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PERFORMANCE OF A PULSE EXTRACTION
COLUMN

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PERFORMANCE OF A PULSE EXTRACTION COLUMN¹

R. M. Cohen and G. H. Beyer

ABSTRACT

A continuous countercurrent liquid-liquid extraction column containing perforated plates was operated with a pulsed liquid phase. The effects of operating variables upon extraction efficiency and column capacity were investigated. A 1-in. Pyrex tube, 20-in. long, served as the column in which an assembly of 10 perforated plates were supported at 2-in. intervals. Each plate contained fifty-three, 0.040-in. perforations, representing 9 per cent of the plate area. Cyclic pulsations were imparted to the liquid in the column through a tee in the stream entering at the bottom by means of a cam-driven bellows pulsator and a diaphragm pump with checks removed. The function of the pulsations was to produce counterflow of both phases through the plate perforations and to provide a high degree of dispersion and turbulence by the continuous formation of fresh interfacial surface.

Extraction runs were made using the system: water-boric acid-isoamyl alcohol, where the direction of boric acid transfer was from the alcohol to the water phase. Efficiencies were expressed in terms of the height of a transfer unit and the height equivalent to a theoretical stage, where the number of theoretical stages were calculated by the McCabe-Thiele method. Over-all heights of a transfer unit as low as 5.7 inches were obtained with water as the continuous phase. Capacities as high as 660 gal./sq ft./hr. were achieved. In general, pulse column operation was found to be most efficient at high alcohol flow rates and moderate to high pulse frequencies (35 to 72 cycles/min.)

INTRODUCTION

Continuous liquid-liquid extraction processes have been used industrially to great advantage as a means of chemical separation and purification where operations such as distillation or adsorption are impractical.

¹ This report is based on a Master's thesis by R. M. Cohen, submitted December, 1952.

Equipment design for continuous countercurrent extraction is largely based upon various methods for obtaining a high interfacial area between the two contacting liquids. Greater efficiency or improved mass transfer is usually achieved by increasing the degree of mixing of the two phases. In spray columns, this is brought about by dispersing one liquid as droplets in the second liquid, while packed columns increase the turbulence of flow and the film surface area by utilizing packing. Mixer-settler equipment takes advantage of stage-wise contact in alternate mixing and settling units, whereas perforated-plate towers are essentially vertical mixer-settlers in which successive dispersion and coalescence is accomplished by perforated plates. In the latter, as well as in spray, packed, and baffle-type columns, low stage efficiencies are encountered due to the poor mixing resulting from counterflow of the two phases past each other by virtue of their density difference alone.

Recently, various mechanically-powered devices having higher throughputs and efficiencies than conventional extraction columns have been built. The Podbielniak centrifugal contactor utilizes a high-speed rotor containing a perforated spiral ribbon for mixing and separating the two liquids, while the Scheibel column consists of alternate mixing and coalescing zones in a vertical tower fitted with a central rotating shaft on which agitators are mounted in the mixing sections. The presence of moving mechanical parts in these and other powered-contactors, poses repair, leakage, and servicing problems which are particularly objectionable if radioactive or highly corrosive solutions are to be processed.

In a patent by Van Dijck (13), a perforated-plate column is described in which the entire plate assembly is vibrated vertically to increase agitation between the two immiscible liquids. The same patent suggests the use of fixed plates and a pulsed liquid phase. This latter modification has been designated as a "pulse column" (2). Several atomic-energy installations have built and operated such perforated-plate pulse columns, but the details have not been published (2,4,6,8,10,11). Feick and Anderson (5) studied the performance of a packed extraction column in which reciprocal motion was imparted to both liquids by means of an eccentric-driven diaphragm at the base of the column. Similar work with a packed pulse column has been performed by Von Berg and Wiegandt (14) at Cornell University.

Their results indicate that the column height required to effect a given extraction is reduced by a factor of five, in some instances, under pulsating conditions. No performance data for perforated-plate pulse columns were found in the unclassified literature.

The plate perforations in a pulse column are small enough so that counterflow of the two phases will not occur because of gravity alone, but an additional force must be applied to overcome the resistance to flow. A cyclic pulse, usually imparted to the light-liquid stream entering the bottom of the column, produces alternate surges of liquid in both directions. Thus countercurrent flow occurs because of density difference in the region between successive plates and because of mechanical pulsing through the plate perforations.

Between pulsations at low pulse frequencies the two phases separate into two distinct layers in each section between adjacent plates. On the upsurge of the pulse cycle the lighter phase beneath each plate is dispersed into the heavier phase above each plate. The droplets rise through this layer and coalesce beneath the plate above. On the downsurge the heavy phase is dispersed downwards through the lighter layer in a similar fashion. Since fresh surface is created with each pulse, mass transfer rates will be greater than for a similar packed or spray column. At higher pulse frequencies re-coalescence between pulses is incomplete, and the degree of dispersion and turbulence are both increased, resulting in higher extraction efficiencies. Greater throughputs are also obtainable since the reduction in droplet size (due to more frequent plate impacts) inhibits dispersed phase coalescence, thus preventing column flooding. By proper combinations of pulse displacement and frequency, a great variation in flow behavior may be achieved. Changes in these variables may be likened to changes in the packing characteristics for packed columns.

The choice of operating and design variables for carrying out a particular extraction in a new apparatus such as a pulse column would ordinarily necessitate a tedious trial-and-error procedure. The major purpose of this investigation was to study the operation and performance of a pulse column as a function of flow rates, pulse amplitude and frequency, capacity, and column hold-up with a convenient test system: water-boric acid-isoamyl

alcohol. The performance data thus obtained may then be used as a basis in predicting optimum operating conditions for other systems having different physical properties by suitable interpretation of the effects of interfacial tensions, density differences and viscosities.

Because of encouraging results with pulse columns in connection with extraction work in the atomic-energy program (2,4,6,11), the construction and investigation of a laboratory-scale pulse column was undertaken. Its potential commercial applications as a highly efficient and versatile extractor having high throughput capacities and combining simplicity of operation with a minimum of maintenance make this performance study all the more desirable.

INVESTIGATION

Description of Apparatus

Physical description

A 20-inch section of 1-inch Pyrex pipe with two 4-inch flanged end sections, 1 1/2 inches in diameter, was assembled and fitted with Saran end plates containing standard 1/4-inch Saran threaded fittings. A central 1/8-inch Lucoflex rod, supporting 10 Lucoflex plates separated at 2-inch intervals by means of 5 mm. glass tubing, was inserted in the 20-inch section of the column. The 1-inch diameter Lucoflex discs were punched from 1 mm. sheet and drilled with fifty-three 0.040 inch perforations per plate. This corresponded to approximately 9 per cent free area. All gaskets were of Teflon or Polythene, and all tubing was either glass, Tygon, Saran or Fluorothene. All metal parts including valves were of stainless steel.

The pulse column and auxiliary equipment are shown in Figure 1. A nitrogen cylinder (A) was used to pressurize a 10-gallon glass-lined steel tank (B) containing isoamyl alcohol-boric acid feed solution. The alcohol feed was metered by means of a rotameter and needle valve (C) before entering a diaphragm pump pulsator (D). By maintaining a pressure of 10 psig. on the feed tank, pulsation of the rotameter float was kept to a minimum. Since the top of

FIG. 1 PHOTOGRAPH OF PULSE COLUMN AND AUXILIARY EQUIPMENT

the column was open to the atmosphere, only the liquid in the column and in the section between the diaphragm pump (D) and the feed entrance (E) was pulsed. A perforated inlet tube at the feed entrance served to disperse the pulsed liquid. The alcohol raffinate stream left the settling section at the top of the column through an overflow tube (F). The heavy liquid, distilled water, was metered through a needle valve and rotameter (G) from an overhead 15-gallon carboy. Since this line was not pulsed, pressurizing was unnecessary and flow was maintained by a hydrostatic head of about ten feet. The water then entered the top of the column (H), and the aqueous extract stream was taken off through a flexible leg (J) consisting of a section of Tygon tubing leading from the bottom of the column to a "Y" connection which was open to the atmosphere and another length of Tygon tubing from the open "Y" down to the receiving vessel. The position of the interface was controlled by varying the height of the flexible leg which changed the ratio of the phase volumes in the column.

For the majority of the runs a diaphragm proportioning pump was used as the pulsator. The inlet and outlet checks were removed from one of the Saran reagent heads of a Proportioners Duplex Heavy Duty Chem-O-Feeder (Model 2-47) in order to produce alternate surges of liquid in both directions. Pulse amplitudes were varied between 0.10 and 0.60 inches by turning a stroke-length adjusting knob. A 3-step cone pulley and belt, connected to a 1/4 HP induction motor, gave pulse frequencies of 17, 35.5 and 72 cycles per minute.

Another pulsator unit was built in order to provide a greater range in pulse amplitude and a continuously-variable frequency control. This mechanism, shown in Figure 2, consisted of a 4.7-inch diameter Fulton-Sylphon brass bellows actuated by a motor-driven cam via a lever. Pulse amplitudes were varied between 0.10 and 2.00 inches by means of a screw control which determined the position of the fulcrum under the lever. A Graham variable-speed transmission was utilized to select the desired frequency. In order to prevent contact of the column liquids with the brass bellows, a diaphragm assembly containing a 7-inch diameter Polythene-lined, Neoprene diaphragm was inserted in the line between the bellows and the column. The bellows-side of the assembly was water-filled so as to transmit the pulse, hydraulically, to the diaphragm without dampening due to secondary pulsations. This unit was satisfactorily

FIG. 2 CAM-DRIVEN BELLOWS PULSATOR

used at low pulse frequencies (17 cycles/min.). However, the output torque of the transmission at higher speeds was not great enough to overcome the inertia of the bellows. Consequently, the diaphragm proportioning pump was used in the runs made at 35.5 and 72 cycles/min.

A similar 1 1/2-inch bellows-diaphragm pulsator was utilized earlier in the investigation. This was actuated by a midget air cylinder operated through an automatic air timer. Because of difficulties in controlling the stroke length, this method of pulsing was abandoned in favor of the cam-driven bellows and the diaphragm pump.

Description of operation

The plate perforations in a pulse column are made small enough so that countercurrent flow under non-pulsating conditions is prevented. This resistance to flow is a function of the plate-wetting characteristics of the system as well as the perforation diameter. Flow through such holes results in a pressure drop which is greater than the pressure drop due to density difference. Thus, imparting a cyclic pulse to the liquids provides the "extra-gravitational" force needed to produce countercurrent flow.

The two phases separate into two distinct layers between pulsations, in each section between adjacent plates, when the column is operated at low pulse frequencies. This condition is shown in Figure 3. The lighter phase beneath each plate is dispersed into the heavier phase above the plate on the upward pulse, and the heavier phase is dispersed downwards into the lower section on the downsurge of the pulse cycle. Neither phase may be considered truly continuous in the column as both move countercurrently from plate to plate by alternate dispersion and recalescence. At higher pulse frequencies recalescence between pulses is incomplete, and the distinction between continuous and discontinuous phases becomes more apparent. Although operation at higher pulse frequencies may appear undesirable from the standpoint of creating less fresh surface per pulse (because of incomplete recalescence) than at low frequencies, the use of higher frequencies is justified by the large increase in the degree of dispersion and turbulence resulting in higher extraction efficiencies. The

FIG. 3 CLOSE-UP OF COLUMN, SHOWING SEPARATION OF PHASES

throughput capacity is also increased at higher frequencies because the tendency towards dispersed phase coalescence (and hence, column flooding) is diminished. The limiting operating conditions are defined by flooding at low pulse frequencies and amplitudes, and emulsification at very high frequencies.

The length of time during which a unit volume of one phase is in dispersed contact with the other phase is always less in a pulse column than in a spray column of the same dimensions operating at the same flow rates. Clearly, pulse column contact time (during which extraction occurs) is equal to spray column contact time multiplied by the fraction of the pulse cycle during which dispersion takes place. Defined in this manner, contact time does not include periods of re-coalescence since the contribution to mass transfer under quiescent conditions is negligible. Thus, the greater efficiency of the pulse column over that of the spray column must be attributed to the continuous formation of fresh surface as well as the high degree of dispersion and turbulence through the plate perforations, rather than increased contact time in the column.

The pulse wave shape also has been shown to have a significant effect on extraction efficiency (6). A sharp pulse with a relatively long time between pulses is more desirable than a sine wave cycle since the former results in more violent dispersion through the plates and allows more time for re-coalescence. Such a "semi-square" wave may be obtained with a cam-driven bellows or an air-actuated bellows pulsator, whereas the pulse wave generated by a diaphragm pump is approximately sinusoidal.

Operating Procedure

The feed tank was filled with isoamyl alcohol-boric acid solution made up to a concentration of approximately 0.008 g./ml. of boric acid. The distilled water valve was opened and the pulsator was started in order to fill the column with the continuous phase. When the liquid level in the column was near the top of the 1-inch diameter section, the liquid flow was shut off and the pulse amplitude was adjusted by measuring the total linear displacement of the upper interface. Pulse amplitudes were checked

similarly at the completion of each run. The feed tank was then pressurized to 10 psig. with nitrogen, and both flow rates were regulated by stainless steel needle valves. Calibrated rotameters were used for metering both liquids, while the flow rates were more accurately adjusted during the early part of each run by timing measured volumes of the effluent streams. Since the distilled water solvent was previously saturated with pure isoamyl alcohol and the alcohol feed was saturated with water, no significant volume changes took place during extraction. The interface was maintained at a constant level by adjusting the height of the flexible aqueous take-off leg. Steady-state operation was achieved after 4-5 changeovers of the continuous phase. Samples were collected from both effluent streams 3 hours after start-up to insure the attainment of equilibrium conditions.² For the low-flow fluid (water), a 3-hour run permitted 5-6 changeovers at 10 cc./min., and 12-14 changeovers at 25 cc./min. Both flows were then shut off and the pulsator disconnected while the column was drained into a graduated cylinder in order to measure the ratio of phase volumes in the column. The liquid in the end sections was included in the holdup inventory, and as such the values obtained were not true holdup ratios. However, since the phase volumes in the end sections remained constant throughout the runs, the measured volume ratios were proportional to the actual holdup ratios and served to indicate the trends in this variable with changes in the other parameters.

Calculation of Efficiency of Transfer

Performance data for design purposes may be expressed in terms of H.E.T.S. (height equivalent to a theoretical stage) or HTU (height of a transfer unit). While H.E.T.S. varies considerably with the properties of the system in an unpredictable manner, HTU data are correlated somewhat better since this method is inherently more consistent with the actual extraction picture. However, the practicality of HTU correlational procedures is limited because of the lack of experimental data on individual film transfer coefficients and film HTU's. Thus, although the H.E.T.S. concept is fundamentally unsound when applied to operations where the concentration changes differentially with height, it is used extensively in practice for designing continuous extraction equipment since H.E.T.S. values are more easily computed than HTU's.

²

Analysis for boric acid was by the procedure recommended by Kolthoff and Sandell (7).

In this investigation values of H.E.T.S. were used to express extraction efficiencies. Over-all HTU's were also calculated for comparative purposes. Since the equilibrium line was shown to be straight (1), and the operating line was assumed to be straight when using alcohol saturated with water and water saturated with alcohol, an analytical solution of the McCabe-Thiele method was used in order to give more accurate results than the usual graphical procedure (1,9,12). The following equations were used for the special case of solute-free solvent with the operating line above the equilibrium line (extraction from alcohol into water):

$$n = \frac{\log \left[1 - \left(\frac{y_2}{y_1} - 1 \right) \left(\frac{m}{a} - 1 \right) \right]}{\log \left(\frac{a}{m} \right)} \quad (1) \text{ where } a \neq m.$$

$$n = \frac{y_2}{y_1} - 1 \quad (2) \text{ where } a = m$$

In the above equations,

n = number of theoretical stages
 a = slope of operating line determined by analysis
 m = slope of equilibrium line = 0.2909
 y = concentration of boric acid in alcohol phase
 The subscripts 1 and 2 refer to the lower and higher concentrations, respectively.

H.E.T.S. values were calculated by dividing the number of theoretical stages thus obtained into the column height. Over-all HTU's were computed directly from values of H.E.T.S. by the following relations which are valid only for straight operating and equilibrium lines:

$$(\text{HTU})_{\text{OG}} = \frac{\left(\frac{m}{a} - 1 \right) (\text{H.E.T.S.})}{\ln \left(\frac{m}{a} \right)} \quad (3) \text{ where } a \neq m$$

$$(\text{HTU})_{\text{OL}} = \left(\frac{a}{m}\right) (\text{HTU})_{\text{OG}} \quad (4) \text{ where } a \neq m$$

$$(\text{HTU})_{\text{OG}} = (\text{HTU})_{\text{OL}} = \text{H.E.T.S.} \quad (5) \text{ where } a = m$$

In the above equations the subscripts OG and OL refer to over-all values based on the dispersed and continuous phases, respectively.

Performance Data

Experimental runs were planned in such a way that the effect of each variable on column performance was investigated separately in a series of runs in which the other variables were held constant. In order to cover the entire range of column operation adequately, the method of attack was to study each variable between its minimum and maximum allowable values for representative low, moderate and high values of the other parameters. Several preliminary runs were made to study flooding behavior under various flow and pulse conditions so that operating limits might be approximated beforehand and extraction runs planned accordingly.

Effect of flow rates

Three series of extraction runs were made in which alcohol (dispersed) flow rates were varied over the entire permissible operating range at constant pulse conditions of 17 cycles/min. and 0.35 inches amplitude. Although the alcohol phase recombined between pulsations into a layer 1/4 - 1/2 inch thick beneath each plate, it was for the most part in a state of dispersion. The three sets of runs were made at constant aqueous phase flow rates of 10, 25, and 50 cc./min., respectively and the maximum alcohol flow rate in each series was just below that producing incipient flooding in the aqueous effluent stream.

Extraction as well as holdup data for these runs are presented in Table 1 where holdup ratios are defined as: volume of discontinuous phase/volume of continuous phase in the column. The results of two similar series of runs made at 72 cycles/min. and 0.20 inches amplitude, for constant continuous phase flow rates of 10 and 25 cc./min., are presented in Table 2.

Figures 4 and 5 show the effect of dispersed phase flow rate on H.E.T.S. at both high and low pulse frequencies for continuous phase flow rates of 10 and 25 cc./min., respectively. These data were also correlated in terms of over-all HTU's, which were plotted in Figure 6 as $(HTU)_{OG}$ versus the ratio of the slope of the equilibrium line to that of the operating line, on logarithmic coordinates. The slope of the operating line was determined by analysis. Since the slope of the equilibrium line is constant ($m = 0.2909$), Figure 6 essentially indicates the dependence of $(HTU)_{OG}$ upon the flow ratio G/L raised to some power. Pulse conditions, as a parameter in such a plot, are entirely analogous to the "packing characteristics" parameter frequently used in similar correlations of packed column performance data. It is to be noted in Figure 6 that, whereas the data at the high pulse frequency appear to be a unique exponential function of G/L regardless of individual flow rates, the data at the lower pulse frequency seem to group into separate lines, each representing a constant continuous phase flow rate. At 72 cycles/min. and 0.20 inches amplitude, the data are best expressed by the equation:

$$(HTU)_{OG} = 8.32 (G/L)^{0.39} \text{ inches.} \quad (6)$$

Figure 7 shows the effect of flow rates on volumetric holdup ratio. An increase in either flow rate increases the dispersed phase holdup, and flooding is approached rapidly with an increase in dispersed phase flow rate at high continuous phase flow rates. Thus for $L = 50$ cc./min. flooding occurred at $G = 45$ cc./min., while for $L = 10$ cc./min. values of G as high as 125 cc./min. were obtained at incipient flooding. For the low pulse frequency used (17 cycles/min.) incipient flooding took place at a holdup ratio of approximately 0.30, regardless of flow rates or ratios. At higher frequencies, clear-stream operation was observed with holdup ratios as high as 0.50, allowing greater throughput.

Table 1. Effect of Flow Rates on Extraction and Holdup at a Low Pulse Frequency

Pulse Frequency = 17 cycles/min.

Pulse Amplitude = 0.35 inches

Continuous Phase: Water

Run No.	Water rate, L (cc./min.)	Alcohol rate, G (cc./min.)	Holdup ratio	H.E.T.S. (inches)	(HTU) OG (inches)	(HTU) OL (inches)	Material balance (% error)
19	10	10	0.130	21.2	12.2	41.8	+ 0.06
16	10	15	0.120	21.6	14.9	33.1	+ 2.04
5	10	25	0.158	20.8	17.8	24.5	+ 0.05
6	10	40	0.173	21.5	22.9	20.2	- 1.29
7	10	60	0.196	19.4	24.9	15.4	- 3.03
8	10	100	0.214	15.1	26.9	9.3	- 0.24
20	10	120	0.283	16.2	32.6	9.2	+ 0.43
17	25	15	0.123	21.0	9.8	58.4	- 3.72
18	25	20	0.143	25.3	13.4	56.6	+ 1.52
9	25	25	0.143	28.3	17.1	51.9	+ 8.54
10	25	50	0.212	26.7	21.4	34.0	+ 4.32
11	25	75	0.294	28.4	26.1	31.0	- 1.57
22	50	15	0.136	154.	59.2	628.	+ 6.39
13	50	25	0.173	35.1	16.1	100.	+ 7.69
23	50	35	0.216	27.9	14.0	68.5	+ 0.21
21	50	42.2	0.262	32.9	17.7	72.0	+ 0.09

Table 2. Effect of Flow Rates on Extraction and Holdup at a High Pulse Frequency

Pulse Frequency = 72 cycles/min.

Pulse Amplitude = 0.20 inches

Continuous Phase: Water

Run No.	Water rate, L (cc./min.)	Alcohol rate, G (cc./min.)	Holdup ratio	H.E.T.S. (inches)	(HTU) OG (inches)	(HTU) OL (inches)	Material balance (% error)
36	10	25	0.194	13.0	11.7	14.5	+ 7.20
25	10	50	0.219	13.8	17.5	11.1	+ 3.63
39	10	75	0.318	11.8	18.6	7.9	+ 2.61
38	10	100	0.311	10.5	19.4	6.3	+ 1.58
41	10	150	0.338	11.1	26.1	5.7	+ 0.97
33	25	25	0.228	13.1	7.8	24.9	+ 6.58
34	25	50	0.263	14.1	11.3	17.9	+ 6.26
35	25	75	0.297	13.5	13.1	14.0	+ 4.46
37	25	100	0.234	14.0	15.7	12.6	+ 3.99
40	25	150	0.340	12.1	17.0	8.9	+ 3.70

FIG.4 EFFECT OF DISPERSED PHASE FLOW RATE ON H.E.T.S. AT CONTINUOUS PHASE FLOW RATE OF 10 cc / MIN.

FIG. 5 EFFECT OF DISPERSED PHASE FLOW RATE ON H.E.T.S. AT CONTINUOUS PHASE FLOW RATE OF 25 cc / MIN.

FIG.6 EFFECT OF FLOW RATE RATIO ON OVER-ALL HEIGHT OF A TRANSFER UNIT

FIG. 7 VARIATION OF HOLDUP RATIO WITH FLOW RATE

Effect of pulse amplitude and frequency

A series of runs was made at constant continuous and discontinuous flow rates of 10 and 50 cc./min., respectively, to determine the effect of pulse amplitude on H.E.T.S. and holdup ratios at frequencies of 35.5 and 72 cycles/min. These data are tabulated in Table 3. From Figure 8, it is seen that extraction efficiency is greatly improved by an increase in either pulse amplitude or frequency. At 72 cycles/min., values of H.E.T.S. dropped rapidly with an increase in pulse amplitude between 0.15 and 0.30 inches, but any further increase had relatively little effect on H.E.T.S. Clear-stream operation at amplitudes greater than 0.45 inches was impossible because of excessive emulsification of the two phases. At 35.5 cycles/min. the operating range was greater, and H.E.T.S. values decreased uniformly with increasing amplitudes at a more gradual rate than at 72 cycles/min.

Because of the manner in which extraction was dependent on both frequency and amplitude, it was decided that neither of the two should be considered independently, but rather that both should be grouped into one variable. Thus it was considered instructive to plot H.E.T.S. data for conditions of constant flow rates as a function of the product (amplitude) $\times$ (frequency), since this quantity is dimensionally proportional to what might be considered "pulse velocity" or "pulse energy". Figure 9 is such a plot, representing the previous data of Table 3 supplemented with additional runs at 17 cycles/min. The points fall along a single curve with little scattering, indicating the validity of this correlating device.

A series of holdup measurements was made at constant flow rates ($G = 50$ cc./min. and $L = 25$ cc./min.) in order to determine the effect of pulse amplitude at low frequencies. The results, shown graphically in Figure 10, indicate that a "critical" minimum amplitude exists for any given frequency and flow rate, which is the limiting value for clear-stream operation. Smaller amplitudes result in flooding, while larger values have relatively little effect on dispersed phase holdup other than a gradual decrease in holdup as pulse amplitudes are increased. This "critical" amplitude was seen to increase as pulse

Table 3. Effect of Pulse Amplitude and Frequency on Extraction and Holdup at Constant Flow Rates

Alcohol Flow Rate = 50 cc./min.

Water Flow Rate = 10 cc./min.

Continuous Phase: Water

Run No.	Pulse frequency (cycles/min.)	Pulse amplitude (inches)	Holdup ratio	H.E.T.S. (inches)	(HTU) OG (inches)	(HTU) OL (inches)	Material balance (% error)
24	72	0.15	0.165	18.4	22.8	15.0	+ 1.82
25	72	0.20	0.219	13.8	17.4	11.1	+ 3.63
29	72	0.30	0.381	12.0	14.7	9.9	+ 0.75
31	72	0.40	0.450	11.5	13.6	9.8	- 2.25
27	35.5	0.15	0.152	22.2	27.2	18.3	+ 0.77
26	35.5	0.20	0.151	17.7	21.6	14.7	+ 0.39
28	35.5	0.35	0.222	15.1	18.8	12.3	+ 2.38
30	35.5	0.45	0.298	12.3	14.9	10.3	- 0.26

FIG. 8 EFFECT OF PULSE AMPLITUDE ON H.E.T.S. AT MODERATE AND HIGH PULSE FREQUENCIES.

FIG. 9 H.E.T.S. AS A FUNCTION OF THE PRODUCT (AMP.)x (FREQ.), AT CONSTANT FLOW RATES

FIG.10 EFFECT OF PULSE AMPLITUDE ON HOLDUP RATIO AND COLUMN FLOODING AT LOW PULSE FREQUENCIES

frequency was decreased, again indicating that the product of the two is related to the pulse energy. Interpreted in this light, the minimum pulse energy (or force) is that which is required to overcome the resistance to flow through the plate perforations, resulting in countercurrent flow of the two phases.

At moderate and high frequencies holdup ratios were found to increase with pulse amplitudes. This increase was more rapid at 72 cycles/min. than at 35.5 cycles/min., as can be seen in Figure 11. At small pulse amplitudes (0.10 - 0.20 inches) and a frequency of 72 cycles/min., the dispersed phase was broken up into a very fine emulsion in the lower section of the column, resulting in excessive light-liquid carryover in the heavy-liquid effluent stream. When operating at high pulse amplitudes and the same frequency, the column appeared to be filled with a coarse emulsion, and flooding occurred in both effluent streams. Thus, the clear-stream operating range at 72 cycles/min. was from 0.20 - 0.45 inches, while at lower frequencies the range was greater.

Effect of continuous phase

The continuous phase in the pulse column was determined by the interface location which was governed by the height of the aqueous takeoff leg. With water as the continuous phase the interface was located at the top of the column, whereas a bottom interface was obtained with the alcohol phase continuous. Table 4 presents the results of two pairs of runs made under identical conditions, operating with top and bottom interfaces, respectively. This qualitative comparison shows that transfer is more efficient in the pulse column for the system water-boric acid-isoamyl alcohol, when the water phase is continuous.

DISCUSSION

Effects of Operating Variables and Plate Characteristics

Flow rates

In Figures 4 and 5, it is seen that values of H.E.T.S. are fairly insensitive to changes in dispersed phase flow

FIG. II EFFECT OF PULSE AMPLITUDE ON HOLDUP RATIO AT MODERATE AND HIGH PULSE FREQUENCIES

FIG.12 GRAPHICAL SOLUTION FOR NUMBER OF STAGES IN SAMPLE EXTRACTION RUN

Table 4. Effect of Continuous Phase on Extraction

Alcohol Flow Rate = 75 cc./min.

Water Flow Rate = 25 cc./min.

Run No.	Pulse frequency (cycles/min.)	Pulse amplitude (inches)	Continuous phase	H.E.T.S. (inches)	Material balance (% error)
35	72	0.20	Water	13.5	- 4.46
42-B	72	0.20	Alcohol	29.0	- 0.88
45	35.5	0.45	Water	9.9	- 1.31
43-B	35.5	0.45	Alcohol	24.7	- 1.79

rate at the higher pulse frequency. At the lower frequency, H.E.T.S. varies over a somewhat wider range. The extraction picture at the lower frequency is complicated by the fact that each phase is alternately dispersed and continuous. Thus, the thickness of the dispersed phase layer under each plate, or the holdup ratio, becomes an important factor in addition to the droplet size and contact time. At very low dispersed phase flow rates, the droplet size is very small; hence, the interfacial area is large, and as a result, transfer rates are high. As the dispersed flow rate is increased, the degree of turbulence increases, tending to improve extraction efficiency. However, this effect is partially counterbalanced by a simultaneous increase in droplet size which tends to reduce the total interfacial area. As flooding is approached, the droplet size becomes so large that extraction efficiency is actually lowered.

The continuous phase flow rate was found to have a greater effect on H.E.T.S. than the discontinuous flow rate. Since the transfer was from the discontinuous to the continuous phase, an increase in continuous phase residence time (decrease in flow rate) resulted in lower H.E.T.S. values. When viewed from the standpoint of film resistances, the mass transfer picture becomes clearer. Since the solute distribution favors the continuous phase (water), and since the viscosity of the dispersed phase is greater than that of the continuous phase (4.5 cp. for amyl alcohol, as compared to 1.0 cp. for water at 20°C.), it might be expected that the principal resistance to diffusion lies in the dispersed phase. As a result, the alcohol phase film can be thought of as thicker than the water phase film, and therefore controlling.

A dispersed droplet is thought to have a "static film", the thickness of which is not appreciably affected by the relative velocity of the two phases, whereas the continuous phase film thickness is considerably affected by relative velocity. The velocity of each dispersed droplet in the column is largely dependent upon its diameter, the density difference between the two phases, and the continuous phase viscosity. Although an increase in dispersed phase flow rate increases the size of each droplet, its velocity is not materially increased since the production of more droplets results in hindered rising. On the other hand, the reduction in the effective cross-sectional area for flow of the continuous phase tends to increase the

relative interfacial velocity somewhat, and in this light one would expect extraction to be improved. An increase in the continuous phase flow rate, however, lowers the dispersed droplet velocity because of the increased frictional resistance encountered in counterflow of the two phases. Therefore, for the latter case the relative interfacial velocity would not change appreciably, and extraction would depend almost entirely upon the residence time of each phase in the column.

The data of Tables 1 and 2 show that a 2.5-fold increase in the water rate at a constant alcohol rate effected a 25 per cent decrease in $(HTU)_{OG}$ and an 80 per cent increase in $(HTU)_{OL}$. That $(HTU)_{OG}$ would be relatively insensitive to changes in the water rate might be predicted on the basis of the "stagnant" nature of the alcohol film and the negligible effect of the continuous flow rate upon the relative interfacial velocity. The slight decrease in $(HTU)_{OG}$ is consistent with the fact that a unit volume of the alcohol phase contacted a greater quantity of fresh solvent per unit time. Similarly, the lowered residence time of the water phase, when its flow rate was increased, was the major factor contributing to the large increase in $(HTU)_{OL}$.

If the alcohol flow rate is increased 2.5-fold, at a constant water rate, the same data show a 40 per cent increase in $(HTU)_{OG}$ and a 45 per cent decrease in $(HTU)_{OL}$. The increase in $(HTU)_{OG}$, in this case, may be accounted for by the decrease in the alcohol residence time; however, the magnitude of this increase in $(HTU)_{OG}$ is lower than would be expected if residence time had been the only significant factor. It is probable that extraction was enhanced to some extent by an increase in the relative interfacial velocity, as was previously suggested. The decrease in $(HTU)_{OL}$ may be explained by the increased quantity of alcohol which contacted a unit volume of the water phase per unit time.

Applying the preceding analysis to the over-all interpretation of the effect of the flow ratio upon extraction, it is seen that a 2.5-fold increase in the ratio G/L (alcohol rate/water rate) results in a 40 per cent increase in $(HTU)_{OG}$ and a 45 per cent decrease in $(HTU)_{OL}$ by either of the following methods:

- 1) a 2.5-fold decrease in L, at constant G,
- or 2) a 2.5-fold increase in G, at constant L.

Thus, for this investigation, where the direction of boric acid transfer was from the alcohol to the water phase, extraction was improved by an increase in the flow ratio, G/L, irrespective of the method by which this ratio was increased. If the transfer of boric acid had been in the opposite direction, the trends in over-all HTU's would have been reversed with respect to the flow ratio.

Figure 6 illustrates an empirical correlation of $(HTU)_{OG}$ with the ratio, mg/L, sometimes called the extraction factor. Although the optimum choice of the extraction factor for a practical extraction and solvent-recovery process is primarily a problem in economics, a large value of mg/L would be advantageous for the particular system investigated. The data at the lower pulse frequency are best represented, in Figure 6, by separate straight lines, each referring to a constant value of continuous phase flow rate. Thus extraction was seen to be a function of each flow rate, individually, rather than the flow ratio. This might be explained on the basis that neither phase was truly continuous at the low frequency, and the interpretation of the calculated values of over-all HTU's as being based entirely on either of the two phases is probably unsound. The type of flow behavior at 72 cycles/min. was similar to that of a spray column, in that no appreciable dispersed phase coalescence was observed beneath each plate. This simplifies the interpretation of HTU data and probably explains the more general correlation of $(HTU)_{OG}$ with the flow ratio at the higher frequency.

Pulse amplitude and frequency

It was shown in Figures 8 and 9 that transfer efficiency is greatly improved by increasing either the pulse displacement or frequency. Both operating variables aid extraction by increasing the degree of dispersion (interfacial area) and turbulence. Neither of the two should be considered independently since they both affect the degree of agitation in an analogous manner to the effect of impeller diameter and speed of rotation for mechanical mixing

equipment. Figure 9 shows that efficiency is markedly improved as the product, amplitude x frequency (equivalent to the pulse energy), is increased. Beyond a certain point, however, a further increase in the pulse energy had no appreciable effect on extraction. Thus the curve was seen to flatten out at a pulse energy of approximately 15. A possible explanation of this is that the droplet size was reduced to such an extent that excessive back-mixing occurred, tending to decrease the effectiveness of the countercurrent action.

Although flooding occurred at holdup ratios of approximately 0.30 at low frequencies, clear-stream operation was observed with holdup ratios as high as 0.50 when higher frequencies were used. This accounts for the increase in throughput capacity at high pulse frequencies and may be explained by the reduced size of the dispersed droplets as well as the prevention of their coalescence because of more frequent impacts with the plates.

The limiting values of pulse amplitude and frequency are dependent on the physical characteristics of the system to a large degree. Thus if the interfacial tension of the two phases is low, as is the case with liquids of high mutual solubility, there exists a definite tendency towards the formation of stable emulsions. Consequently, the system would not be operable at high pulse rates. On the other hand, if the interfacial tension is high, the upper limit of operating pulse frequency and amplitude would probably be determined by flooding in the effluent streams due to excessive dispersed phase coalescence in the column, occurring at the high holdup ratios encountered.

Still another phenomenon might occur at high pulse frequencies. This effect, known as cavitation, would cause the system to be inoperable because of bubble formation in the line from the column to the pulse generator due to the development of localized pressures which would be lower than the vapor pressure of the pulsed fluid. In order for this to occur, the algebraic sum of the atmospheric, hydrostatic and pulse acceleration pressures must be less than the vapor pressure. The acceleration pressure reaches its most negative value at the pulse generator when the direction of flow changes from positive to negative, and at this point in the pulse cycle cavitation is most likely

to take place. Cooper and Groot (3) have shown that the pulse acceleration pressure is directly proportional to the pulse displacement and the square of the frequency. Thus the use of high frequencies might be prohibitive for systems having high vapor pressures.

Choice of continuous phase

The location of the interface determines which of the two phases in the column is to be the continuous one. In general, the physical properties of the system which affect the film thickness, the degree of dispersion and the droplet velocity, as well as the chemical properties which affect the plate-wetting characteristics, determine the optimum choice of the interface location. Usually, the phase which preferentially wets the plates is chosen as the continuous phase since finer dispersions of the discontinuous phase would then be obtainable. However, if the interfacial tension is low, dispersion will usually be adequate in either direction, and viscosity will probably be the determining factor in choosing the continuous phase. This was the case with the system: water-boric acid-isoamyl alcohol, where higher rates of extraction were observed with the water phase continuous. The dispersed droplet size was approximately the same with either phase continuous, but the greater viscosity of the alcohol phase resulted in slower settling rates of the dispersed droplets when the alcohol phase was continuous. Thus, because of hindered settling of the dispersed phase, mass transfer rates were lower. Also contributing to the lowered efficiency, is the fact that the low-flow fluid was dispersed, making less interfacial area available, per pulse, than with the high-flow fluid dispersed.

Plate characteristics

Although only one plate assembly was tested in this performance study, several generalizations may be made regarding the effects of hole diameter, number of holes per plate and plate spacing on extraction and throughput. The hole diameter has the greatest effect on dispersed droplet size, and hence, on interfacial area. Thus extraction efficiency is improved by the use of smaller holes.

The lowered velocity of the dispersed droplets also contributes to higher transfer rates by increasing column holdup (residence time). The use of very small holes, however, would tend to cause either emulsification or flooding at low throughputs. An increase in the number of holes per plate probably has little effect on extraction at optimum operating conditions since the same number of dispersed droplets having the same diameter would be formed by each plate per pulse, regardless of the number of holes (above, say, 10 per cent free area per plate). Plate thickness, on the other hand, is an important factor and should be kept to a minimum in order to obtain better dispersion and to lower the pressure drop through the perforations. Close plate spacing generally results in high extraction efficiency at the expense of a lowered throughput capacity. However, throughputs may be increased by using a wider plate spacing, and the lowered efficiency brought about by this may be improved by increasing the pulse frequency. Thus a great versatility in pulse column operation may be achieved by the suitable combination of operating and design variables.

Application of Performance Data to Other Systems

In order to avoid much of the experimental work in selecting the optimum conditions for pulse column operation with an untested system, a generalized procedure for investigation, based upon the performance data obtained with the system: water-boric acid-isoamyl alcohol, may be formulated. A knowledge of the qualitative effects of the physical properties of the system upon pulse column variables is helpful in limiting the permissible operating range and predicting a logical region for systematic study.

Prior to any experimental work, column and plate assembly design should be investigated from the standpoint of desired throughput capacities. In general, it may be stated that pulse columns are capable of handling between two and three times the volumetric throughput of similar packed columns. As a starting point, an optimum throughput of 500 gal./ft.²/hr. may be used in approximating the required column diameter, if the unit is to be used as a laboratory tool where high efficiencies are of prime importance. On the other hand, if its intended use is as

a plant extractor where high throughputs as well as efficiencies are necessary, a basis of 1000 gal./ft.²/hr. may be used for selecting the column diameter.

The generalizations made in the previous section, regarding plate characteristics, apply to any system and therefore may be utilized in choosing a suitable plate design. Usually, hole diameters between 0.03 and 0.05 inches will be adequate. Where dispersion is difficult due to high viscosity or high interfacial tension, the larger hole diameter would be beneficial. If the density difference is high and the viscosity low, small perforations will yield low values of H.E.T.S. without considerable reduction in throughput capacity. Where coalescence is rapid (systems having a low viscosity, high density difference and high interfacial tension), a plate spacing of one inch may be desirable. However, in this is not the case, and especially if the system exhibits a tendency towards the formation of stable emulsions, larger plate spacings may be warranted.

For any given system the phase in which the solute is more soluble should flow at a slower rate. Ordinarily, the low-flow fluid would be the continuous phase; however, several comparative extraction runs should be made in order to validate the optimum choice of continuous phase. If packed or spray column data is available for the particular system, optimum flow rate ratios found on these extractors may be used as a basis for studying the system using a pulse column. If such data is unavailable, it would be desirable to carry out a few series of extraction runs, keeping flow rates of the low-flow fluid constant and varying the other flow rate. Flooding conditions should be approached in each series of runs in order to insure investigation of the region of high throughput where extraction efficiency is usually high. Pulse frequency and amplitude should be kept constant throughout the series of runs. Moderate pulse conditions should be used (e.g. 50 cycles/min. and 0.30 inches amplitude). Only three or four runs need be made in each series in order to determine the optimum flow ratio. Once this is found, a series of extraction runs can be made to determine the pulse frequency and amplitude which give the lowest values of H.E.T.S.

If the viscosity is high or if the density difference or interfacial tension is low, the dispersed droplets will

coalesce slowly. Hence, a low frequency should be chosen (in the neighborhood of 30 cycles/min.), and a series of runs should be made at the optimum flow ratio, at constant flow rates, varying the pulse amplitude in the range above 0.50 inches. Pulse displacements as high as the distance between successive plates would probably give optimum results at this low frequency. If, on the other hand, the physical characteristics of the system are such that coalescence is fairly rapid, the region of high pulse frequencies should be investigated (about 50 cycles/min.). In either case runs should be planned to cover as wide a range in the product, (amplitude) x (frequency), as possible, keeping the flow rates constant. This way optimum operating conditions may be established with a minimum of trial-and-error experimentation.

Advantages and Limitations of the Pulse Column

Advantages

1. Because of its high efficiency and low column height (approximately $1/3$ that of a similar packed column performing the same separation), the pulse column is particularly advantageous where low head room or shielding requirements (for radioactive solutions) prohibit the use of larger columns.
2. High throughput capacities are obtainable, allowing the use of small-diameter columns.
3. Column construction is relatively simple, and the absence of moving mechanical parts within the column keep leakage, maintenance and repair problems to a minimum. The entire system can be made corrosion-resistant by using a plate assembly of a suitable plastic material and separating the external pulse mechanism from the column liquids by means of an inert diaphragm.
4. The pulse column is a versatile piece of equipment in that the "packing characteristics" (and hence, the flow behavior) may be drastically changed by varying either the displacement or frequency of pulsation, or both. Various

plate assembly cartridges, having different plate spacings and hole diameters may readily be installed or removed to alter the degree of dispersion and coalescence for different systems.

Limitations

1. The initial cost of the pulse column (essentially, the cost of the pulse generator) might be prohibitive for installations in which relatively inexpensive spray, packed or wetted-wall towers are economically feasible. However, the high initial cost may be offset by the savings due to increased throughput and lowered height requirements.

2. A mechanical problem which will probably limit the applicability of large-diameter pulse columns, is the difficulty in pulsing large volumes of fluid at a rapid and constant rate. To do this, an efficient and economical plant-size pulse generator must be developed which will provide reproducible operation over a long period without failure. At the present time, large-diameter piston pumps appear to be most feasible for this application.

3. The pulsing requirements for highly viscous liquids may be excessive. Similarly, for highly volatile systems, cavitation at the pulse generator might inhibit column operation.

4. Where coarse slurries are to be processed, the pulse column would not be applicable due to the possible clogging of the plate perforations by suspended particles.

Discussion of Errors

The material balance was the only quantitative index of experimental error in this investigation. This error represented the degree of attainment of steady-state conditions in the column, as well as experimental error in flow rate measurement. Analyses did not cause a significant error as these were usually reproducible within 0.2 per cent accuracy. The maximum material balance error was + 8.54 per cent, and the average error for all the runs was ± 2.63 per cent.

Since the internal column diameter was not uniform, the plates did not fit tightly, and a small amount of liquid channeling took place between the plates and the column wall. This probably brought about a loss in efficiency. Channeling could have been avoided by the use of "precision-bore" pipe and carefully machined plates, or by the use of a column composed of short, flanged sections of pipe bolted together, with a gasket-plate assembly clamped between each section.

Deviations in the pulse frequency and amplitude, during the course of each run, did not constitute a serious source of error. These were checked at the beginning and at the end of each run and were found to be essentially constant. The pulse wave generated by the diaphragm pump was approximately sinusoidal, whereas the bellows pulsator generated a "semi-square" wave. The latter type of wave shape produces more turbulence and allows more time for recalescence between surges, thus improving extraction. Hence, HTU data obtained with a sine wave cycle might be expected to be higher than similar data obtained with a "semi-square" cycle, all other variables remaining constant.

CONCLUSIONS

1. For the system: water-boric acid-isoamyl alcohol, transfer is most efficient in the pulse column with the water phase continuous.

2. At high pulse frequencies, over-all HTU's are a function only of the flow ratio, whereas at low frequencies, over-all HTU's vary with the individual flow rates (at constant pulse frequency and amplitude). In general, values of $\{HTU\}_{OG}$ increase with the flow ratio G/L while values of $\{HTU\}_{OL}$ decrease.

3. Extraction efficiency may be improved at low frequencies by decreasing the flow rate of the phase in which the solute is more soluble (in this case, the continuous phase). An increase in the dispersed phase flow rate also improves extraction.

4. At high frequencies extraction is more dependent upon the pulse conditions than upon flow rates or ratios. Generally, an increase in pulse displacement and/or pulse frequency results in lower values of H.E.T.S.

5. Throughput capacity is greatly improved at high frequencies, although the use of high frequencies and amplitudes may tend to cause emulsification of the two liquids. For the system investigated, the pulse column was found to be most efficient at high throughput rates of the dispersed phase, operating at moderate to high pulse frequencies (35 - 72 cycles/min.).

6. For the one-inch diameter column used in this investigation, a cam-driven bellows pump and a diaphragm proportioning pump were successfully used as pulse generators. Both pulsators provided trouble-free, reproducible operation during the course of the runs.

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