensionless
y = weight fraction of solute in organic phase, dimensionless
y^* = weight fraction of solute in organic phase which could be in equilibrium with x_2

Greek Letters

η = extraction efficiency defined by Equation 4
σ = interfacial tension, dynes per cm.
ρ = density, pounds per cu. foot
$\Delta\rho$ = density difference, grams per cc.

Subscripts

F = flooding conditions
1,2 = input and output compositions of aqueous phase, respectively
o = organic phase
w = aqueous phase
c = continuous phase
d = dispersed phase

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BENEFICIATION OF FLORIDA HARD-ROCK PHOSPHATE

Selective Flocculation

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Beneficiation of Florida hard-rock phosphate has been limited to washing and screening the ore to recover the plus 20-mesh fraction which contains about 40% of the P_2O_5. Attempts were made to recover phosphate from the smaller fractions. Flotation of the sand was impractical because the phosphate was too soft. Preferential grinding followed by selective flocculation proved to be a technically feasible method for recovering an additional 40% of the ore P_2O_5. The product, on a dry basis, contained 32% P_2O_5 and 7% R_2O_3. This high R_2O_3 content and the cost of dewatering (40% H_2O) probably would make recovery under present conditions unfavorable.

THE hard-rock phosphate field in northwest Florida extends from Suwannee and Columbia Counties southward to Citrus and Hernando Counties, an area approximately 100 miles long and varying from 2 to 30 miles in width (Kibler, 1941, 1944). The phosphate deposits are irregular in shape and scattered. They range up to several acres in area and from a few up to 100 feet in thickness and lie under overburden ranging in thickness from a few to 100 feet. The phosphate occurs as coarse sand, pebbles, and boulders interspersed with quartz sand and clay (Kibler, 1941, 1944). About 40% of the P_2O_5 can be recovered in the plus 20-mesh material as a high-grade concentrate (up to 38% P_2O_5). However, the hard rock is more costly to mine than pebble ore (Ruhlman, 1958) and, as a result, there is no commercial production at present.

This paper gives detailed information on the composition and size distribution of ore from a number of hard-rock phosphate deposits and describes tests of the feasibility of recovering the phosphate from the minus 20-mesh fines.

One third of the minus 20-mesh phosphate was in the sand fraction (−20 +325 mesh) and two thirds was in the slime. Flotation of the sand was found to be impractical because the phosphate was too soft. Preferential grinding followed by selective flocculation (Haseman, 1951) proved to be a technically feasible method of recovering an additional 40% of the ore P_2O_5. However, the quality of the concentrate and the cost of dewatering it probably would make recovery under present conditions economically unfavorable.

Composition and Properties of Ore

Most of the experimental work was done on core samples taken while prospecting various deposits of the hard-rock phosphate in a systematic manner. Core samples from each drill hole were combined in the proper proportions to yield a representative hole sample. Ore from each hole was classified as minable or marginal on the basis of the amount and grade of phosphate in the plus 20-mesh fraction, the ratio of overburden to ore, and the continuity of the ore body. The hole samples then were combined to yield respresentative samples of the minable and marginal ore occurring in a 40-acre tract of land. Ore from 29 tracts scattered over that portion of the field lying

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