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Studies of Controlled Cyclic Distillation: I. Computer Simulations and the Analogy with Conventional Operation

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Summary

Computer simulations of a controlled cycling rectification still were run to determine the theoretical effects of local point efficiency, slopes of the equilibrium and operating lines, amount of liquid dropped during the liquid-flow period, and other parameters on over-all column and individual plate efficiencies. It is shown that, although the Murphree vapor efficiency of a plate at any instant of time is assumed to be constant and equal to the local point efficiency, the effective plate efficiency based on the resulting liquid-phase plate compositions is usually significantly greater than the point efficiency. This leads to the improved separating ability achieved in controlled cyclic operation. The existence of a precise analogy between controlled cyclic distillation and conventional distillation with liquid-phase concentration gradients across the plates of the column is shown. In essence, this analogy reduces to the substitution of time as the independent variable in the former case for distance in the latter case.

The concept of controlled cycling and its application to various chemical engineering operations has received considerable attention in recent years. As compared to conventional countercurrent operations with simultaneous flow of two phases, controlled cyclic operation consists of alternating flow of each phase over a controlled time interval, with or without a coalescence period between each flow interval. This concept derives its origin from Cannon (*1*,*2*), who was the first to apply controlled cycling to a number of operations, including screening (*3*), extraction (*4*–*6*) and distillation (*7*–*9*).

Numerous investigators have since applied controlled cycling or a variation of it to a variety of separations and operations. These include absorption (*10,11*), in which an increase in throughput of a factor of three and a simultaneous improvement in efficiency have been observed, and extraction (*6,12*), in which throughput increases of an order of magnitude have been reported. Pulsing, which may be considered as a form of controlled cycling, has also been applied to fractional crystallization (*13*) and chemical reactions (*14*). Examples of the application of controlled cycling in the area of heat transfer include welding (*15*) and film boiling (*16*). In the latter case, up to 100% increases in the heat-transfer rate were observed when cycling was applied to stable film boiling. All this research indicates substantial advantages to be gained from the successful application of controlled cycling to separations and rate processes in a variety of disciplines.

More recently, McWhirter (*17*) and McWhirter and Lloyd (*18*) have carried out extensive theoretical and experimental investigations of controlled cyclic distillation. This mode of operation consists of alternating periods of vapor flow only and liquid flow only. In the physical sense, this is accomplished in a column fitted with, typically, perforated trays with large open areas and no downcomers. McWhirter demonstrated, using laboratory columns ranging up to 6 inches in diameter, that the separating ability and capacity of a controlled cycling column could each be simultaneously increased by approximately a factor of two relative to those for the same column operating in conventional fashion. Schrodt (*19*) has reported similar results from his laboratory studies.

Although the nature of the increased capacity of a controlled cycling column is easily rationalized by the fact that such a column is operating in essentially a flooded condition during the vapor-flow period, and hence excessive entrainment becomes the only limiting condition here, the reasons for the increased efficiency of such a column have yet to be given. From his simulations, McWhirter (*17,18*) shows that the average driving forces for mass transfer in a cyclic column are considerably greater than those in a conventional column, but concludes that the high stage efficiencies of a cyclic column are difficult, if not impossible, to rationalize in terms of conventional operation.

In this paper the results of analog- and digital-computer simulations of controlled cyclic distillation, the purpose of which was to

TABLE 1
Definition of Various Efficiences

Efficiency	Symbol	Definition
Murphree point efficiency	E	Local vapor efficiency at a point in time and space [see Eq. (2)]
Instantaneous plate efficiency		Over-all vapor efficiency of a plate at a point in time (always assumed to be equal to E in these simulations)
Effective plate efficiency	E_0	Over-all efficiency of a plate computed on the basis of liquid-phase plate compositions
Over-all column efficiency	E^0	Number of theoretical stages ($E_0 = 100\%$) corresponding to a given separation divided by the number of actual plates in the column

investigate the theoretical effects of various parameters on the separating ability of a controlled cycling column, are presented. Using analytical results derived for certain simplified cases via matrix methods (*20*), an analogy is then developed between controlled cyclic distillation, on the one hand, and conventional distillation with transverse concentration gradients across the plates of the column, on the other. The analogy, in essence, involves the mere replacement of distance as the independent variable in the latter case with time in the former case. The beneficial effects of transverse concentration gradients on the separating ability of a distillation column were shown by Lewis (*21*) more than twenty-five years ago. Using this analogy, the theoretical performance of a controlled cycling column may be accurately predicted from that of its conventional counterpart.

Before proceeding further, it may be beneficial to define the various efficiencies that will be referred to throughout this paper. Although the reasons for doing this may not be immediately obvious at this time, it is hoped that this will serve to reduce the amount of possible confusion brought about by the necessary use of various efficiencies. The definitions of these are given in Table 1.

DYNAMIC EQUATIONS

Dynamic material-balance equations for the vapor-flow and liquid-flow periods of controlled cyclic distillation of a binary mixture in a rectification still and the assumptions underlying them have been given earlier by McWhirter and Lloyd (*18*). The same equations were used in this study, and hence only brief mention of them is made here. For the *n*th stage of the column (reboiler = stage 1) during the vapor-flow period of the cycle, we have

$$H\frac{dx_n}{dt} = Vy_{n-1} - Vy_n \qquad (1)$$

where H is the liquid-phase molar holdup on the stage (assumed here to be the same and constant for all plates in the column), V is the constant molar boilup rate, x_n is the liquid-phase mole fraction of the more volatile component on the *n*th stage, and y_n, the mole fraction of the more volatile component in the vapor leaving the *n*th stage, is given by the definition of the Murphree (vapor) point efficiency:

$$E = \frac{y_n - y_{n-1}}{y_n^* - y_{n-1}} \qquad (2)$$

where y_n^* is the composition of the vapor that would be in equilibrium with the liquid on the *n*th stage and is given by the particular vapor-liquid equilibrium relationship assumed. The Murphree point efficiency, E, with which the plate efficiency at any instant of time is equated, is assumed to be the same and equal for all plates in the column. Equations (3) and (4) describe the dynamics during the vapor-flow period for the special cases of the still pot and condenser, respectively:

$$\frac{d(Sx_1)}{dt} = -Vy_1 = -Vy_1^* \qquad (3)$$

$$\frac{d(Cx_c)}{dt} = Vy_{N+1} \qquad (4)$$

where S and C are the liquid-phase holdups of the still pot and condenser, respectively, at time t, and N is the number of actual plates in the column. It will be noted in Eq. (3) that the still pot is assumed to be equivalent to one theoretical stage.

During the liquid-flow period of the cycle, it is assumed that no mass transfer occurs and that constant and equal amounts of liquid flow from each stage in plug-flow fashion. With these assumptions, the material-balance equations for the liquid-flow period become

$$x_n^L = \phi x_{n+1}^V + (1-\phi)x_n^V \qquad (0 \leq \phi \leq 1) \qquad (5)$$

where the superscripts V and L refer to conditions at the ends of the vapor-flow and liquid-flow periods, respectively, and ϕ is the amount of liquid that flows during the liquid-flow period, expressed as a fraction of a plate holdup. For the still pot and condenser, we have

$$x_1^L = \frac{S^V x^V + \phi H x_2^V}{S^V + \phi H} \qquad (0 \leqslant \phi \leqslant 1) \tag{6}$$

$$x_c^L = x_c^V \tag{7}$$

The conditions denoted by the superscript L also correspond to the initial conditions for the vapor-flow period of the next cycle.

Equations (5) and (6) are valid only for $0 \leqslant \phi \leqslant 1$. For larger values of ϕ, the following equations result:

For $1 \leqslant \phi \leqslant 2$:

$$x_1^L = \frac{S^V x_1^V + H x_2^V + (\phi - 1) H x_3^V}{S^V + \phi H} \tag{8}$$

$$x_n^L = (\phi - 1) x_{n+2}^V + (2 - \phi) x_{n+1}^V \qquad (n \leqslant N) \tag{9}$$

$$x_{N+1}^L = x_c^V \tag{10}$$

For $2 \leqslant \phi \leqslant 3$:

$$x_1^L = \frac{S^V x^V + H x_2^V + H x_3^V + (\phi - 2) H x_4^V}{S^V + \phi H} \tag{11}$$

$$x_n^L = (\phi - 2) x_{n+3}^V + (3 - \phi) x_{n+2}^V \qquad (n \leqslant N - 1) \tag{12}$$

$$x_N^L = x_{n+1}^L = x_c^V \tag{13}$$

where the $(N + 2)$th stage corresponds to the condenser. Equations similar in form can easily be developed for values of $\phi > 3$. In all cases there is no change in the condenser composition during the liquid-flow period.

In the experimental studies of McWhirter (*17,18*) it was shown that the condition of plug flow during the liquid-flow period was fairly realizable in columns as large as 6 inches in diameter.

The duration of the vapor-flow period (τ) is determined by such parameters as plate holdup (H), boilup rate (V), fraction of a plate holdup dropped during the liquid-flow period (ϕ), and reflux ratio (R). In conventional distillation, the reflux ratio is defined as

$$R = \frac{L}{D} = \frac{L}{V - L} \tag{14}$$

where L and D are the reflux and distillate rates, respectively, expressed as certain amounts of material per unit time. In controlled cyclic distillation, the reflux ratio is given by consideration of one complete cycle. The total amount of boilup in one cycle is $V\tau$, whereas the amount of liquid reflux at the end of the cycle is ϕH. Thus the reflux ratio becomes

$$R = \frac{\phi H}{V\tau - \phi H} \tag{15}$$

whence

$$\tau = \frac{R+1}{R}\,\frac{\phi H}{V} \tag{16}$$

Alternatively, for given values of V, H, and τ, specification of ϕ defines R. At total reflux ($R \rightarrow \infty$),

$$\tau = \frac{\phi H}{V} \tag{17}$$

Although the duration of the liquid-flow period is determined by the hydrodynamics of a real column, it is apparent that this period is of no relevance from a purely mathematical point of view.

ANALOG-COMPUTER SIMULATIONS

To see how the plate compositions of a controlled cycling column vary with time during the vapor-flow period, and also how the column approaches its pseudo-steady-state condition, analog-computer simulations of controlled cyclic distillation were run. The pseudo-steady-state condition is defined to be that condition at which the composition profile in a cycling column is the same at the end of successive cycles. Obviously, such factors as time constants for the plates (H/V), the number of plates in the column, and the fraction of a plate holdup dropped during the liquid-flow period will have a significant effect upon the number of cycles required to achieve this condition. Nonetheless, it will be seen that a controlled cycling column, much like its conventional counterpart, does indeed achieve a form of a steady-state condition.

A binary system with a constant relative volatility (α) of 1.2 was chosen for study. The simulation was run at total reflux. The following values for the various system parameters were assumed:

$V = 0.1$ g mole/sec
$H = 0.2$ g mole

$$S^0 = 10 \text{ g moles}$$
$$E = 1.0$$
$$\phi = 1.0$$
$$N = 5$$

Thus from Eq. (17) it is seen that $\tau = 2$ sec. The analog simulation was run in real time. For initial conditions it was assumed that the column was operating in conventional fashion at total reflux, whence, with $E = 1.0$,

$$x_i = y_{i-1} = \frac{\alpha x_{i-1}}{1 + (\alpha - 1)x_{i-1}} \tag{18}$$

The initial composition of the still pot (x_1^0) was assumed to be 0.5.

Two consoles of PACE 131-R analog-computing equipment were used in this study. The first console, which simulated the operation of the controlled cycling column, integrated Eqs. (1), (3), and (4) for a time interval slightly greater than τ, at the end of which it was automatically put into the reset mode and then back into the operate mode for another cycle. In the reset mode it obtained its initial conditions for the next cycle from the second console, which, operating in track-and-hold fashion, had been automatically put into the hold mode at $t = \tau$, and returned to the operate and track mode shortly after the initiation of the new cycle. Thus the second console served as a memory device and, in addition, performed the algebraic operations denoted by Eqs. (5) and (6).

Composition-time profiles for the five plates of the column and the condenser, as followed with a six-channel recorder, are presented in Fig. 1, for the conditions given above. It is seen that each plate composition decreases during the vapor-flow period as the more volatile component is stripped out and then returns to a new higher level during the liquid-flow period. The condenser receives only vapor from the top plate, so its composition first increases during the vapor-flow period as it receives richer vapor, and then decreases as the composition of the vapor from the top plate decreases. Thus the condenser composition goes through a maximum during the vapor-flow period of each cycle (except the first cycle). The composition levels for each plate and the condenser increase from the conventional condition up to the pseudo-steady-state condition. At this point the composition on each plate (except the first plate) at the end of the vapor-flow period is exactly equal to that on the plate immediately below at the beginning of this period. Also, the condenser composition at the end of the vapor-flow period

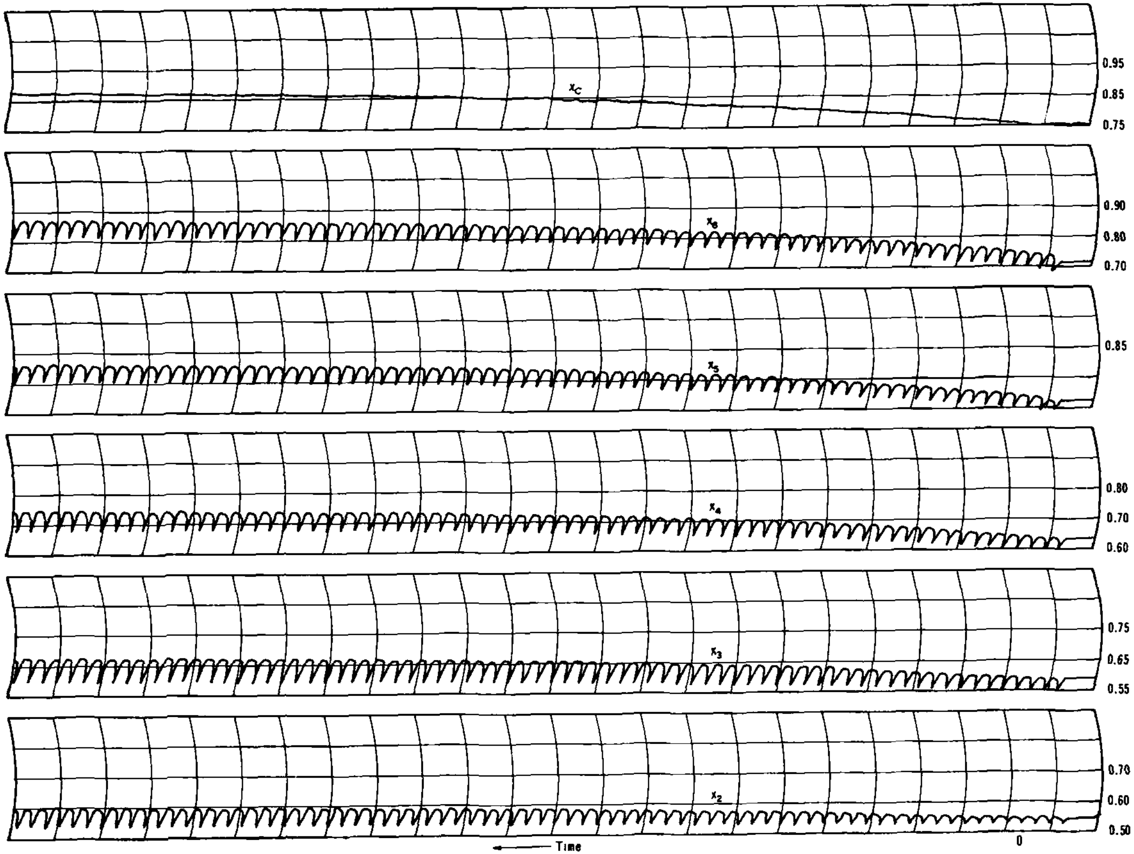

FIG. 1. Results of analog-computer simulation of controlled cyclic distillation in a five-plate rectification still at total reflux. ($V = 0.1$ g mole/sec; $H = 0.2$ g mole; $S^0 = 10$ g moles; $E = 100\%$; $\phi = 1.0$; $\alpha = 1.2$; $x_1^0 = 0.5$).

is the same as at the beginning of this period. The composition of the still pot, because of the large holdup associated with the latter, decreases only slightly during any vapor-flow period, and also experiences only a slight permanent decrease in the approach to the pseudo-steady-state condition (less than 0.001 mole fraction). The flat parts of the curves in Fig. 1 merely correspond to the time during which the first console is in the reset mode.

DIGITAL-COMPUTER SIMULATIONS

The results of the analog-computer simulations provided a graphic demonstration of the manner in which a controlled cycling

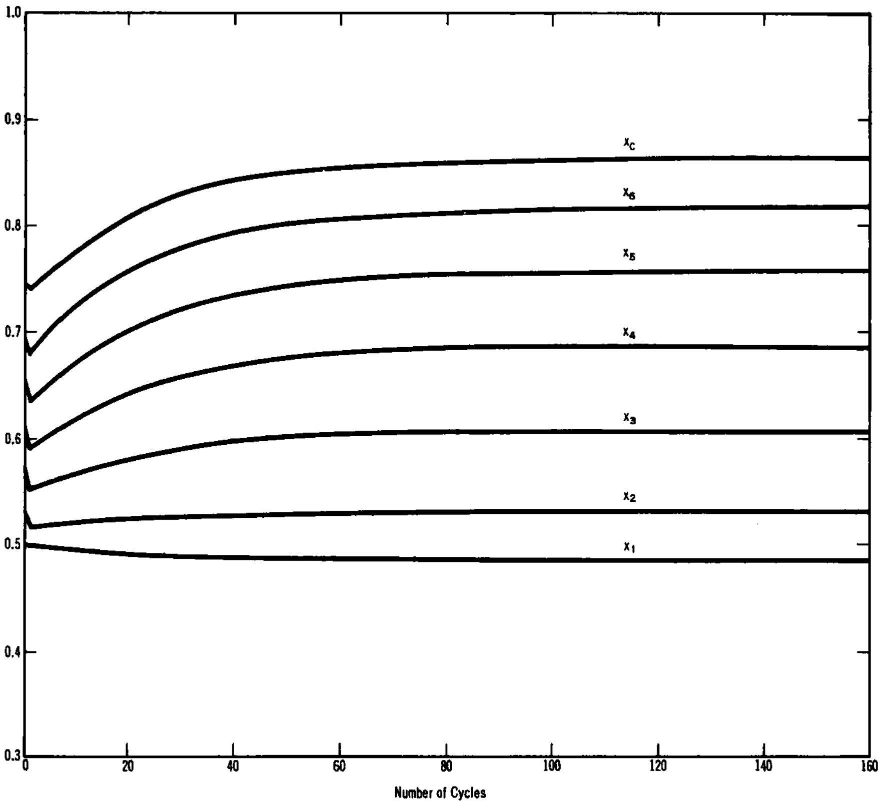

FIG. 2. Results of digital-computer simulation of controlled cyclic distillation in a five-plate rectification still at total reflux. Compositions refer to conditions at the end of the vapor-flow period. ($V = 0.1$ g mole/sec; $H = 0.2$ g mole; $S^0 = 10$ g moles; $E = 100\%$; $\phi = 1.0$; $\alpha = 1.2$; $x_1^0 = 0.5$).

distillation column operates. Having established that a difference in separation stems fundamentally from a difference in mode of operation, a program was initiated to study the effects of various parameters on the separating ability of such a column via digital-computer simulation. For this purpose, Eqs. (1), (3), and (4) were converted to finite-difference form suitable for numerical integration on an IBM-704 digital computer. The study was confined to the simulation of controlled cycling rectification stills; distillation columns with intermediate feed streams were not investigated. The normal time step (value of Δt in the finite-difference equations) in all these simulations was 0.01 sec; it was found that very little change in the results occurred for time steps smaller than this.

The results of the digital-computer simulation corresponding to the same conditions at which the analog simulation was made are presented in Fig. 2. These curves represent the computed values of the various compositions at the end of the vapor-flow period as a function of number of cycles. The pseudo-steady-state condition is, for all practical purposes, achieved after 150 cycles. This was generally true for most of the simulations.

Controlled Cyclic Distillation at Total Reflux

The effects of fraction of a plate holdup dropped during the liquid-flow period, mixing during the liquid-flow period, relative volatility, actual slope of the equilibrium curve, Murphree point efficiency, and number of actual plates on the separating ability of a controlled cycling rectification still operating at total reflux were studied. The following parameters were held constant during all these simulations: $S^0 = 20$ g moles, $V = 0.1$ g mole/sec, $H = 0.2$ g mole. The results of these studies are presented below.

Effect of fraction a plate holdup dropped. Values of ϕ ranging from 0 up to 3.0 were investigated. Values of the other parameters were: $\alpha = 1.2$, $E = 1.0$, $N = 5$, and $x_1^0 = 0.5$. The effective number of theoretical plates in the column (N_{eff}) was calculated from the values of the still-pot and condenser compositions at the end of the vapor-flow period at the pseudo-steady-state condition, using the Fenske equation (22):

$$N_{\text{eff}} = \left(\log\left[\frac{x_c}{1-x_c}\,\frac{1-x_1}{x_1}\right]\Big/\log\alpha\right) - 1 \qquad (19)$$

where the effect of the still pot, which is assumed to be equivalent to one theoretical plate, has been subtracted out. The over-all column efficiency (E^0) is then determined by dividing N_{eff} by the number of actual plates. The results of these investigations are presented in Fig. 3.

These results agree with those obtained by McWhirter (*17*) in his original theoretical studies. Maxima occur at integral values of ϕ, with the maximum of these maxima occurring at $\phi = 1$. Presumably, other peaks would result for integral values of ϕ greater than 3, although they would become less and less distinct. The value of $\phi = 0$ corresponds to conventional operation.

Effect of mixing during the liquid-flow period. To ascertain the effect of mixing during the liquid-flow period on the separating ability of a controlled cycling column, Eqs. (5) and (6) were re-

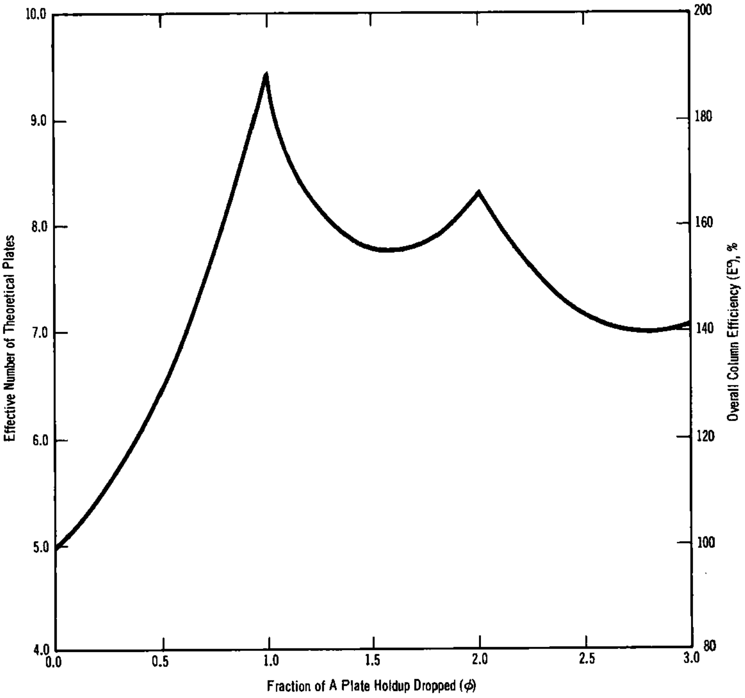

FIG. 3. Effect of fraction of a plate holdup dropped during the liquid-flow period (ϕ) on the over-all efficiency (E^0) of a controlled cycling rectification still at total reflux. ($V = 0.1$ g mole/sec; $H = 0.2$ g mole; $S^0 = 20$ g moles; $E = 100\%$; $N = 5$; $\alpha = 1.2$; $x_1^0 = 0.5$).

placed by differential equations which would describe the dynamics of the plates and the still pot for complete mixing during the liquid-flow period:

$$H \frac{dx_n}{dt} = Lx_{n+1} - Lx_n \tag{20}$$

$$\frac{d(Sx_1)}{dt} = Lx_2 \tag{21}$$

where L is the liquid molar flow rate during the liquid-flow period, and at total reflux is equal to V if τ_L, the duration of the liquid-flow period, is equal to the duration of the vapor-flow period, τ. As with the equations for the vapor-flow period, Eqs. (20) and (21) were converted to finite-difference form and integrated numerically in the digital-computer simulations. Values of τ (and also τ_L) equal to 0.5, 1.0, and 2.0 sec were investigated; these correspond to $\phi = 0.25$, 0.5, and 1.0, respectively, in the case of liquid plug flow. The results of these simulations are presented in Table 2.

A comparison of the data of Table 2 and Fig. 3 shows the importance of plug flow during the liquid-flow period of controlled cyclic distillation. Complete mixing during this period obliterates the separation advantages to be gained by controlled cyclic operation, and results in essentially conventional operation. Thus close approach to liquid plug flow down the column is necessary in controlled cyclic distillation.

Effect of relative volatility. The results of these simulations (Table 3) showed the over-all column efficiency of a controlled cycling column to vary with the relative volatility. Thus for a con-

TABLE 2

Effects of Mixing during the Liquid-Flow Period on the Separating Ability of a Controlled Cycling Rectification Still at Total Reflux

($S^0 = 20$ g moles, $H = 0.2$ g mole, $V = L = 0.1$ g mole/sec, $\alpha = 1.2$, $E = 1.0$, $N = 5$, $x_1^0 = 0.5$)

Duration of the vapor-flow period, $\tau(=\tau_L)$, sec	Effective number of theoretical plates, N_{eff}	Over-all column efficiency, E^0, %
0.5	4.96	99.1
1.0	4.93	98.7
2.0	4.83	96.6

TABLE 3
Effect of Relative Volatility on the Over-All Column Efficiency of a Controlled Cycling Rectification Still at Total Reflux ($S^0 = 20$ g moles, $H = 0.2$ g mole, $V = 0.1$ g mole/sec, $\phi = 1.0$, $E = 1.0$, $N = 5$, $x_1^0 = 0.5$)

Relative volatility, α	Effective number of theoretical plates, N_{eff}	Over-all column efficiency, E^0, %
1.05	9.56	191.1
1.10	9.54	190.8
1.20	9.46	189.2
1.30	9.35	187.0
1.40	9.23	184.6
1.50	9.12	182.4
1.50[a]	9.26	185.3

[a] $x_1^0 = 0.3$.

stant initial value of the still-pot composition of $x_1^0 = 0.5$, the over-all column efficiency (E^0) decreases monotonically as the relative volatility (α) increases from 1.05 to 1.5; the value of E^0 increases slightly at $\alpha = 1.5$ as x_1^0 is reduced to 0.3. These results indicate that E^0 for a controlled cycling column is a function of the slope of the equilibrium line, $m = dy^*/dx$. Moreover, it would appear that E^0 decreases with decreasing m, because it may be shown that for any value of x greater than 0.5,

$$m(x, \alpha_1) < m(x, \alpha_2), \ \alpha_1 > \alpha_2$$

This would also explain why a greater column efficiency is realized at $\alpha = 1.5$ when x_1^0 is decreased to 0.3, because, at the generally lower plate composition levels in this case, larger values of m result (m increases monotonically with decreasing x for a given value of α).

Recall that these simulations were all run for a constant plate efficiency equal to 100% at any instant of time. In conventional distillation this circumstance would require that the over-all column efficiency also be 100%, regardless of the slope of the equilibrium line (to be more general, regardless of the value of the stripping factor, $\lambda = mV/L$) (23). Thus as an apparent consequence of the dynamic operation, the over-all (at the pseudo-steady-state condition) efficiency of a given plate is not necessarily equal to the instantaneous plate efficiency.

Effect of Murphree plate efficiency. In these simulations, various constant values of the instantaneous Murphree plate efficiency, E, were assumed to determine the effect of this parameter on the over-all column efficiency. Together with the assumption of complete mixing of the liquid contents on all plates during the vapor-flow period, it was also assumed that the instantaneous plate efficiency was the same for all plates and equal to the Murphree point efficiency. The results of these simulations are plotted in Fig. 4. Three different curves are presented there, corresponding to: (1) $\alpha = 1.2$, $x_1^0 = 0.5$; (2) $y^* = 1.02x$; (3) $\alpha = 1.2$, $x_1^0 = 0.5$, conventional distillation. Thus m is a constant for the second set. The effective number of theoretical plates for the cases of this second set was calculated from the following general formula for total reflux conditions:

$$N_{\text{eff}} = \left(\log\left[\frac{(K-1)x_c + b}{(K-1)x_1 + b}\right] \Big/ \log K\right) - 1 \qquad (22)$$

which, for b (in the equation, $y^* = Kx + b$) $= 0$, merely reduces to

$$N_{\text{eff}} = \frac{\log (x_c/x_1)}{\log K} - 1 \qquad (23)$$

The value of K for these cases was 1.02.

These results show that the over-all column efficiency of controlled cyclic distillation increases rapidly as the individual plate efficiencies are increased. This conclusion is in good agreement with the results of McWhirter's earlier studies (*18*). The first two curves of Fig. 4 also demonstrate again the effect of the slope of the equilibrium line on over-all column efficiency. Thus the curve corresponding to $\alpha = 1.2$, $x_1^0 = 0.5$, for which equilibrium relationship and composition range the value of m is always less than 1.02, lies generally below the curve corresponding to cyclic distillation for a straight-line equilibrium relationship with a slope of 1.02. The third curve in this figure, which corresponds to conventional distillation at total reflux with $\alpha = 1.2$, $x_1^0 = 0.5$, serves as a direct comparison of conventional and controlled cyclic distillation. This curve is essentially a 45° line, which, in view of the fact that λ here is close to unity, is what one would expect (23).

Effect of number of plates. These studies were made assuming a

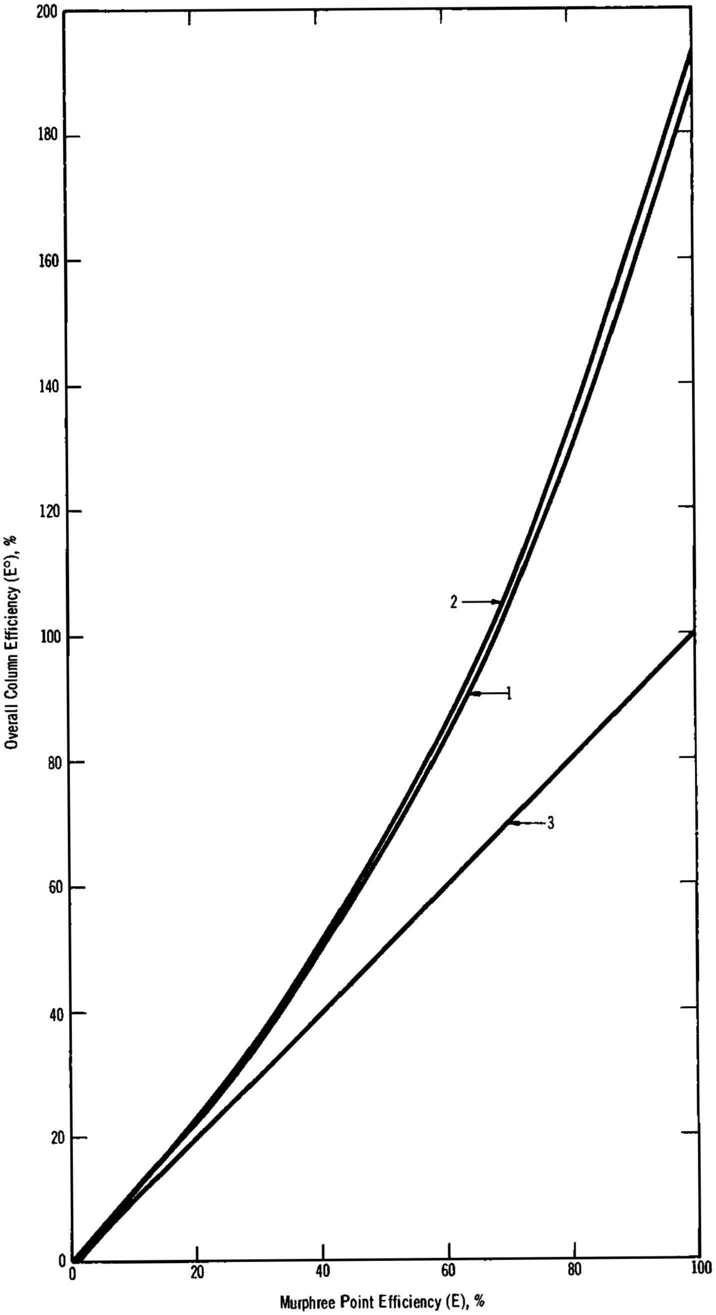

FIG. 4. Effect of Murphree point efficiency (E) on the over-all column efficiency (E^0) of a controlled cycling rectification still at total reflux: 1 – $\alpha = 1.2$, $x_1^0 = 0.5$; 2 – $y^* = 1.02x$; 3 – $\alpha = 1.2$, $x_1^0 = 0.5$, conventional distillation. ($V = 0.1$ g mole/sec; $H = 0.2$ g mole; $S^0 = 20$ g moles; $\phi = 1.0$; $N = 5$).

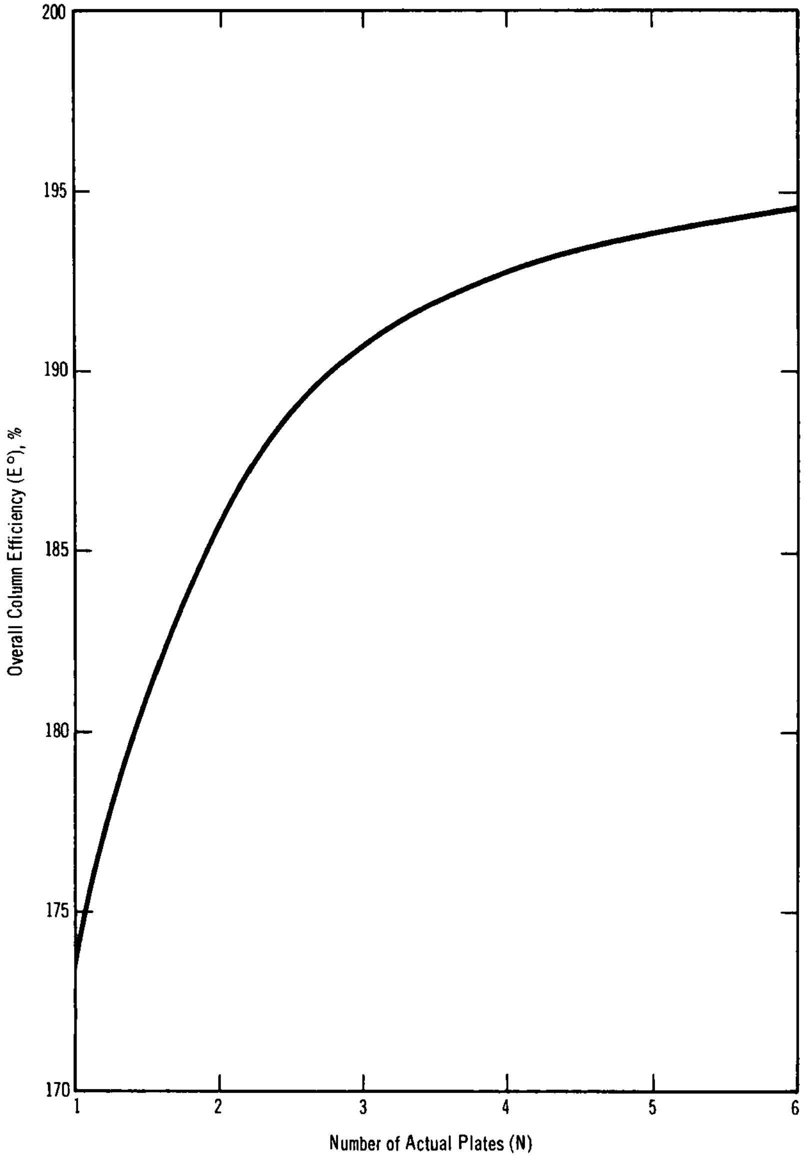

FIG. 5. Effect of number of plates (N) on the over-all column efficiency (E^0) of a controlled cycling rectification still at total reflux. ($V = 0.1$ g mole/sec; $H = 0.2$ g mole; $S^0 = 20$ g moles; $\phi = 1.0$; $E = 100\%$; $y^* = 1.02x$).

straight-line equilibrium relationship in order to eliminate the effect of the slope of the equilibrium line on the over-all column efficiency. From these results (Fig. 5), it appears that the over-all column efficiency of a controlled cycling rectification still increases to an asymptotic value as the number of actual plates in the still increases. In an effort to determine the reason for this behavior, effective efficiencies for the individual plates were computed. A total-reflux modification of Eq. (2) was used for these computations:

$$E_0 = \frac{y_n - y_{n-1}}{y_n^* - y_{n-1}} = \frac{x_{n+1}^V - x_n^V}{Kx_n^V - x_n^V} \tag{24}$$

wherein, as the superscripts indicate, the pseudo-steady-state compositions at the end of the vapor-flow period were used. The results of these computations are presented in Fig. 6, which includes the case of the five-plate rectification still in Fig. 5, as well as addi-

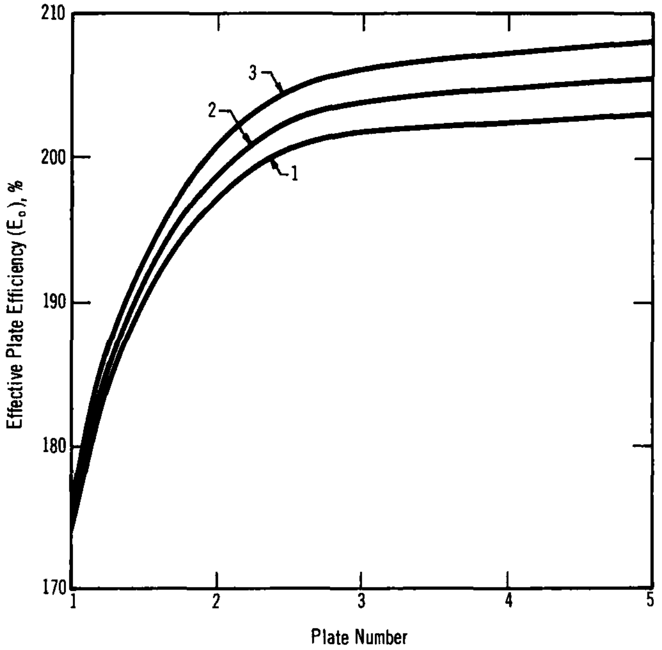

FIG. 6. Effective plate efficiencies (E_0) in a controlled cycling rectification still at total reflux: 1 – $y^* = 1.02x$; 2 – $y^* = 1.04x$; $y^* = 1.06x$. ($V = 0.1$ g mole/sec; $H = 0.2$ g mole; $S^0 = 20$ g moles; $\phi = 1.0$; $E = 100\%$; $N = 5$).

tional simulations run for values of $K = 1.04$ and 1.06. The data of Fig. 6 show a striking resemblance to those of Fig. 5; that is, the effective plate efficiencies also increase from plate to plate up the column to an asymptotic value. Moreover, these plate efficiencies themselves are functions of the slope of the equilibrium line, increasing as the latter is increased.

Controlled Cyclic Distillation at Finite Reflux Ratio

In the preceding section it was seen that the over-all column efficiency of a controlled cycling rectification still, as well as the effective efficiencies of the plates themselves, despite the assumption of perfect mixing, is a function of the slope of the equilibrium line. In conventional distillation the over-all column efficiency is more generally a function of the ratio of the slope of the equilibrium line to that of the operating line ($\lambda = mV/L$), so the effect of the latter on the over-all efficiency in controlled cyclic distillation was investigated. In conventional distillation, the slope of the operating line is L/V, which for rectification is equal to $R/(R+1)$. From Eq. (16) it is seen that the latter quantity is equal to $\phi H/V\tau$ in the case of cyclic distillation. Thus, for given values of ϕ, H, and V, specification of R determines τ and vice versa.

For simplicity in these simulations, the holdup of the still pot was assumed to be so large relative to that of a plate holdup that the composition of the former could be assumed to be constant at all times. Among other advantages, this assumption facilitated the approach to the pseudo-steady-state condition, while preserving an accurate representation of continuous rectification at finite reflux.

These simulations were also run assuming a straight-line equilibrium relationship. Thus the effective number of theoretical plates in the continuous controlled cycling rectification still could be determined from the following equation:

$$N_{\text{eff}} = \log\left[\frac{K(1-\lambda)(x_c^V - x_1^V)}{(K-1)x_c^V + b} + \lambda\right] \Big/ -\log\lambda \qquad (25)$$

Equation (25) is an adaptation to distillation of Colburn's equation (*24*), which was originally derived for absorption:

$$N(E_0 = 1) = \log\left[(1-\lambda)\,\frac{y_b - y_t^*}{y_t - y_t^*} + \lambda\right] \Big/ -\log\lambda \qquad (26)$$

where y_b and y_t are the mole fractions of the solute in the gas entering at the bottom of the absorption column and leaving at the top, respectively, and y_t^* is the composition of the gas phase that would be in equilibrium with the solvent entering at the top. In distillation then, with the assumption that the still pot is equivalent to one theoretical plate, y_b becomes $Kx_1 + b = y_1^*$, y_t^* becomes $Kx_c + b = y_c^*$, and y_t becomes x_c (for a total condenser). The over-all column efficiency is then readily determined by dividing the result of Eq. (25) by the actual number of plates in the still.

The effective (or over-all) plate efficiency of the nth stage is determined by consideration of the steady-state material-balance equation for this stage when the column is operating under conventional conditions:

$$Vy_{n-1} + Lx_{n+1} = Vy_n + Lx_n \qquad (27)$$

whence

$$y_n = y_{n-1} + \frac{R}{R+1}(x_{n+1} - x_n) \qquad (28)$$

where $L/V = R/(R+1)$. For $n = 2$, $y_{n-1} = y_1^*$. Thus a combination of Eqs. (2) and (28) yields, for the over-all efficiency of the nth stage,

$$E_0 = \frac{[R/(R+1)](x_{n+1}^V - x_n^V)}{y_n^* - y_{n-1}} \qquad (29)$$

The results of simulations of controlled cyclic distillation at finite reflux ratios are presented in Figs. 7 and 8. From the first of these figures it is seen that the over-all column efficiency generally decreases with increasing reflux ratio (or increasing slope of the operating line). However, two different factors are contributory here: (1) the relationship between the over-all efficiency of a column, be it conventional or controlled cycling, and the individual plate efficiencies is a function of the reflux ratio (23), and (2) the relationship between the over-all plate efficiencies of a controlled cycling column and the instantaneous plate efficiency is also dependent upon the reflux ratio. The second effect is seen quite clearly in Fig. 8. The over-all plate efficiencies, as determined from Eq. (29), are seen to depend quite markedly upon the reflux ratio, decreasing rapidly with increasing reflux ratio (or slope of the oper-

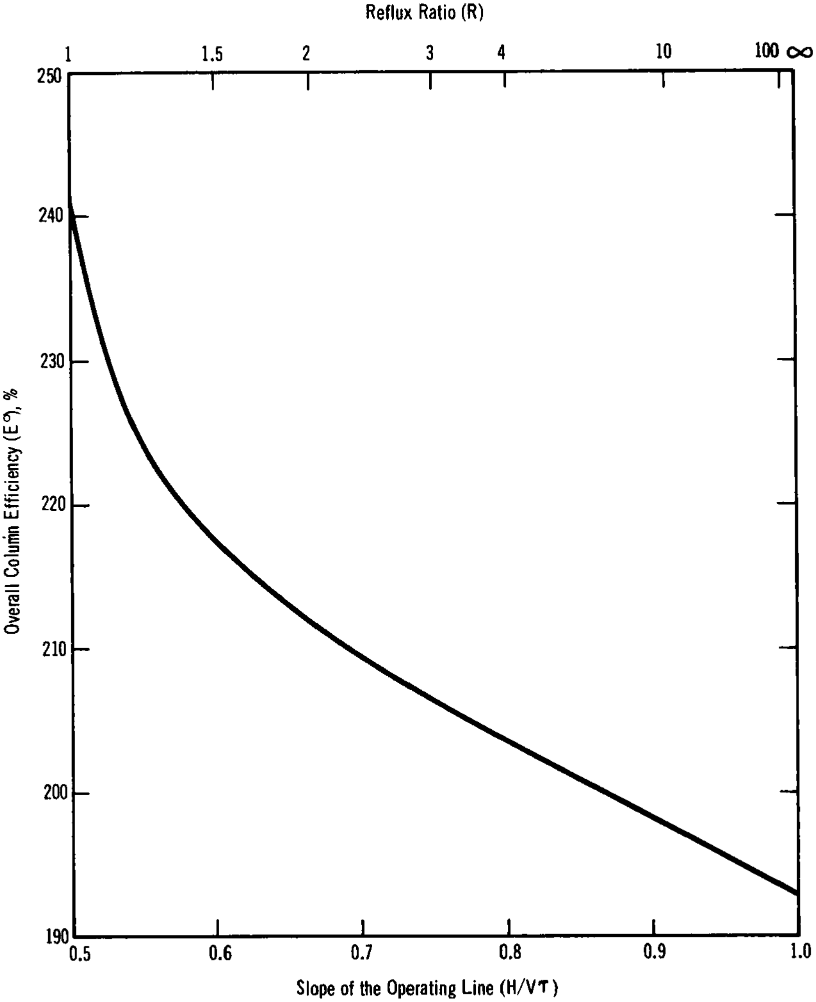

FIG. 7. Effect of reflux ratio (R) on the over-all column efficiency (E^0) of a controlled cycling rectification still. ($V = 0.1$ g mole/sec; $H = 0.2$ g mole; $S = \infty$; $\phi = 1.0$; $E = 100\%$; $N = 5$; $y^* = 1.02x$).

ating line), even though the assumed instantaneous point efficiency in all cases was 1.0. Thus, in a more general fashion, it may be postulated that the over-all plate efficiencies in a controlled cycling column are a function of the stripping factor, $\lambda = mV/L$.

It is also seen from Fig. 8 that, for a given reflux ratio, the over-

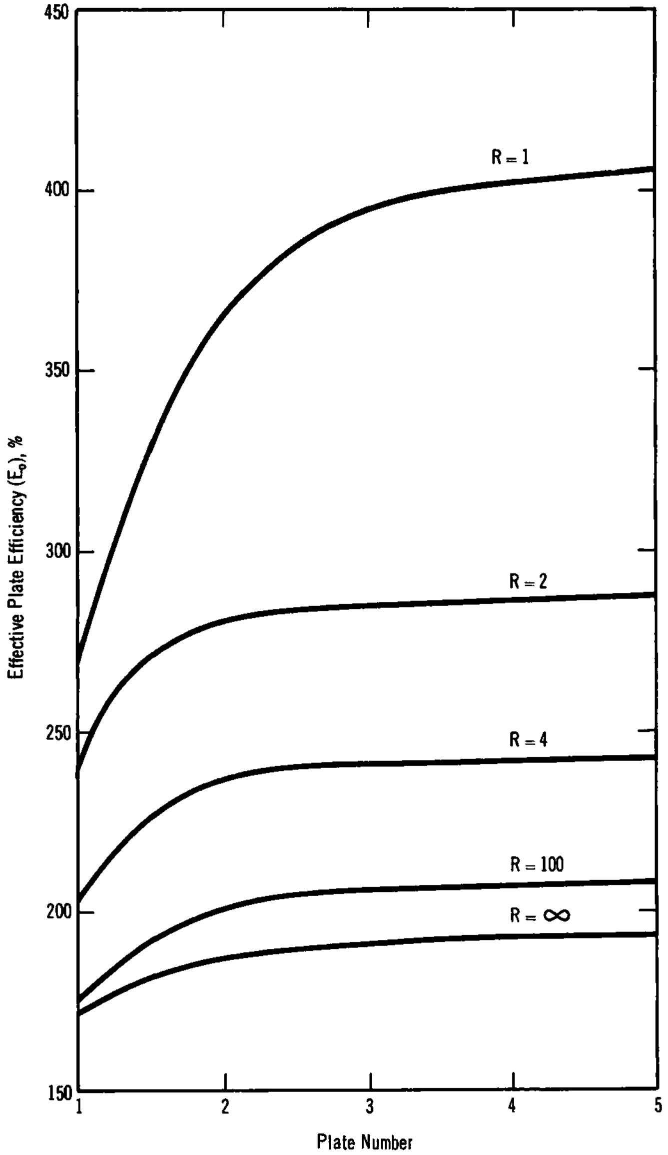

FIG. 8. Effective plate efficiencies (E^0) in a controlled cycling rectification still. ($V = 0.1$ g mole/sec; $H = 0.2$ g mole; $S = \infty$; $\phi = 1.0$; $E = 100\%$; $N = 5$; $y^* = 1.02x$.)

all plate efficiencies increase as one proceeds up the column—the same behavior that was observed in Fig. 6.

Controlled Cyclic Absorption

Several simulations were run to show the extension of the concept of controlled cycling to absorption. The following assumptions were made here: (1) straight-line equilibrium relationship, (2) the carrier gas for the solute (only one) is insoluble in the solvent, (3) the solvent is essentially nonvolatile, and (4) the amount of solute-free solvent holdup on each plate is the same and constant. The last three assumptions result in a constant rate of solute-free gas from each plate during the gas-flow period, and a constant amount of solute-free holdup being dropped from each plate during the liquid-flow period. The dynamic material-balance equations for each plate during the gas-flow period were written in terms of mole ratios:

$$H_s \frac{dX_n}{dt} = G_s(Y_{n-1} - Y_n) \tag{30}$$

where H_s is the solute-free liquid holdup on a plate, G_s is the solute-free gas rate up the column, $X_n = x_n/(1 - x_n)$ is the mole ratio of the solute in the solvent on the nth plate, and Y_n is the mole ratio of the solute in the carrier gas leaving the nth plate. Since all the simulations were run for a value of $\phi = 1$, Eq. (5) was applicable for the liquid (solvent)-flow period.

From the pseudo-steady-state conditions achieved in the simulations, effective plate efficiencies for controlled cyclic absorption as a function of L_s/G_s were computed using Eq. (29), with $R/(R + 1)$ replaced by L_n/G_n. The results (Fig. 9) are quite analogous to those of cyclic distillation, although the actual value of the slope of the operating line for a given plate, $L_n/G_n = [L_s(1 + X_n)/G_s(1 + Y_n)]$, varies from plate to plate because of the absorption of solute. Nonetheless, the theoretical application of controlled cycling to absorption is seen even though the separation improvement to be gained in a real absorption column (the plates of which are usually characterized by poor efficiencies) might be difficult to achieve in practice (cf. Fig. 4). There is no reflux, so a

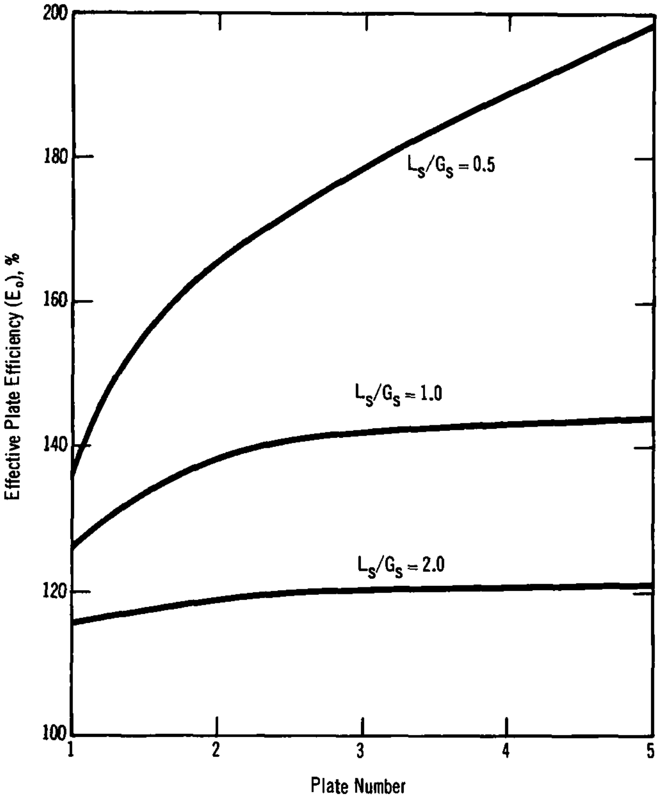

FIG. 9. Effective plate efficiencies in controlled cyclic absorption. ($G_s = 0.1$ g mole/sec; $H_s = 0.2$ g mole; $\phi = 1.0$; $E = 100\%$; $N = 5$; $y^* = 0.5x$; $y_b = 0.3$; $x_t = 0.0$.)

controlled cycling absorption column comes to its pseudo-steady-state condition much more rapidly than its distillation counterpart.

Controlled Cyclic Distillation in a Packed Column

With the fact of improved separating ability of a plate distillation column operating in controlled cyclic fashion established, the question arises whether similar behavior could be expected in a packed column. Simulation of controlled cyclic distillation in a packed column is not as simply handled as for a plate column, because the behavior of such an operation is described by a system of partial differential equations:

$$A_L \frac{\partial x}{\partial t} = L \frac{\partial x}{\partial z} - k_g a(y^* - y) \tag{31}$$

$$A_V \frac{\partial y}{\partial t} = -V \frac{\partial y}{\partial z} + k_g a(y^* - y) \tag{32}$$

where A_L and A_V are the holdups per unit volume of packing of the liquid phase and vapor phase, respectively, and $k_g a$ is the combined mass-transfer–interfacial area coefficient. At steady-state conventional operation, Eqs. (31) and (32) reduce to the standard material-balance equation for a packed column:

$$L \frac{dx}{dz} = V \frac{dy}{dz} = k_g a(y^* - y) \tag{33}$$

If it is assumed that the vapor-phase holdup is negligible, the right equality of Eq. (33) may be used for calculating the distribution of y's up the column under transient conditions. During the vapor-flow period of controlled cyclic distillation, $L = 0$, and thus Eq. (31) may be written

$$-A_L \frac{\partial x}{\partial t} = k_g a(y^* - y) \tag{34}$$

The following procedure was used in the digital simulations of controlled cyclic operation of a packed distillation column. The column was broken up into a finite number of Δz elements, and the right equality of Eq. (33) was then written in finite-difference form. From an initial distribution of x values through the column, a distribution of y values (assuming y = the still-pot vapor composition = y_s^*) was calculated from this finite-difference equation. The driving force at the top of a given element was used to calculate the composition of vapor leaving that element. After this distribution of y values had been calculated, a new distribution of x values after a short time step (duration of Δt) was calculated from Eq. (34), which had also been written in finite-difference form. This procedure was then repeated until the amount of material accumulated in the condenser during this vapor-flow period equalled the amount to be dropped during the liquid-flow period (all simulations were for total reflux operation).

The equations for the liquid-flow period were essentially the same as those for a plate column. That is, if the number of Δz elements to be dropped during the liquid-flow period was k (always an integer), then the composition of the ith element after this period, x_i^L, was

$$x_i^L = x_{(i+k)}^V \tag{35}$$

where $x_{(i+k)}^V$ is the composition of the $(i+k)$th element at the end of the vapor-flow period. The complete procedure described by Eqs. (33) to (35) was then repeated for a number of cycles until the compositions at the ends of successive cycles were essentially invariant.

The performance of controlled cyclic operation of a packed column was evaluated as follows. For a straight-line equilibrium relationship, integration of Eq. (34) under conventional steady-state conditions yields

$$\ln\left[\frac{x_c(K-1)+b}{x_b(K-1)+b}\right] = \frac{(K-1)k_g aZ}{V} \tag{36}$$

where Z is the total height of packing and x_b is the composition of the first (or bottom element). Also, it can be shown for a plate column at total reflux that

$$\ln\left[\frac{x_c(K-1)+b}{x_b(K-1)+b}\right] = N \ln K \tag{37}$$

Here x_b is the composition of the first plate and N is the number of theoretical plates in the column. Combining Eqs. (36) and (37) then yields

$$N = \frac{(K-1)k_g aZ}{V \ln K} \tag{38}$$

for the number of theoretical plates in a packed column. The actual (or effective) number of theoretical plates in the simulations was determined from Eq. (22), and the over-all column efficiency, relative to that of conventional operation, was computed by dividing this result by the number given by Eq. (38).

The results of simulations of a controlled cycling packed column are presented in Table 4. Although these results are not quite as unequivocal as those for plate columns, several important conclusions may nonetheless be derived therefrom. The first of these is

TABLE 4

Results of Simulations of Controlled Cyclic Operation of a Packed Distillation Column at Total Reflux ($S^0 = 20.0$ moles, $A_L = 0.04$ moles/ft^3, $A_V = 0$, $k_g a = 0.25$ moles/ft^3-sec, $V = 0.1$ moles/ft^2-sec, $y^* = 1.02x$, $Z = 2$ ft, $N = 5.05$)

Number of Δz elements dropped	Height of a Δz element, ft	Duration of a time step, Δt, sec	Effective number of theoretical plates, N_{eff}	Over-all column efficiency, $100\ N_{\text{eff}}/N$
0[a]	0.04	0.01	4.59	90.9
0[a]	0.04	0.001	4.58	90.7
12.5	0.004	0.01	5.14	101.7
2.5	0.04	0.01	4.91	97.2
5.0	0.04	0.01	4.90	97.0
10.0	0.04	0.001	4.68	92.7
10.0	0.04	0.01	4.81	95.2
20.0	0.02	0.01	4.93	97.6
40.0	0.01	0.01	4.99	98.8
100.0	0.004	0.01	4.02	99.5
20.0	0.04	0.01	4.43	87.7
30.0	0.04	0.01	3.94	78.0

[a] Simulations of conventional operation.

that the separating ability of a controlled cycling packed column decreases monotonically as the amount of liquid dropped during the liquid-flow part of the cycle (or the duration of the vapor-flow period) increases. Also, although the exact values of the over-all column efficiencies presented may be somewhat in doubt, the considerable separation improvements obtained through cyclic operation of plate columns cannot be achieved by similar operation of packed columns (assuming that the value of $k_g a$ remains unchanged). The difficulty in obtaining accurate results via simulation lies in the approximation of a set of partial differential equations with a set of finite-difference equations. Only about 91% of theoretical separation was obtained by simulation of conventional operation (the first two entries of Table 4). Conceivably this discrepancy could be reduced by decreasing the elemental height (Δz) of packing. However, considerations of stability and/or computer time interfere here. Nonetheless, the principal conclusion remains that controlled cyclic operation of a packed column should not materially improve the separation (unless greater turbulence is concurrently promoted), and that the primary advantage of such operation would be increased throughout. This conclusion is in good agreement with the results of experiments (*19*) in which it was found that the ratio of the maximum capacity of a packed column under controlled cyclic operation to that for conventional operation was about 3, whereas the separating ability of the cyclic column was essentially the same or at best slightly higher than that of the conventional column.

Indeed, it may be postulated that the actual upper limit of the separating ability of a cyclic packed column, neglecting hydrodynamic considerations, should merely be that of a conventional packed column. The basis of this idea is that a packed column may be thought of as an infinite sequence of infinitesimal stages each with zero efficiency, and hence, in accordance with Fig. 4, no improvement may be obtained through cyclic operation.

THE ANALOGY WITH CONVENTIONAL OPERATION

Using matrix algebra, analytical representations of the pseudo-steady-state condition are possible for certain simplified conditions. Let us define a composition vector, $\mathbf{x}_p(t)$, which represents the compositions of the more volatile component on the stages dusing the vapor-flow period of the *p*th cycle. A transition matrix, $\mathbf{J}(t)$, is defined which transforms the initial composition vector, $\mathbf{x}_p(0)$, to its value at time *t*:

$$\mathbf{x}_p(t) = \mathbf{J}(t)\mathbf{x}_p(0) \tag{39}$$

$\mathbf{J}(t)$ is a square matrix and $\mathbf{J}(0)$ is, of course the identity matrix. At the end of the vapor-flow period, we have

$$\mathbf{x}_p^V = \mathbf{x}_p(\tau) = \mathbf{J}(\tau)\mathbf{x}_p(0) \tag{40}$$

For the liquid-flow period we define a square matrix, D, which is independent of time and which transforms the composition vector at the beginning of the liquid-flow period, $\mathbf{x}_p^V$, to the composition vector at the end of this period:

$$\mathbf{x}_p^L = \mathbf{D}\mathbf{x}_p^V \tag{41}$$

However, the compositions at the end of the liquid-flow period are also the compositions at the beginning of the next vapor-flow period. Thus

$$\mathbf{x}_{p+1}(0) = \mathbf{x}_p^L = \mathbf{D}\mathbf{x}_p^V = \mathbf{D}\mathbf{J}(\tau)\mathbf{x}_p(0) \tag{42}$$

Now, at the pseudo-steady-state condition (as p becomes very large),

$$\mathbf{x}_{p+1}(0) = \mathbf{x}_p(0) \tag{43}$$

or

$$\mathbf{x}^L = \mathbf{D}\mathbf{J}(\tau)\mathbf{x}^L \tag{44}$$

and finally,

$$[\mathbf{D}\mathbf{J}(\tau) - \mathbf{I}]\mathbf{x}^L = 0 \tag{45}$$

The foregoing equation may then be solved for $\mathbf{x}^L$, presuming the condition $\det[\mathbf{D}\mathbf{J}(\tau) - \mathbf{I}] = 0$ is satisfied (*20*). This solution will then yield the complete composition profile for a controlled cycling rectification still. Alternatively, analytical expressions for each plate composition can be derived which, in conjunction with the equations given earlier for over-all plate efficiencies, may be used to obtain analytical expressions for the latter as functions of operating parameters.

Let us consider first the second stage (first plate) of a controlled cycling rectification still. The still pot is assumed to be very large, so that the compositions of the liquid in the pot and of the vapor leaving therefrom are constant at all times. The boilup rate (V) and liquid-phase holdup (H) are also assumed to be constants for each plate in the still. Then, under the condition of $\phi = 1$, the effective efficiency of this first plate is (*20*)

$$E_0 = \frac{e^{E\lambda} - 1}{\lambda} \tag{46}$$

Equation (46) is identical to one derived by Lewis (*21*) in his studies of the relationship between the over-all efficiencies of bubble-cap plates and point efficiencies. Lewis showed that the over-all plate efficiency can be greater than the local point efficiency if concentration gradients in the liquid phase could be set up across the plate, that is, if backmixing could be reduced or eliminated. Thus, for example, plate efficiencies greater than 100% can be realized. It must be realized here that efficiencies greater than 100% do not imply a violation of thermodynamic equilibrium; rather, they result from the definition of plate efficiency, and merely imply that one actual plate may, under certain conditions, be equivalent to more than one theoretical stage of separation. Lewis found that the amount of improvement in the over-all plate efficiency is dependent upon, among other things, the downcomer configuration and the degree of vapor-phase mixing. In particular, he considered three cases:

1. Vapors enter each plate completely mixed.
2. Vapors rise from plate to plate without mixing and the liquid flows in the same direction on all plates.
3. Vapors rise from plate to plate without mixing and the liquid flows in opposite directions on alternate plates.

In all three cases it is assumed that no backmixing occurs in the liquid phase. Equation (46) was then derived by Lewis for case 1. Thus, although this equation corresponds to conventional distillation with a vapor composition constant with respect to distance, it is also seen to be valid for controlled cyclic distillation with a time-invariant vapor composition.

We consider now the case wherein the composition of the vapors entering a certain plate does vary with time during the vapor-flow period. Typically, this would correspond to an upper plate of a rectification still with many plates, so that any effects of a constant still-pot composition would be damped out. As before, it is assumed that E and H are constants and that $\phi = 1$. Based on the solution of Eq. (45), the over-all efficiency for such a plate is given by the following expression (*20*):

$$\frac{E^2\lambda}{\exp(\Psi + E - 1)} = \frac{\exp(E\lambda)}{\Psi} \tag{47}$$

where

$$\Psi \equiv 1 + E_o(\lambda - 1) \tag{48}$$

Thus, from Eq. (48),

$$E_0 = \frac{\Psi - 1}{\lambda - 1} \tag{49}$$

By taking logarithms of Eq. (47) and rearranging, one obtains the following equation for the parameter Ψ as a function of E and λ:

$$\lambda = \left(\frac{1}{E} + \frac{1}{\Psi - 1}\right) \ln \Psi \tag{50}$$

Equations (49) and (50) were obtained by Lewis (*21*) for the over-all plate efficiency in a conventional distillation column under the conditions of case 2, that is, where the composition of the vapors entering the plate varies with distance in the same fashion as the liquid composition on the plate changes (as opposed to case 3). In this connection, Lewis' case 3, which is probably the most common in conventional operation because of designers' understandable reluctance to install downcomers in the configuration of case 2, appears to have no relevance to controlled cyclic distillation.

The above results represent a mathematical demonstration of the analogy between controlled cyclic distillation and conventional distillation with transverse concentration gradients across the plates. A sketch of the pertinent features of this analogy is presented in Figure 10. The existence of a liquid-phase concentration gradient across the nth plate of a distillation column with downcomers and operating in conventional fashion is schematically shown in Fig. 10(a). Distance across the plate is denoted by z and the total length of liquid flow across the plate by z_0. The value of $z = 0$ corresponds to the point at which liquid in the downcomer from plate $n + 1$ enters the nth plate. Hence the concentration at this point, $x_n(0)$, is also equal to the concentration at the end of the plate immediately above, $x_{n+1}(z_0)$, providing of course that no mass transfer occurs in the downcomer. If it is assumed that there is little or no liquid backmixing on the plate, then the liquid will be progressively depleted of the more volatile component by contact with the vapor from plate $n - 1$ as it flows across the plate. At the end of its traverse across the plate ($z = z_0$), it will have the composition $x_n(z_0)$ and will be discharged to plate $n - 1$, and the same process will be repeated on this plate with $x_{n-1}(0) = x_n(z_0)$.

Consider now Fig. 10(b). The independent variable in this graph is time (t) and the length under consideration is the duration of the vapor-flow period of the cycle (τ). If there is no enrichment of the liquid phase on the nth plate by liquid flowing down from plate $n + 1$ (i.e., no liquid backmixing in the time domain), as indeed is the case during the vapor-flow period, depletion of the more volatile component will occur on each plate during the course of this period. The concentration of this component will thus decrease monotonically with time. The liquid on each plate is now assumed to be perfectly mixed; that is, no concentration gradients with respect to distance exist. If the amount of material dropped during the liquid-flow period is exactly equal to one plate holdup (i.e., $\phi = 1$), then the analogy becomes precise. The concentration on the nth

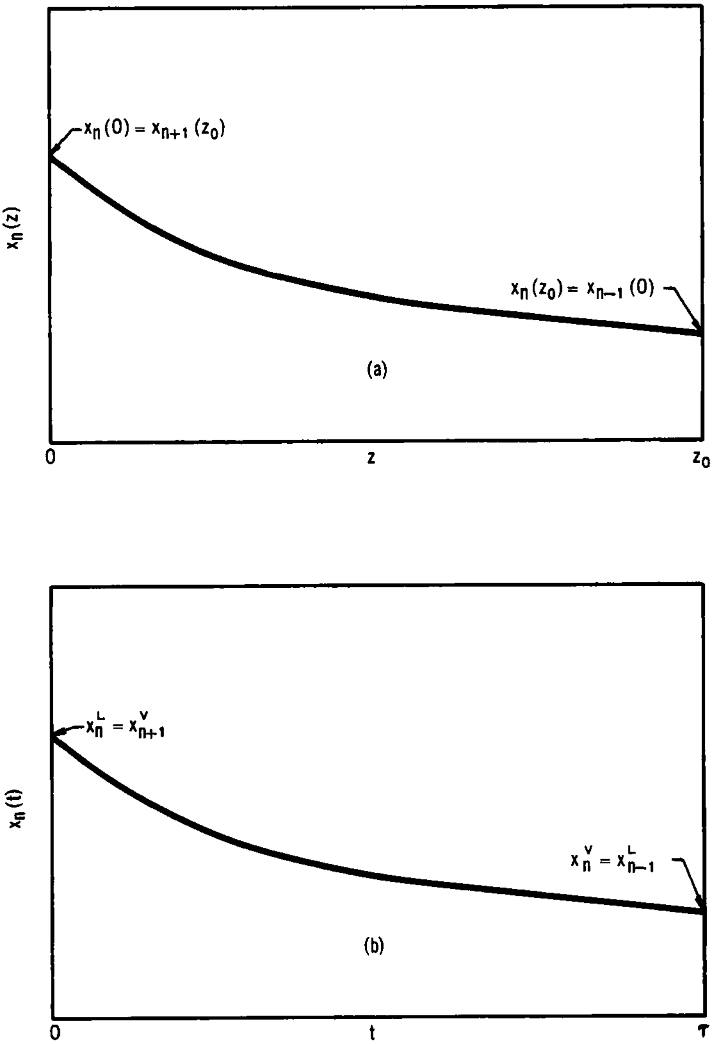

FIG. 10. Sketch of the analogy between (a) conventional distillation with a liquid-phase concentration gradient on the *n*th plate and (b) controlled cyclic distillation ($\phi = 1.0$).

plate at the beginning of the vapor-flow period, $x_n(0)$, corresponds to that at the end of the liquid-flow period, x_n^L, but this is also equal to the concentration on plate $n + 1$ at the end of the vapor-flow period, x_{n+1}^V.

Similarly, at the end of the vapor-flow period $x_n(\tau) = x_n^V$, which is also equal to x_{n-1}^L. It is readily seen that this analogy is constructed by merely substituting, with the restriction of $\phi = 1$, time for distance as the independent variable and is independent of the particular modification of vapor flow, that is, regardless of whether one considers case 1 or case 2. The only distinction is that, as Lewis (*21*) showed for conventional operation and as was seen earlier (see Figs. 6 and 8) for controlled cyclic distillation, for given values of E and λ, E_0 will be larger in case 2.

The existence of transverse concentration gradients and the beneficial effects to be derived therefrom in conventional operation are not mathematical figments. Recent publications (*25,26*) have presented experimental data showing the improvement in over-all efficiency of a sieve plate resulting from concentration gradients. Also, the construction of trays with special baffles to minimize backmixing and thus improve tray efficiency has been reported (*27*). Thus there are both theoretical and experimental bases for the application of this analogy in the analysis of controlled cyclic distillation phenomena.

ANALYSIS OF SIMULATION RESULTS

The analogy developed above can be used to explain in greater detail some of the results of computer simulations presented earlier. In Fig. 4 it was seen that the over-all column efficiency (E^0) of a five-plate rectification still operating in controlled cyclic fashion varied almost exponentially with the local point efficiency, E. All these simulations were run at total reflux and for slopes of the equilibrium line close to unity; thus $\lambda = m \cong 1$ and the over-all column efficiency should then be close to the over-all plate efficiencies (*23*). This is readily seen to be true in the results of simulations of conventional distillation (with perfect mixing on each plate), which are also presented in this figure. In this case, of course, the over-all plate efficiency should be identical to the local point efficiency.

There is, however, another factor to be considered in the analysis of over-all column efficiencies of controlled cyclic distillation, and that is the transition from the conditions of case 1 to those of case 2. For given values of E and λ, the over-all plate efficiency for case 2 will always be larger than that for case 1. Thus, for a controlled cycling rectification still, the effective plate efficiency will increase from a minimum for the first plate above the still pot and approach some limiting value [given by Eqs. (49) and (50)] for the plates near the top of the still, where the conditions of case 2 predominate. This will then have a corresponding effect on the over-all column efficiency, and the latter should slowly increase (for $\lambda \cong 1$) with an increasing number of plates in the still. Indeed, this effect is clearly seen in Fig. 5, in which λ was held constant at 1.02 and only the number of plates in the still was varied.

Because the analogy is concerned with over-all plate efficiencies rather than column efficiencies, it is of interest to investigate the variation of the former with column operating parameters. In Fig. 6 individual plate efficiencies for a five-plate controlled cycling rectification still operating at total reflux were presented. In all these simulations both E and ϕ are equal to unity. The transition from case 1 to case 2 in these results is clearly evident. These numbers may be compared with those resulting from the equations of the analogy. For example, for $\lambda(=m) = 1.02$ and $E = 1.0$, Eq. (46), which corresponds to case 1, yields a value for E_0 of 173.8%, which compares with the simulation result of 173.4% for the first plate. Similarly, for the same values of λ and E, solution of Eq. (50) yields $\Psi = 1.0406$, from which, together with Eq. (49), a limiting value (case 2) for E_0 of 203% is obtained. This compares favorably with a simulation result of 202.9% for the fifth (top) plate.

The results of simulations of controlled cyclic distillation in a five-plate rectification still operating at finite reflux ratios ($\phi = 1$, $E = 1$, $m = 1.02$) were presented in Fig. 8. Individual plate efficiencies are given there also. Since the slope of the operating line $[R/(R + 1)]$ diminishes with decreasing reflux ratio (R), the stripping factor, λ, which is the ratio of the slope of the equilibrium line to the slope of the operating line, must increase with decreasing R. Then, in accordance with the analogy, the individual plate efficiencies of a controlled cycling rectification still should increase with decreasing reflux ratio. This effect is clearly seen in the data of this figure. Similar results were also obtained from simulations of controlled cyclic absorption with varying liquid-to-gas ratios (see Fig. 9).

CONCLUSION

The physical realization of the separation improvements in controlled cyclic distillation as predicted by this analogy depends upon the satisfaction of the various assumptions made in its development. These were: no liquid flow during the vapor-flow period, plug flow (no mixing) down the column and no mass transfer during the liquid-flow period, and the simultaneous dropping of exactly one plate holdup during this latter period. These assumptions, of course, are considerations of a hydrodynamic nature, and cannot be validated by simulation and/or mathematical analysis as easily as were the questions regarding separation. Nonetheless, it has been shown experimentally (*18,19*) that these conditions can be sufficiently approximated in small columns (up to 6 inches in diameter), and a significant separation improvement achieved. In a sense, then, the analogy presented herein represents a way of estimating the maximum improvement that may be realized. Far more important though, it puts the concept of controlled cyclic operations on a firm theoretical ground, and thus provides sufficient justification for exploring the possibilities of its large-scale application.

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