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Study of Controlled Cyclic Distillation: II. Analytical Transient Solution and Asymptotic Plate Efficiencies

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Summary

The dynamic equations of the composition variables of a controlled cycling distillation column are solved to obtain the transient solutions for the vapor-flow period. These solutions are then used to establish asymptotic expressions for the compositions at the pseudo-steady-state condition of the cycling column. Analytical expressions for the asymptotic plate efficiencies in terms of the operating conditions, equilibrium data, and local point efficiencies are derived to show quantitatively the amount of improvement in the separating ability that can be achieved in an ideal cycling column. A method of numerical iterative solution for a nonlinear equilibrium relationship is demonstrated, and a simplified graphical method for calculating the number of stages required for a given separation is presented.

In this paper the analytical expressions describing the dynamics of a distillation column operated in controlled cyclic fashion have been derived. Using this relationship, it is possible to predict the time history of the compositions at every plate, and furthermore to obtain the asymptotic pseudo-steady-state values of the compositions. The plate efficiencies of the pseudo-steady-state operation can then be calculated as a function of the local point efficiency, the equilibrium relationship, and the operating parameters. This efficiency information may then be used in the design of controlled cyclic distillation columns.

Matrix notations are, in general, employed here to make the presentation more compact and the concept easier to follow for those who are used to matrix notations.

DESCRIPTION OF THE METHOD

Let the composition of the more volatile component of a binary system on the *i*th stage be denoted by x_i. The condenser is the *n*th stage and the reboiler is the first stage. Boldface **x** is used to denote the composition vector.

Let us first consider the vapor-flow period. At the beginning of this period, the composition vector has a value $\mathbf{x}(0)$. A transition matrix $\mathbf{J}(t)$ is defined which transforms the initial composition vector $\mathbf{x}(0)$ to its value at time t, $\mathbf{x}(t)$:

$$\mathbf{x}(t) = \mathbf{J}(t)\mathbf{x}(0) \tag{1}$$

Equation (1) is equivalent to its component form:

$$x_i(t) = \sum_{j=1}^{n} J_{ij}(t)x_j(0)$$

$\mathbf{J}$ is an $n \times n$ matrix and $\mathbf{J}(0)$ is an identity matrix. The form of $\mathbf{J}$ is discussed in the next section. At the end of the vapor-flow period, $t = \tau$, the composition vector will be

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

where the subscript p refers to the pth cycle.

During the liquid-flow period, one again may describe the change of the state by a transition matrix, which shall be called the "drop matrix, **D**." The drop matrix transforms the composition vector at the beginning of the liquid-flow period, $\mathbf{x}_p^V$, to the composition vector at the end of the period, $\mathbf{x}_p^L$; i.e.,

$$\mathbf{x}_p^L = \mathbf{D}\mathbf{x}_p^V \tag{2}$$

However, the compositions at the end of the liquid-flow period are just the compositions at the beginning of the next vapor-flow period. Using Eqs. (1) and (2), one obtains

$$\mathbf{x}_{p+1}(0) = \mathbf{x}_p^L = \mathbf{D}\mathbf{x}_p^V = \mathbf{D}\mathbf{J}_p(\tau)\mathbf{x}_p(0) \tag{3}$$

Using the recursion formula (3) together with (1), the compositions at any time can be calculated. As p becomes very large, Eq. (3) approaches

$$\mathbf{x}^L = \mathbf{D}\mathbf{J}\mathbf{x}^L \tag{4}$$

Here $\mathbf{x}^L$ denotes the asymptotic pseudo-steady-state composition vector at the end of the liquid-flow period. The pseudo-steady-state compositions at any time during the vapor-flow period can be obtained using Eq. (1).

When the equilibrium relationship is nonlinear, the J matrix will be a function of $\mathbf{x}$ also:

$$\mathbf{J} = \mathbf{J}(t; \mathbf{x})$$

However, when the cycle time, τ, is not very large, $\mathbf{x}$ does not change very much during the vapor-flow period. One may use the average value of $\mathbf{x}$ or simply take $\mathbf{x}(0)$ in calculating $\mathbf{J}$. The nonlinear cases will be discussed in greater detail later.

Equation (4) defines n equations for the n unknown compositions. The solution $\mathbf{x}^L$ is the characteristic vector of the matrix $\mathbf{DJ}$ with an eigenvalue of unity. Any multiple of the solution, $\mathbf{x}^L$, is also a solution of Eq. (4). However, once one of the compositions is fixed, say x_1, the rest of the compositions will all be determined.

For Eq. (4) to yield a solution, it is necessary to have

$$\det [\mathbf{DJ} - \mathbf{I}] = 0 \tag{5}$$

Condition (5) may be considered as the necessary condition for the cyclic distillation operation to have an asymptotic steady-state value.

THE UNIQUENESS OF THE SOLUTION

The reader will find in the next section that the matrix $\mathbf{DJ}$ is a so-called nonnegative matrix. Such matrices have important applications in the theory of probability, Markov processes, etc.

The theorem of Frobenius (*1,2*) ensures that a nonnegative matrix has a positive characteristic root which is also the maximum among all the roots. To that positive maximal root there corresponds a characteristic vector with positive entries. This is the existence theorem of a solution to Eq. (4).

In (*2*), page 63 of Vol. 2, it is also shown that a nonnegative matrix cannot have two linearly independent nonnegative characteristic vectors. This is the uniqueness theorem of a solution to Eq. (4).

DERIVATION OF THE TRANSITION MATRIX

In our derivation we shall use the approach of immediately making simplifying assumptions and to provide the very specific derivation which hopefully will be easier to follow. Later these assumptions will be removed and the steps of the derivation for more general cases will either be given in greater detail or the possibility of derivation merely indicated.

Consider the case where $y_i^* = k_i x_i$ and the k_i's are constants; however, every plate has its own value of k_i.

The column during the vapor-flow period can be described by the following differential equations:

$$\text{Reboiler:} \quad \frac{d(H_1 x_1)}{dt} = -V_1 y_1 \tag{6}$$

$$\text{Tray:} \quad H_i \frac{dx_i}{dt} = -V_i y_i + V_{i-1} y_{i-1} \qquad i = 2, \ldots, n-1 \tag{7}$$

$$\text{Condenser:} \quad \frac{d(H_n x_n)}{dt} = V_{n-1} y_{n-1} \tag{8}$$

Assume here that the local Murphree efficiencies for all of the stages are 100%, and assume further that

$$V_i = V \text{ for all } i = 1, \ldots, n-1$$
$$H_i = H \text{ for all } i = 2, \ldots, n-1$$

Then

$$\frac{d(H_1 x_1)}{d\theta} = -k_1 H x_1 \tag{9}$$

$$\frac{dx_i}{d\theta} = -k_i x_i + k_{i-1} x_{i-1} \qquad i = 2, \ldots, n-1 \tag{10}$$

$$\frac{d(H_n x_n)}{d\theta} = H k_{n-1} x_{n-1} \tag{11}$$

after the dimensionless time, $\theta = Vt/H$, is introduced.

The assumption that all V_i's and all H_i's are constant and identical except H_1 and H_n is not at all necessary. Variations in the V_i's can easily be absorbed in the k_i's and variations in H_i merely introduce multipliers to the off-diagonal terms of the **J** matrix.

Consider the reboiler. Since $H_1 = H_1^0 - Vt = H_1^0 - H\theta$, then

$$\frac{d(H_1 x_1)}{d\theta} = H_1 \frac{dx_1}{d\theta} - H x_1 \tag{12}$$

Therefore, combining Eqs. (9) and (12), one has

$$\frac{H_1}{H} \frac{dx_1}{d\theta} = (1 - k_1) x_1 \tag{13}$$

The solution to Eq. (13) is

$$x_1 = x_1^0 \left(\frac{H_1}{H_1^0}\right)^{k_1-1} = x_1^0 \left(1 - \frac{H}{H_1^0}\,\theta\right)^{k_1-1} \tag{14}$$

Usually, H_1^0, the initial reboiler holdup, is very large in comparison with the tray holdup, H. The solution may then be expanded into a series.

$$x_1 = x_1^0 \left[1 - (k_1 - 1)\left(\frac{H\theta}{H_1^0} + \frac{1}{2}\left(\frac{H\theta}{H_1^0}\right)^2 + \cdots\right)\right]$$

$$\approx x_1^0 \left[1 + (1 - k_1)\,\frac{H\theta}{H_1^0}\right] = x_1^0(1 + \beta\theta) \tag{15}$$

Now consider the plates. Let us define a vector

$$\bar{\mathbf{x}} = \begin{bmatrix} x_2 \\ \cdot \\ \cdot \\ \cdot \\ x_{n-1} \end{bmatrix}$$

to be the plate-composition vector. Then Eq. (10) may be written

$$\frac{d}{d\theta}\,\bar{\mathbf{x}} = \mathbf{A}\bar{\mathbf{x}} + \bar{\mathbf{b}} \tag{16}$$

where the elements of the A matrix, a_{ij}, are

$$a_{ii} = -k_{i+1} \qquad a_{i,i-1} = k_i \qquad i = 1, \ldots, n-2$$

All the other elements are zero. The $\bar{\mathbf{b}}$ vector has $\bar{b}_1 = k_1x_1$, $\bar{b}_i = 0$; $i = 2, \ldots, n-2$.

For $n = 5$, or a three-plate column, Eq. (16) is

$$\frac{d}{d\theta}\begin{bmatrix} x_2 \\ x_3 \\ x_4 \end{bmatrix} = \begin{bmatrix} -k_2 & 0 & 0 \\ k_2 & -k_3 & 0 \\ 0 & k_3 & -k_4 \end{bmatrix}\begin{bmatrix} x_2 \\ x_3 \\ x_4 \end{bmatrix} + \begin{bmatrix} k_1x_1 \\ 0 \\ 0 \end{bmatrix} \tag{17}$$

One may solve Eq. (16) by the Laplace transform method. Let

$$\bar{\mathbf{z}}(p) \equiv L[\bar{\mathbf{x}}(\theta)] \qquad \text{and} \qquad \bar{\mathbf{b}}' \equiv L[\bar{\mathbf{b}}]$$

Equation (16) then becomes, after transformation,

$$p\bar{\mathbf{z}} - \bar{\mathbf{x}}(0) = \overline{\overline{\mathbf{A}}}\bar{\mathbf{z}} + \bar{\mathbf{b}}'$$

or

$$\bar{\mathbf{z}} = (p\mathbf{I} - \bar{\mathbf{A}})^{-1}[\bar{\mathbf{x}}(0) + \bar{\mathbf{b}}'] \tag{18}$$

Again, take (17) as an example:

$$\begin{bmatrix} z_2 \\ z_3 \\ z_4 \end{bmatrix} = \frac{1}{\det} \begin{bmatrix} (p+k_3)(p+k_4) & 0 & 0 \\ k_2(p+k_4) & (p+k_2)(p+k_4) & 0 \\ k_2k_3 & k_3(p+k_2) & (p+k_4) \end{bmatrix} \begin{bmatrix} x_2(0) \\ x_3(0) \\ x_4(0) \end{bmatrix} + \begin{bmatrix} k_1z_1 \\ 0 \\ 0 \end{bmatrix} \tag{19}$$

where

$$\det \equiv (p+k_2)(p+k_3)(p+k_4)$$

After inverting Eq. (18) and using Eq. (15), the solution is in the form

$$x_i(\theta) = \sum_{l=1}^{i} j_{il}x_l(0) \qquad i = 2, \ldots, n$$

The general form of j_{ij} is shown in Table 1.

TABLE 1

J Matrix for $y_i^* = k_ix_i$

$$j_{11} = 1 + \beta\theta \quad j_{ll} = e^{-k_l\theta};\ l = 2, \ldots, n-1$$

$$j_{nn} = \frac{H_n^0}{H_n}$$

$$j_{l1} = \left(\prod_{i=1}^{l-1} k_i\right)\left[\int_0^\theta \sum_{j=2}^{l} \frac{e^{-k_j\tau}\,d\tau}{\prod_{i=2}^{l}{}'\,(k_i - k_j)} + b\int_0^\theta\int_0^\tau \sum_{j=2}^{l} \frac{e^{-k_j\lambda}\,d\lambda\,d\tau}{\prod_{i=2}^{l}{}'\,(k_i - k_j)}\right]$$

$$j_{lm} = \left(\prod_{i=m}^{l-1} k_i\right)\left[\sum_{j=m}^{l} \frac{e^{-k_j\theta}}{\prod_{i=m}^{l}{}'\,(k_i - k_j)}\right];\ l = 2, \ldots, n-1;\ m = 2, \ldots, l-1$$

$$j_{n1} = \frac{Hk_{n-1}}{H_n}\int_0^\theta j_{n-1,1}(\lambda)\,d\lambda$$

$$j_{nm} = \frac{Hk_{n-1}}{H_n}\int_0^\theta j_{n-1,m}(\lambda)\,d\lambda$$

$j_{lm} = 0$ for all $m > l$

Note: $\prod_{i=m}^{l}{}'\,(k_i - k_j) \equiv \prod_{\substack{i=m \\ i\neq j}}^{l} (k_i - k_j)$

TABLE 2

J Matrix for $k_i = k_j = k$

$$j_{11} = 1 + \beta\theta, j_{ll} = e^{-k\theta};\ l = 2, \ldots, n-1$$

$$j_{nn} = \frac{H_n^0}{H_N}$$

$$j_{l1} = k^{l-1}\left[\frac{1}{(l-2)!}\left(\int_0^\theta \tau^{l-2}e^{-k\tau}\, d\tau + b\int_0^\theta\int_0^\tau \lambda^{l-2}e^{-k\lambda}\, d\lambda\, d\tau\right)\right]$$

$$j_{lm} = k^{l-m}\frac{1}{(l-m)!}\theta^{l-m}e^{-k\theta};\ l = 2, \ldots, n-1;\ m = 2, \ldots, l-1$$

$$j_{nm} = \frac{Hk}{H_n}\int_0^\theta j_{n-1,m}(\lambda)\, d\lambda$$

For an infinite reboiler, $\beta = 0$, and using the formula

$$\int_0^\theta \tau^m e^{-k\tau}\, d\tau = \frac{m!}{k^{m+1}} - \left(e^{-k\theta}\sum_{i=0}^{m}\frac{m!}{(m-i)!}\frac{\theta^{m-i}}{k^{i+1}}\right)$$

we have

$$j_{l1} = 1 - e^{-k\theta}\sum_{s=0}^{l-2}\frac{1}{s!}(k\theta)^s$$

$$j_{n1} = \frac{H}{H_n}\left[k\theta - \sum_{s=0}^{n-3}\left(1 - e^{-k\theta}\sum_{i=0}^{s}\frac{(k\theta)^i}{i!}\right)\right]$$

Consider the condenser:

$$\begin{aligned} H_n x_n &= H_n^0 x_n^0 + H\int_0^\theta k_{n-1}x_{n-1}(\lambda)\, d\lambda \\ &= H_n^0 x_n^0 + H\int_0^\theta k_{n-1}\left(\sum_{l=1}^{n-1} j_{n-1,l}(\lambda)x_l^0\right) d\lambda \end{aligned} \qquad (20)$$

Table 2 gives the J matrix when all the k_i's are equal. Table 3 shows the J matrix when the V_i's and H_i's are not equal. The derivation of these cases will not be shown, because it involves only minor changes from the derivation of the J matrix of Table 1. It is to be remembered that, except for H_1 and H_n, all H_i's are assumed to be constant here during the vapor-flow period.

Consider the case where $y_i^* = k_i x_i + b_i$. We have always assumed the k_i's are constants during one cycle. Although the k_i's are allowed to differ from plate to plate, it is still better to use $y_i^* = k_i x_i + b_i$ as the equilibrium relationship for obvious reasons. Using such a rela-

TABLE 3

J Matrix for $H_i \neq H_j \neq H$, $V_i \neq V_j$

Let $\dfrac{V_i k_i}{H_i} = q_i$

$$j_{11} = 1 + (1 - k_1)\,\frac{V_1 t}{H_1^0} = 1 + \beta^* t, \qquad j_{ll} = \exp(-q_l t)$$

$$j_{nn} = \frac{H_n^0}{H_n}$$

$$j_{l1} = \frac{H_1}{H_l}\left(\prod_{i=1}^{l-1} q_i\right)\left[\int_0^t \sum_{j=2}^{l} \frac{e^{-q_j t}\,d\tau}{\prod_{i=2}^{l}{}'\,(q_i - q_j)} + b^* \int_0^t\!\!\int_0^\tau \sum_{j=2}^{l} \frac{e^{-q_j \lambda}\,d\lambda\,d\tau}{\prod_{i=2}^{l}{}'\,(q_i - q_j)}\right]$$

$$j_{lm} = \frac{H_m}{H_l}\left(\prod_{i=m}^{l-1} q_i\right) \sum_{j=m}^{l} \frac{e^{-q_j t}}{\prod_{i=m}^{l}{}'\,(q_i - q_j)}$$

$$j_{n,m} = \frac{H_{n-1}}{H_n}\,q_{n-1} \int_0^t j_{n-1,m}(\lambda)\,d\lambda$$

Note: β^* has dimensions of (1/time)

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tionship, k_i actually approximates the local slope of the equilibrium line. Later, when we demonstrate the nonlinear cases, it will be shown that this approximation converges faster in the iterations. The accuracy is also better and the range of cycle times can also be larger.

Equations (6), (7), and (8) still apply. The solution (1) becomes

$$\mathbf{x}(t) = \mathbf{J}(t)\mathbf{x}(0) + \mathbf{M}(t)\boldsymbol{\beta} \tag{21}$$

Equation (4) then becomes

$$\mathbf{x}^L = \mathbf{D}(\mathbf{J}\mathbf{x}^L + \mathbf{M}\boldsymbol{\beta}) \tag{22}$$

or

$$\mathbf{x}^L = (\mathbf{I} - \mathbf{D}\mathbf{J})^{-1}\mathbf{D}\mathbf{M}\boldsymbol{\beta} \tag{23}$$

Here, because of the nonhomogeneity of the equations, the solution is no longer a characteristic root. To establish the existence and uniqueness of a positive solution is very difficult. We shall simply assume that a positive solution exists. Although Eq. (23) is quite different from Eq. (4), the **J** and **D** matrices are still the same. The reader must realize that the numerical values of the k_i's used in **J** are different from those of the previous case. We shall define **M** and $\boldsymbol{\beta}$ below.

The equation for the reboiler is

$$\frac{H_i}{H}\frac{dx_1}{d\theta} = (1 - k_1)x_1 - b_1 \tag{24}$$

the solution to which is

$$\begin{aligned} x_1 &= \left(x_1^0 - \frac{b_1}{1 - k_1}\right)\left(\frac{H_1}{H_1^0}\right)^{k_1 - 1} + \frac{b_1}{1 - k_1} \\ &\approx \left(x_1^0 - \frac{b_1}{1 - k_1}\right)\left[1 - (k_1 - 1)\frac{H\theta}{H_1^0}\right] + \frac{b_1}{1 - k_1} \\ &\approx x_1^0\left[1 - \left(1 - \frac{b_1}{(1 - k_1)x_1^0}\right)(k_1 - 1)\frac{H}{H_1^0}\theta\right] \\ &= x_1^0(1 + \beta\theta) \end{aligned} \tag{25}$$

For the plates Eq. (16) becomes

$$\frac{d}{d\theta}\bar{\mathbf{x}} = \mathbf{A}\bar{\mathbf{x}} + \bar{\mathbf{b}} + \bar{\boldsymbol{\beta}} \tag{26}$$

where

$$\bar{\boldsymbol{\beta}} = \begin{bmatrix} b_1 - b_2 \\ b_2 - b_3 \\ \cdot \\ \cdot \\ \cdot \\ b_{n-2} - b_{n-1} \end{bmatrix}$$

For $n = 5$, or a three-plate column, the equation is

$$\begin{bmatrix} x_2 \\ x_3 \\ x_4 \end{bmatrix} = \begin{bmatrix} -k_2 & 0 & 0 \\ k_2 & -k_3 & 0 \\ 0 & k_3 & -k_4 \end{bmatrix}\begin{bmatrix} x_2 \\ x_3 \\ x_4 \end{bmatrix} + \begin{bmatrix} k_1x_1 \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} b_1 - b_2 \\ b_2 - b_3 \\ b_3 - b_4 \end{bmatrix}$$

Equation (18) then becomes

$$\bar{\mathbf{z}} = (p\mathbf{I} - \bar{\mathbf{A}})^{-1}\left[\bar{\mathbf{x}}(0) + \bar{\mathbf{b}}' + \frac{1}{p}\bar{\boldsymbol{\beta}}\right]$$

The general forms of M and β are given in Table 4.

For the condenser,

$$H_n x_n = H \int_0^\theta (k_{n-1} x_{n-1} + b_{n-1})\, d\lambda + H_n^0 x_n^0 \tag{27}$$

The reader may have noted that, except for the first column,

$$m_{lm} = \int_0^\theta j_{lm}\, d\tau \qquad \text{for } m \neq 1$$

By redefining the quantity β in Eq. (25), it is possible to make

$$\mathbf{M} = \int_0^\theta \mathbf{J}\, d\tau$$

But it turns out that the resulting expression is much more complicated.

Given the **J** and **M** matrices, the compositions of the liquid on every stage at any time during the vapor-flow period are completely defined. The assumption that the k_i's and b_i's are constants (but not necessarily equal) is valid as long as the time τ is not very large, i.e., the compositions do not change drastically.

In the following section the transition matrix **D** for the liquid-flow period is derived.

TABLE 4

General Forms of the **M** Matrix and $\boldsymbol{\beta}$ Vector

$$\beta_1 = 0, \qquad \beta_i = b_{i-1} - b_i;\ i = 2,\ \ldots,\ n-1$$

$$\beta_n = b_{n-1}$$

$$M_{11} = 0, \qquad M_{ll} = \int_0^\theta e^{-k_l \tau}\, d\tau;\ i = 2,\ \ldots,\ n-1$$

$$M_{lm} = \left(\prod_{i=m}^{l-1} k_i\right)\left[\int_0^\theta \sum_{j=m}^{l} \frac{e^{-k_j \tau}\, d\tau}{\prod_{i=m}{}' (k_i - k_j)}\right];\ l = 2,\ \ldots,\ n-1;\ m = 2,\ \ldots,\ n-1$$

$$M_{l1} = 0;\ l = 1,\ \ldots,\ n$$

$$M_{nn} = \frac{H\theta}{H_n}$$

$$M_{nm} = \frac{Hk_{n-1}}{H_n} \int_0^\theta \int_0^\tau \prod_{i=m}^{n-2} k_i \left[\sum_{j=m}^{n-1} \frac{e^{-k_j \lambda}}{\prod_{i=m}^{n-1}{}' (k_i - k_j)}\right] d\lambda\, d\tau$$

THE D DROP MATRIX

Having derived the **J** and **M** matrices, we need only to find **D** to solve Eq. (4) [or Eq. (23) for $y^* = kx + b$]. Unlike matrix **J**, which is a function of time, we shall only attempt to relate the composition vector at the end of the liquid-flow period to the composition vector at the beginning of the liquid-flow period. It is assumed that no mass transfer occurs during the liquid-flow period, so the **D** matrix can be obtained simply by considering the plate-to-plate material balance at the end of the liquid-flow period. Let us define ϕ to be the fraction of the equivalent tray holdup dropped during the liquid-flow period from the condenser. We shall again, for simplicity, assume that all tray holdups are equal.

The matrix **D** is defined by

$$\mathbf{x}^L = \mathbf{D}\mathbf{x}^V \tag{28}$$

We shall demonstrate the case when $0 < \phi < 1$; the general form of D may be found in Table 5.

$$x_1^L = \frac{H_1}{H_1 + \phi H}\, x_1^V + \frac{\phi H}{H_1 + \phi H}\, x_2^V$$

$$x_i^V = (1 - \phi)x_i^V + \phi x_{i+1}^V \qquad i = 2, \ldots, n - 1$$

$$x_n^L = x_n^V$$

TABLE 5

General Form of the **D** Matrix

$$FN = [\phi]$$

$$D_{11} = \frac{H_1}{H_1 + FN(H)}$$

$$D_{1l} = \frac{H}{H_1 + FN(H)};\ l = 2, \ldots, FN + 1$$

$$\left.\begin{array}{l} D_{i,FN+1} = FN + 1 - \phi \\ D_{i,FN+i+1} = \phi - FN \end{array}\right\} i = 2, \ldots, n - FN - 1$$

$$D_{i,n} = 1;\ i = n - FN, \ldots, n$$

All others are zero.

Note: $[\phi]$ is the largest integer less than or equal to ϕ

Again it is to be emphasized that the assumption of identical tray holdups is not at all necessary. However, if they are not all the same, another set of total material-balance equations must be solved for all the ϕ_i's, ϕ_1 being the fraction of the ith tray holdup dropped to the $(i-1)$th tray.

EXAMPLE

In this section a sample calculation will be given for a three-tray rectification still. The still-pot size is assumed to be infinite, and all k_i's are assumed to be equal.

Using Table 2 the **J** matrix is as follows:

$$\mathbf{J} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 1 - e^{-k\theta} & e^{-k\theta} & 0 & 0 & 0 \\ 1 - e^{-k\theta}(k\theta + 1) & k\theta e^{-k\theta} & e^{-k\theta} & 0 & 0 \\ 1 - e^{-k\theta}(k\theta + 1) - \dfrac{k^2\theta^2}{2} e^{-k\theta} & \dfrac{k^2\theta^2}{2} e^{-k\theta} & k\theta e^{-k\theta} & e^{-k\theta} & 0 \\ \begin{gathered} \dfrac{H}{H_5}\left\{k\theta + e^{-k\theta} - 1 + \dfrac{k^2\theta^2}{2} e^{-k\theta} \right. \\ \left. - 2[1 - e^{-k\theta}(k\theta + 1)]\right\} \end{gathered} & \begin{gathered} \dfrac{H}{H_5}\left[-\dfrac{k^2\theta^2}{2} e^{-k\theta} \right. \\ \left. + 1 - e^{-k\theta}(k\theta + 1)\right\} \end{gathered} & \dfrac{H}{H_5}[1 - e^{-k\theta}(k\theta + 1)] & \dfrac{H}{H_5}(1 - e^{-k\theta}) & \dfrac{H_5^0}{H_5} \end{bmatrix} \tag{29}$$

For $0 \leqslant \phi \leqslant 1$, the **D** matrix is

$$\mathbf{D} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1-\phi & \phi & 0 & 0 \\ 0 & 0 & 1-\phi & \phi & 0 \\ 0 & 0 & 0 & 1-\phi & \phi \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{30}$$

Let $\phi = 1$ and using $y^* = kx$ as the equilibrium relationship, Eq. (4) becomes

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 1 - e^{-\lambda}(\lambda + 1) & \lambda e^{-\lambda} - 1 & e^{-\lambda} & 0 & 0 \\ 1 - e^{-\lambda}(\lambda + 1) - \frac{\lambda^2}{2} e^{-\lambda} & \frac{\lambda^2}{2} e^{-\lambda} & \lambda e^{-\lambda} - 1 & e^{-\lambda} & 0 \\ \frac{H}{H_5}\left[\lambda + e^{-\lambda} - 1 + \frac{\lambda^2}{2} e^{-\lambda} - 2[1 - e^{-\lambda}(\lambda + 1)]\right] & \frac{H}{H_5}\left[-\frac{\lambda^2}{2} e^{-\lambda} + 1 - e^{-\lambda}(\lambda + 1)\right] & \frac{H}{H_5}[1 - e^{-\lambda}(\lambda + 1)] & \frac{H}{H_5}(1 - e^{-\lambda}) - 1 & \frac{H_5^0}{H_5} \\ \frac{H}{H_5}\left[\lambda + e^{-\lambda} - 1 + \frac{\lambda^2}{2} e^{-\lambda} - 2[1 - e^{-\lambda}(\lambda + 1)]\right] & \frac{H}{H_5}\left[-\frac{\lambda^2}{2} e^{-\lambda} + 1 - e^{-\lambda}(\lambda + 1)\right] & \frac{H}{H_5}[1 - e^{-\lambda}(\lambda + 1)] & \frac{H}{H_5}(1 - e^{-\lambda}) & \frac{H_5^0}{H_5} - 1 \end{bmatrix} \mathbf{x}^L = 0 \qquad (31)$$

The solution for total reflux after simplification may be written

$$\begin{aligned} x_2^L &= [e^{\lambda}(\lambda - 1) + 1]x_1 \\ x_3^L &= [e^{\lambda}(e^{\lambda} - \lambda)(\lambda - 1) + 1]x_1 \\ x_4^L &= \left[e^{\lambda}\left(e^{2\lambda} + \frac{\lambda^2}{2} - 2\lambda e^{\lambda}\right)(\lambda - 1) + 1\right] \\ x_5^L &= x_4^L \end{aligned} \qquad (32)$$

where $\lambda = k(V_T/H)$. For total reflux

$$V_T = \phi H \qquad (33)$$

and since $\phi = 1$ in this case, the λ's in Eq. (32) are equal to k's. When the column is operated at finite reflux with feed to the still pot, or

$$\frac{V_T}{H} > \phi$$

then Eq. (32) is no longer valid; the correct solution will be shown in a later section.

Since $\phi = 1$, this implies that

$$\begin{aligned} x_3^V &= x_2^L \\ x_4^V &= x_3^L \\ x_5^V &= x_4^L = x_5^L \end{aligned}$$

The last relation shows that the condenser composition at the beginning of the vapor-flow period is the same as at the end of the vapor-flow period. This is one of the characteristics of a pseudo-steady-state operation.

The composition x_2^V may be calculated in the following way:

$$x_2^V = \sum_{m=1}^{5} j_{2,m}x_m^L = (1 - e^{-k})x_1 + e^{-k}[e^k(k-1) + 1]x_1 = kx_1$$

It is rather interesting to observe that the composition of the first plate above the still pot at the end of the vapor-flow period is the same as the composition obtained in the conventional column. This is equivalent to stating that the still-pot efficiency in a cycling column is identical to that for the still pot of a conventionally operated column. We shall explore the significance of theoretical efficiencies further in a later section. The derivation of $\mathbf{x}^L$ for columns of larger size or for a more general situation (e.g., k_i's are not identical) is quite straightforward, although the algebraic manipulations to simplify the final form of the solution become rather involved. It is easier to use Eq. (4) as it is and solve the matrix equation with the numerical values of the constants inserted. As the size of the matrix gets larger, the problem may have to be solved on a computer.

When $\phi = 1$ in a cycling column operated at total reflux, Eq. (32) not only applies for the three-plate column, but is valid regardless of the total number of plates in the column. In fact, for $0 < \phi < 1$ at total reflux operation, the compositions of any plate can be shown to be independent of the total number of plates in the column. An explanation of this phenomenon is discussed in another paper.

THE TRANSITION MATRIX WHEN THE LOCAL PLATE EFFICIENCY IS NOT UNITY

In all the preceding sections the local Murphree (or point) efficiency has always been assumed to be equal to unity. The purpose of such an assumption was to simplify the algebra and to concentrate on the concept of the approach. It certainly would be very limited in application if this assumption could not be relaxed. The derivation of the **J** matrix becomes very long, tedious, and almost intractable. It was quite a surprise when the result turned out to be so compact. The reason for all the complexity in derivation is that now the rate of change of the composition of the ith plate depends not only on y_i and y_{i-1}, but also on all y_m, $m = 1, \ldots, i$.

In the following, only the differential equations of the tray composition variables are presented. The solution of the differential equation again is listed in a table.

Assume first that all the plates have the same point efficiency E and that the still pot has an efficiency of unity. The point efficiency E is defined as usual to be

$$E = \frac{y_i - y_{i-1}}{y_i^* - y_{i-1}} \tag{34}$$

which, after rearranging, gives

$$y_i = Ey_i^* + (1-E)y_{i-1} \tag{35}$$

Writing out all the y_i's, we have

$$\begin{aligned}
y_1 &= k_1x_1 \\
y_2 &= Ek_2x_2 + (1-E)y_1 = Ek_2x_2 + (1-E)k_1x_1 \\
y_3 &= Ek_3x_3 + (1-E)Ek_2x_2 + (1-E)^2k_1x_1 \\
y_4 &= Ek_4x_4 + (1-E)Ek_3x_3 + (1-E)^2Ek_2x_2 + (1-E)^3k_1x_1 \\
&\cdot \\
&\cdot \\
&\cdot \\
y_l &= E\sum_{i=2}^{l} k_ix_i(1-E)^{l-i} + (1-E)^{l-1}k_1x_1
\end{aligned} \tag{36}$$

We shall consider the equations of the plates, since the equations for the still pot and the condenser are the same as before:

$$\begin{aligned}
\frac{dx_2}{d\theta} &= y_1 - y_2 = k_1x_1 - Ek_2x_2 - (1-E)k_1x_1 \\
&= -Ek_2x_2 + Ek_1x_1 \\
\frac{dx_3}{d\theta} &= -Ek_3x_3 + E^2k_2x_2 + E(1-E)k_1x_1 \\
&\cdot \\
&\cdot
\end{aligned} \tag{37}$$

$$\begin{aligned}\frac{dx_l}{d\theta} &= E\left(\sum_{i=2}^{l-1}\{k_ix_i[(1-E)^{l-1-i}-(1-E)^{l-i}]\}-k_lx_l\right)\\ &\qquad\qquad\qquad\qquad + (1-E)^{l-2}k_1x_1E \qquad (37)\\ &= E\left[(1-E)^{l-2}k_1x_1-k_lx_l+\sum_{i=2}^{l-1}k_ix_i(1-E)^{l-i-1}E\right]\end{aligned}$$

Equation (16) is

$$\frac{d\bar{\mathbf{x}}}{d\theta} = \mathbf{A}\bar{\mathbf{x}} + \bar{\mathbf{b}} \qquad (16)$$

where **A** and $\bar{\mathbf{b}}$ are given by

$$\begin{aligned} a_{ii} &= -Ek_{i+1}\\ a_{ij} &= (1-E)^{i-j-1}E^2k_{j+1} \qquad \text{for all } j < i;\ i = 2, \ldots, n-2 \quad (38)\\ b_i &= Ek_1x_1(1-E)^{i-1}\end{aligned}$$

In their full form,

$$\mathbf{A} = \begin{bmatrix} -Ek_2 & 0 & 0 & 0 & \cdots & 0\\ E^2k_2 & -Ek_3 & 0 & 0 & \cdots & 0\\ (1-E)E^2k_2 & E_2k_3 & -Ek_4 & 0 & \cdots & \cdot\\ \cdot & \cdot & \cdot & \cdot & & \cdot\\ \cdot & \cdot & \cdot & \cdot & & \cdot\\ \cdot & \cdot & \cdot & \cdot & & \cdot\\ (1-E)^{n-4}E^2k_2 & (1-E)^{n-5}E^2k_3 & \cdots & & \cdots & -Ek_{n-1}\end{bmatrix}$$

$$\bar{\mathbf{b}} = \begin{bmatrix} Ek_1x_1\\ E(1-E)k_1x_1\\ \cdot\\ \cdot\\ \cdot\\ \cdot\\ E(1-E)^{n-3}k_1x_1\end{bmatrix}$$

Note again that **A** is a $(n-2)\times(n-2)$ matrix and that $\bar{\mathbf{x}}$ is the composition vector of the trays, the total of which is $n-2$.

The transition matrix $\mathbf{J}(\theta)$ of the vapor cycle may be obtained from the solution of the above differential equations; it is shown in Table 4.

It is to be noted that the definition of j_{1m} is

$$j_{lm} = E_l E_m k_m \sum_{j=m}^{l} \frac{e^{-E_j k_j \theta} \prod_{i=m+1}^{l-1} [E_i k_i + (1 - E_i) E_j k_j]}{\prod_{i=m}^{l}{}' \, (E_i k_i - E_j k_j)} \tag{39}$$

for a system where the individual Murphree efficiencies of each plate are not the same. The above solution is obtained simply by carrying the subscript i for the E's in the derivation. The rest of the terms of the **J** matrix may be obtained in similar fashion.

We did not include a table for the **J** matrix with unequal E_i's, because the individual E_i's are rarely known. However, it is to be pointed out that the assumption of equal E's for the derivation of **J** (Table 6) is not necessary.

When $k_i = k_j = k$ the j_{lm} assumes the form

$$j_{lm} = kE^2 e^{-Ek\theta} \sum_{i=2}^{l-m+1} \frac{(E^2 k)^{i-2} (1 - E)^{l-m+1} \theta^{i-1} (l - m - 1)!}{(l - m + 1 - i)!(i - 1)!(i - 2)!} \tag{40}$$

TABLE 6

The **J** Matrix when $E \leqslant 1$

$$j_{11} = 1, j_{ll} = e^{-Ek_l\theta} (1 < l < n), j_{nn} = \frac{H_n^0}{H_n}$$

$$j_{lm} = Ek_m \sum_{j=m}^{l} \frac{e^{-Ek_j\theta} \prod_{i=m+1}^{l-1} [k_i - (1 - E)k_j]}{\prod_{i=m}^{l}{}' \, (k_i - k_j)}; 1 < l < n, 1 < m < l$$

$$j_{l1} = k_1 \sum_{j=2}^{l} \frac{[(1 - e^{-Ek_j\theta})/k_j] \prod_{i=2}^{l-1} [k_i - (1 - E)k_j]}{\prod_{i=2}^{l}{}' \, (k_i - k_j)}$$

$$j_{nm} = \frac{H}{H_n} k_m \sum_{j=m}^{n-1} \frac{[(1 - e^{-Ek_j\theta})/k_j] \prod_{i=m+1}^{n-1} [k_i - (1 - E)k_j]}{\prod_{i=m}^{n-1}{}' \, (k_i - k_j)}$$

$$j_{n1} = \frac{H}{H_n} k_1 \left\{ \theta + \sum_{j=2}^{n-1} \frac{[(e^{-Ek_j\theta} - 1)/E^2 k_j^2] \prod_{i=2}^{n-1} [k_i - (1 - E)k_j]}{\prod_{i=2}^{n-1}{}' \, (k_i - k_j)} \right\}$$

NONLINEAR EQUILIBRIUM RELATIONSHIP

There is a point reached at which derivation of analytical relationships become completely intractable or impossible. A change in philosophy of investigation is clearly indicated. This point is reached for controlled cycling when one attempts to handle nonlinear equilibrium relationships. When the equilibrium relationship is nonlinear, the k_i in $y_i^* = k_i x_i$ (or $y_i^* = k_i x_i + b_i$) is a function of x_i. For example, in the case of a constant relative volatility,

$$y^* = \frac{\alpha}{1 + (\alpha - 1)x_i} x$$

or

$$k_i = \frac{\alpha}{1 + (\alpha - 1)x_i} \tag{41}$$

Although the assumption that k_i remains constant during the vapor-flow period is still a good approximation, to estimate the correct k_i's in $\mathbf{J}$ in the solution at the pseudo-steady-state compositions no doubt requires an iterative procedure. Of course, one could also use the very basic recursion equation (3), in which k_i's may be calculated using the initial value of x at the beginning of the vapor-flow period, and recalculate the k_i's at every new cycle until pseudo steady state has been reached. The number of cycles or, equivalently, the number of times a new $\mathbf{J}$ matrix has to be evaluated will depend upon the initial composition vector and the total number of plates in the column. Usually the iterative method using the asymptotic equation (4) is more efficient, in spite of the fact that the recursion formula does not require iteration, provided, of course, the iterative procedure converges.

The iterative procedure is first to guess a set of k_i's and to calculate the composition vector. Next a new set of k_i's are computed using the composition vector just obtained, and a new composition vector is calculated. The same procedure is repeated until the compositions do not change.

A digital program was written to solve iteratively Eq. (4) [or Eq. (23) in cases where $y_i^* = k_i x_i + b_i$ is assumed] on an IBM 704 for a nonlinear equilibrium relationship. In the early stages of the work it was found that the iteration diverges when the size of the $\mathbf{x}$ is greater than 5. It was determined later that the trouble results from the roundoff error, a problem that must be quite familiar to all digital-computer users.

The difficulty was traced back to two terms.

1. $\prod_{i=m}^{l}{}' \, (k_i - k_j)$

Since k_i is not much different from k_j, the product of the differences soon becomes very very small when $l - m$ is large; e.g., when $l - m$ is 4 and $k_i - k_j$ is about 10^{-2}, the product is about 10^{-10}.

2. $\prod_{j=m}^{l} \frac{e^{-k_j\theta}}{\Pi' \, (k_i - k_j)}$

Since k_j is not much different from k_{j+1}, all the $e^{-k_j\theta}$ have about the same magnitude. The terms under the summation have both positive and negative values, which, together with the reason mentioned in 1, causes very serious roundoff errors when $n > 5$.

After a triple-precision arithmetic routine was used to compute

$$\sum_{j=m}^{l} \frac{e^{-k_j\theta}}{\Pi' \, (k_i - k_j)}$$

the convergence of the iterative procedure was usually very fast. It required approximately $\frac{1}{4}$ minute to obtain an iterative solution for an eight-plate column (or 10 × 10 matrix), although the total number of iterations obviously depends upon the initial k_i's guessed. Since $\phi = 1$ is of the greatest interest (it will be shown later to be the most efficient mode of controlled cyclic operation), the following cases are cited as examples of the total number of iterations required for an accuracy of 10^{-5} in the compositions. The initial k_i's are computed using compositions corresponding to conventional column operation. Total reflux is assumed ($\phi = V\tau/H$) and a constant relative volatility of $\alpha = 1.2$ is used. k_i's are computed using the average composition of x_i^V and x_i^L as the base composition,

TABLE 7

Total Number of Iterations

n	$y_i^* = k_i x_i$	$y_i^* = k_i x_i + b_i$
5	8	3
6	9	
7	10	4
10	13	4

Table 7. When $y_i^* = k_i x_i + b_i$ is used, we choose

$$k_i = \left(\frac{dy^*}{dx}\right)_i = \frac{\alpha}{[1 + (\alpha - 1)x_i^2]} \tag{42}$$

$$b_i = \frac{\alpha(\alpha - 1)x_i^2}{[1 + (\alpha - 1)x_i]^2} \tag{43}$$

As the value of ϕ becomes greater than unity, the solution oscillates very badly when using the first form for equilibrium relationships. The total number of iterations goes up to 30 or even 40. However, when using the second relationship ($y_i^* = k_i x_i + b_i$) the solution converges very rapidly (three or four iterations), although the program must compute the **M** matrix in addition to the original **J** matrix. The advantage of using the second relationship when ϕ is large is obvious, since k_i is apt to be more nearly constant as the composition changes during the vapor-flow period are considerably larger. Tables 8 and 9 each contain a typical solution for a three-plate column using methods 1 and 2, respectively. Figure 1 shows the compositions as a function of ϕ.

When $0 \leqslant \phi \leqslant 1$, and the column is operating at total reflux, the

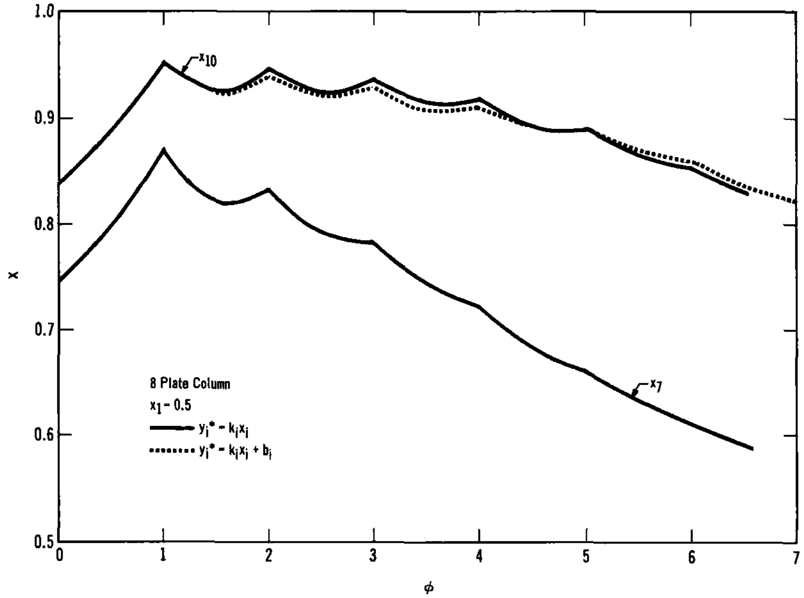

FIG. 1. x_{10}^F and x_7^F as a function of fraction of a plate holdup dropped (ϕ).

TABLE 8

Typical Entries for a Three-Plate Column ($y_i^* = k_i x_i$, $\alpha = 1.2$, $\phi = 1.0$)

			J Matrix		
	1	0	0	0	0
	0.66849	0.34134	0	0	0
	0.29740	0.36955	0.34630	0	0
	0.09565	0.19732	0.36977	0.35109	0
	0.00294	0.00918	0.02839	0.06489	0.9
			Solution		
x_i^L	0.5	0.61876	0.69707	0.76732	0.76732
x_j^V	0.5	0.54545	0.61876	0.69707	0.76732

TABLE 9

Typical Entries for a Three-Plate Column ($y_i^* = k_i x_i + b_i$, $\alpha = 1.2$, $\phi = 1.0$)

			J Matrix		
	1	0	0	0	0
	0.63687	0.38198	0	0	0
	0.26011	0.37244	0.39207	0	0
	0.07505	0.17654	0.37155	0.04162	0
	0.00197	0.00690	0.02364	0.05984	0.9
			M *Matrix*		
	0	0	0	0	0
	0	0.64218	0	0	0
	0	0.26228	0.64928	0	0
	0	0.07568	0.25912	0.65594	0
	0	0.00199	0.00916	0.03441	0.1
			Solution		
x_i^L	0.5	0.62104	0.69979	0.76945	0.76945
x_i^V	0.5	0.54545	0.62104	0.69979	0.76945

compositions x_i are not a function of the total number of plates in the column. Figure 2 shows the relation between x_i and ϕ. Here α is again chosen to be 1.2 and an infinite still pot and total reflux have been assumed.

At total reflux one may define the effective plate efficiency in the following way:

$$E_{0,i} = \frac{y_{i_{\mathrm{av}}} - y_{i-1_{\mathrm{av}}}}{y_i^*(\tau) - y_{i-1_{\mathrm{av}}}} \tag{44}$$

Since

$$V\tau y_{\mathrm{av}} = \phi H x_{i+1}^V \qquad \text{for } 0 \leq \phi \leq 1 \tag{45}$$

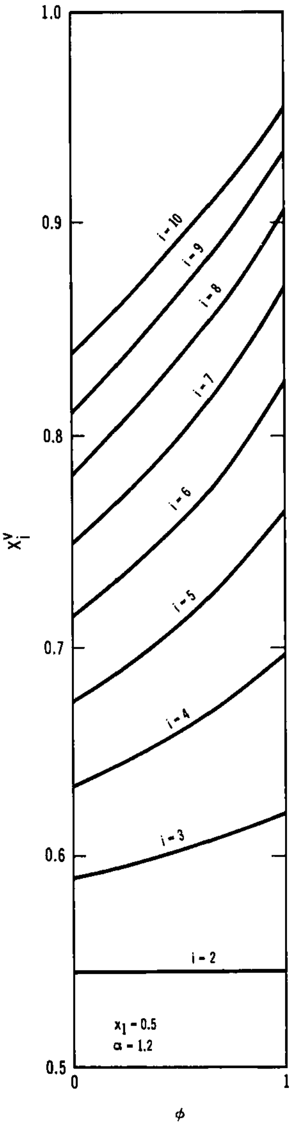

FIG. 2. Compositions x_i^v as a function of fraction of a plate holdup dropped (ϕ).

and $\phi = V\tau/H$ for total reflux, we have

$$E_{0,i} = \frac{x_{i+1}^V - x_i^V}{k_i x_i^V - x_i^V} \tag{46}$$

Figure 3 shows the E_0 versus plate number using ϕ as a parameter. Since $\phi \leqslant 1$ in this plot, the E_0 is not a function of the total number of plates in the column (which follows from the conclusion regarding the independence of compositions on the number of plates for $\phi \leqslant 1$). However, as ϕ becomes greater than 1, Eq. (46) is no longer true, even at total reflux. We have plotted E_0 versus ϕ ($1 \leqslant \phi \leqslant 3$) in Fig. 4, where E_0 is defined by Eq. (44). Since $y_{i-1_{av}}$ can be greater than y_i^* (τ) for large ϕ, the efficiencies of the second and third plates have singular points at which $E_{0,3}$ and $E_{0,4}$ jump from $+\infty$ to $-\infty$. $E_{0,2}$, or the efficiency of the first plate, does not exhibit such behavior, because y_2^* (τ) is always greater than y_1, which is assumed to be a constant. Figure 5 is rather misleading, because it shows that the efficiency for a given plate increases very rapidly with ϕ (for ϕ greater than 1 but less than that value corresponding to the point at which the efficiency becomes negative); yet the composition x_5^V decreases as ϕ exceeds unity. Actually, $x_{5_{av}}$, the average over the whole vapor-flow period, indeed increases when ϕ increases; nevertheless, it is the x_5^V which is more significant to the separation achieved. Therefore, it is more realistic and informative to plot E_0 versus ϕ using Eq. (46) as the definition of E_0.

This is to extend the definition of E_0 for $0 \leqslant \phi \leqslant 1$ to all $\phi \geqslant 0$; the plot is shown in Fig. 5.

As ϕ increases above unity, as shown in Fig. 4 for a three-plate

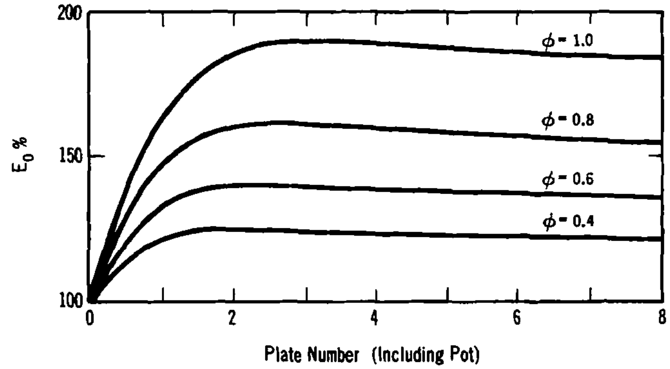

FIG. 3. Effective plate efficiency (E_0) as a function of plate number; $\alpha = 1.2$.

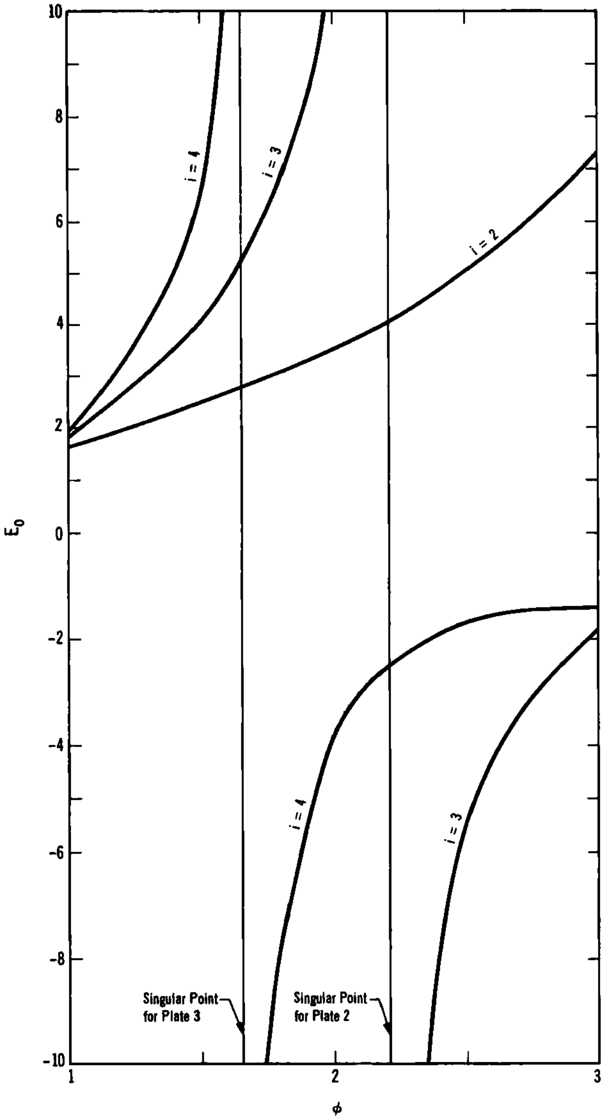

FIG. 4. Effective plate efficiency (E_0) as a function of fraction of a plate holdup dropped (ϕ).

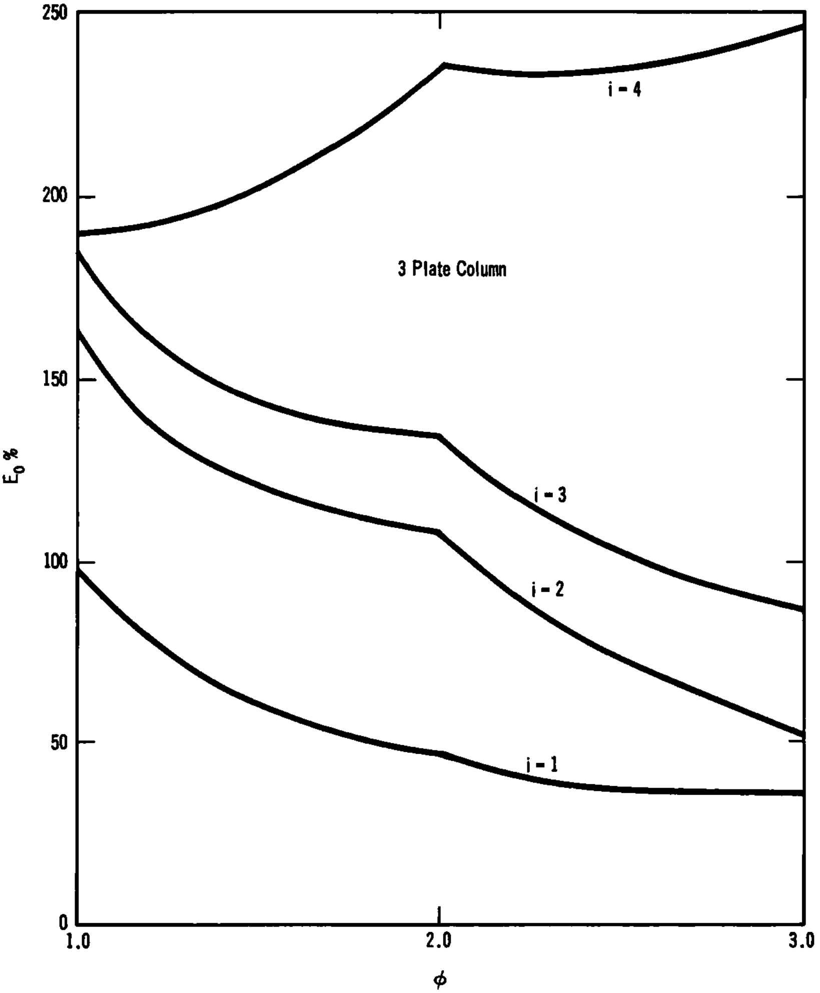

FIG. 5. Difficulty in the definition of E_0 when $\phi > 1$.

column, the top plate efficiency also increases. However, the overall column or efficiency decreases, because all the other plate efficiencies drop significantly. These phenomena will also be explained in another paper.

CONTINUOUS OPERATION

Most of the examples shown in the preceding sections have assumed total reflux to simplify the computation. We are to demonstrate in the following the applicability of this matrix method to cases where one does not have total reflux $V_T > \phi H$.

Now the compositions in the column become a function of the total number of stages. For example, Eq. (32), which is valid for any size of the column at total reflux, now changes to the following set of equations:

One-plate column:

$$x_2^L = \left[\frac{\lambda-\theta}{e^{-\lambda}-(1-\theta)}+1\right]x_1$$

Two plates:

$$x_2^L = \left[\frac{e^{-\lambda}(\lambda-\theta)}{e^{-2\lambda}-(1-\theta)(1-\lambda e^{-\lambda})}+1\right]x_1$$

$$x_3^L = \left[\frac{(1-\lambda e^{-\lambda})(\lambda-\theta)}{e^{-2\lambda}-(1-\theta)(1-\lambda e^{-\lambda})}+1\right]x_1$$

Three plates:

$$x_2^L = \left[\frac{e^{-2\lambda}(\lambda-\theta)}{e^{-3\lambda}-(1-\theta)[(1-\lambda e^{-\lambda})^2-(\lambda^2/2)e^{-2\lambda}]}+1\right]x_1$$

$$x_3^L = \left[\frac{e^{-2\lambda}(1-\lambda e^{-\lambda})(\lambda-\theta)}{e^{-3\lambda}-(1-\theta)[(1-\lambda e^{-\lambda})^2-(\lambda^2/2)e^{-2\lambda}]}+1\right]x_1$$

$$x_4^L = \left[\frac{[(1-\lambda e^{-\lambda})^2-(\lambda^2/2)](\lambda-\theta)}{e^{-3\lambda}-(1-\theta)[(1-\lambda e^{-\lambda})^2-(\lambda^2/2)e^{-2\lambda}]}+1\right]x_1$$

ϕ is assumed to be unity in all these derivations; hence

$$x_i^V = x_{i-1}^L \qquad i > 2$$

x_2^V can be recovered from

$$x_2^V = (1-e^{-\lambda})x_1 + e^{-\lambda}x_2^L$$

Equations for the efficiencies which may be derived without the assumption of total reflux will remain the same. Nonlinear continuous cases have also been tested on the IBM 704. The results indicate that the matrix-iterative method, as described in detail previously, works as well for the continuous cases. However, roundoff error becomes more serious, especially if the total number of trays is large. The reasons are not only those mentioned before, but also because of the fact that when the total number of plates increases, the differences between the lower plate compositions (or equivalently the k_i's) get smaller and smaller.

Table 10 contains the results of a three-plate column with $\alpha = 1.2$ and Table 11 gives the results of an eight-plate column.

TABLE 10

Continuous Operation

($n = 5$; $\alpha = 1.2$; $x_1 = 0.5$; $\phi = 1.0$)

$\frac{V_T}{H}$	i	x_i^L	x_i^V	E_i	k_i
1.1	1	0.5	0.5	1.0	0.9917
	2	0.5813	0.5275	1.798	0.9724
	3	0.6495	0.5813	2.026	0.9514
	4	0.7244	0.6495	2.034	0.9276
	5	0.7244	0.7244		
1.5	1	0.5	0.5	1.0	0.9917
	2	0.5177	0.5040	2.300	0.9878
	3	0.5515	0.5177	2.696	0.9794
	4	0.6284	0.5515	2.708	0.9601
	5	0.6284	0.6284		
2.0	1	0.5	0.5	1.0	0.9917
	2	0.5035	0.5005	3.160	0.9910
	3	0.5186	0.5035	3.816	0.9878
	4	0.5904	0.5186	3.844	0.9724
	5	0.5904	0.5904		

TABLE 11

Continuous Operation

($n = 10$; $\alpha = 1.2$; $x_1 = 0.5$; $V_T/H = 1.1$, $\phi = 1.0$)

i	x_i^L	x_i^V	E_i	k_i
1	0.5	0.5	1.0	0.9917
2	0.5417	0.5141	1.805	0.9818
3	0.5775	0.5417	2.050	0.9706
4	0.6189	0.5775	2.074	0.9572
5	0.6644	0.6189	2.057	0.9426
6	0.7128	0.6644	2.034	0.9271
7	0.7625	0.7128	2.010	0.9113
8	0.8120	0.7625	1.987	0.8957
9	0.8594	0.8120	1.965	0.8809
10	0.8594	0.8594		

THEORETICAL PLATE EFFICIENCY OF A CONTROLLED CYCLIC DISTILLATION COLUMN

Having derived expressions for pseudo-steady-state compositions in controlled cyclic distillation, we shall attempt to calculate individual plate efficiencies, which are defined by

$$E_{0,i} = \frac{y_{i_{\text{av}}} - y_{i-1,_{\text{av}}}}{y_i^*(\tau) - y_{i-1,_{\text{av}}}} \tag{47}$$

The efficiency of the first plate, $E_{0,2}$, when the still pot is infinite in size, is very easy to derive. In fact, one does not need to know exactly the expression for the composition of the first plate. As defined earlier,

$$y_2 = Ey_2^* + (1-E)y_1$$
$$y_2^* = k_2x_2 = k_2(j_{21}x_1^0 + j_{22}x_2^0)$$

Substituting for j_{21} and j_{22} from Table 6, one has

$$y_2^* = k_1(1 - e^{-Ek_2\theta})x_1 + k_2e^{-Ek_2\theta}x_2^0$$

The average value of y_2 is

$$y_{2_{\text{av}}} = \frac{1}{\tau}\int_0^\tau y_2\, d\theta = (k_2x_2^0 - k_1x_1)\,\frac{1-e^{-E\lambda_2}}{\lambda_2} + y_1$$
$$y_2^*(\tau) = (k_2x_2^0 - k_1x_1)\, e^{-E\lambda} + k_1x_1$$

Recognizing that $y_1 = k_1x_1$, one has

$$E_0 = \frac{e^{E\lambda_2} - 1}{\lambda_2} \tag{48}$$

where

$$\lambda_2 = k_2\frac{V\tau}{H}$$

Note that the derivation does not involve ϕ; hence Eq. (48) is valid for any ϕ. This is due to the fact that y_1 is assumed constant regardless of the value of ϕ. All the other plates do not have this property, because $y_{i-1_{\text{av}}}(i > 2)$ is strongly dependent upon the value of ϕ.

The same method may be used sequentially to obtain the efficiencies for the other plates of the column, but the procedure soon becomes too complicated. However, as the plate number increases the efficiency rapidly approaches some asymptotic value, which is a function of the various operating parameters of the column. We shall first derive the expression for the asymptotic efficiency, assuming ϕ to be unity and the local (or point) efficiency to be 100%, to demonstrate the method. Cases wherein ϕ is not unity and E is not 100% will be derived later.

Let us assume the following:

1. $y^* = kx + b$ for all $x_1 \leqslant x \leqslant x_n$.
2. $\phi = 1$.
3. $E = 1$.

Since $\phi = 1$, the material balance for any plate of the column at pseudo steady state yields

$$y_{i-1_{\mathrm{av}}} = \frac{H}{\tau V}\, x_i^V + \frac{D}{\tau V}\, x_n^V$$

where D is the total amount of product removed from the condenser at the end of the vapor-flow period with a composition x_n^V.

Substituting the above expression in Eq. (47) we have

$$E_{0,i} = \frac{x_{i+1}^V - x_i^V}{(kx_i + b)(V\tau/H) - x_i^V - (D/H)x_n^V} \tag{49}$$

Let us redefine b to be

$$b\,\frac{V\tau}{H} - \frac{D}{H}\, x_n^V \tag{50}$$

Equation (49) then becomes

$$E_{0,i} = \frac{x_{i+1}^V - x_i^V}{(\lambda - 1)x_i^V + b} \tag{51}$$

Solving for x_{i+1}^V in the above equation, one has

$$x_{i+1}^V = [1 + E_{0,i}(\lambda - 1)]x_i^V + E_{0,i}b$$

Assume i to be very large, or

$$E_{0,i} = E_{0,i+1} = E_0$$

and define Ψ to be

$$\Psi = 1 + E_0(\lambda - 1) \tag{52}$$

The above equation then becomes

$$\begin{aligned} x_i^V &= \Psi x_{i-1}^V + E_0 b \\ &= \Psi^{i-j} x_j^V + \sum_{k=1}^{i-j} \Psi^{k-1} E_0 b \qquad j \leqslant i \end{aligned} \tag{53}$$

$$= \Psi^{i-j} x_j^V + \frac{1 - \Psi^{i-j}}{1 - \Psi} E_0 b \tag{54}$$

or

$$x_j^V = \Psi^{j-i} x_i^V + \frac{1 - \Psi^{j-1}}{1 - \Psi} E_0 b \tag{55}$$

The *i*th row of the matrix equation (22), when $\phi = 1$ and $i \neq n$, is

$$x_i^V = \sum_{l=1}^{i} j_{i+1,l} x_l^V + x_{i+1}^V e^{-\lambda}$$

or

$$x_{i+1}^V = e^{\lambda} \left(- \sum_{l=1}^{i} j_{i+1,l} x_l^V + x_i^V \right) \tag{56}$$

Inserting x_i^V and x_{i+1}^V, Eq. (51) becomes

$$E_0 = \frac{-e^{\lambda}}{(\lambda - 1) x_i^V + b} \left(\sum_{i=1}^{i} j_{i+1,l} x_l^V - x_i^V - \sum_{l=1}^{i-1} j_{i,l} x_l^V + x_{i-1} \right) \tag{57}$$

Substituting for $j_{i,j}$ from Table 2 we have

$$E_0 = \frac{1}{(\lambda - 1) x_i^V + b} \left[\sum_{j=1}^{i-1} \frac{\lambda^{i-j}}{(i-j)!} x_j^V - \sum_{j=1}^{i} \frac{\lambda^{i+1-j}}{(i+1-j)!} x_j^V + e^{\lambda} (x_i^V - x_{i-1}^V) \right]$$

In the above equation we did not use different forms for the $j_{i+1,1}$ and $j_{i,1}$ as should be done, but when *i* is large the order of magnitude of these quantities is small enough to justify the approximation. By the same token, we may assume that Eq. (55) is valid for all *j* and substitute it in the above expression to get

$$\begin{aligned} E_0 = \frac{1}{(\lambda - 1) x_i^V + b} \Bigg[& (1 - \Psi) \sum_{p=1}^{i-1} \frac{(\lambda/\Psi)^p}{p!} x_i^V - x_i^V \Psi \frac{(\lambda/\Psi)^i}{i!} \\ & - \sum_{p=1}^{i-1} \frac{(\lambda/\Psi)^p}{p!} E_0 b - E_0 b \frac{\lambda^i}{i!} \frac{1 - \Psi^{1-i}}{1 - \Psi} + (x_i^V - x_{i-1}^V) e^{\lambda} \Bigg] \end{aligned}$$

As *i* becomes large, the above equation reduces to

$$E_0 \approx \frac{1}{(\lambda - 1) x_i^V + b} [(1 - \Psi) x_i^V - E_0 b] (e^{\lambda/\Psi} - 1) + \frac{e^{\lambda}}{\Psi} E_0$$

This may be simplified again to

$$\frac{e^{\lambda}}{\Psi} = e^{\lambda/\Psi} \tag{58}$$

For a given $\lambda = kV\tau/H$, the above equation yields the asymptotic efficiency as $i \to \infty$. Actually, since λ/Ψ is always less than or equal to 1, the above equation is a fairly good approximation for $i \geqslant 4$, i.e., all the plates above and including the third plate.

It is interesting to note that Eq. (57) does not involve b defined in Eq. (50); the plate efficiency is only a function of the stripping factor. Hence one would expect that the derivation using an equilibrium expression of the form $y^* = kx$ or at total reflux would give the same result. Furthermore, apparently the efficiency of the ith plate involves only three or four plate compositions beneath it (the assumption that $y^* = kx + b$ is valid with a single k for all the plates is, after all, not a bad approximation).

As was mentioned earlier, the derivation of the asymptotic efficiency for cases where the point efficiency E is less than 1 may be obtained in almost similar fashion. We have elected not to present the detailed derivation but simply the final equation. It can be shown that the plate efficiency satisfies the following equation, as i approaches infinity, and $\phi = 1$.

$$\exp\left(\frac{E^2\lambda}{\Psi + E - 1}\right) = \frac{e^{E\lambda}}{\Psi} \tag{59}$$

It can also be shown that when $\lambda = 1$, i.e., parallel equilibrium and operating lines, the above equation reduces to

$$E_0 = \frac{2E}{2 - E} \tag{60}$$

Figures 6 and 7 give a plot of Eq. (59) in two different forms for easy reference. Unlike Eq. (48), Eq. (59) is only valid for $\phi = 1$.

To illustrate the correctness of Eqs. (48) and (59), the following is a comparison of the calculated efficiencies and the efficiencies obtained from the solution of the matrix equation (Table 9):

	i		
	2	3	4
E_0 from the matrix solution	1.6905	1.8810	1.8900
E_0 calculated using (48) or (59)	1.681	1.917	1.886

These calculated $E_{0,i}$'s were obtained with k_i's computed from the arithmetic average of x_i^V and x_i^L (or λ_i if the column is not at total

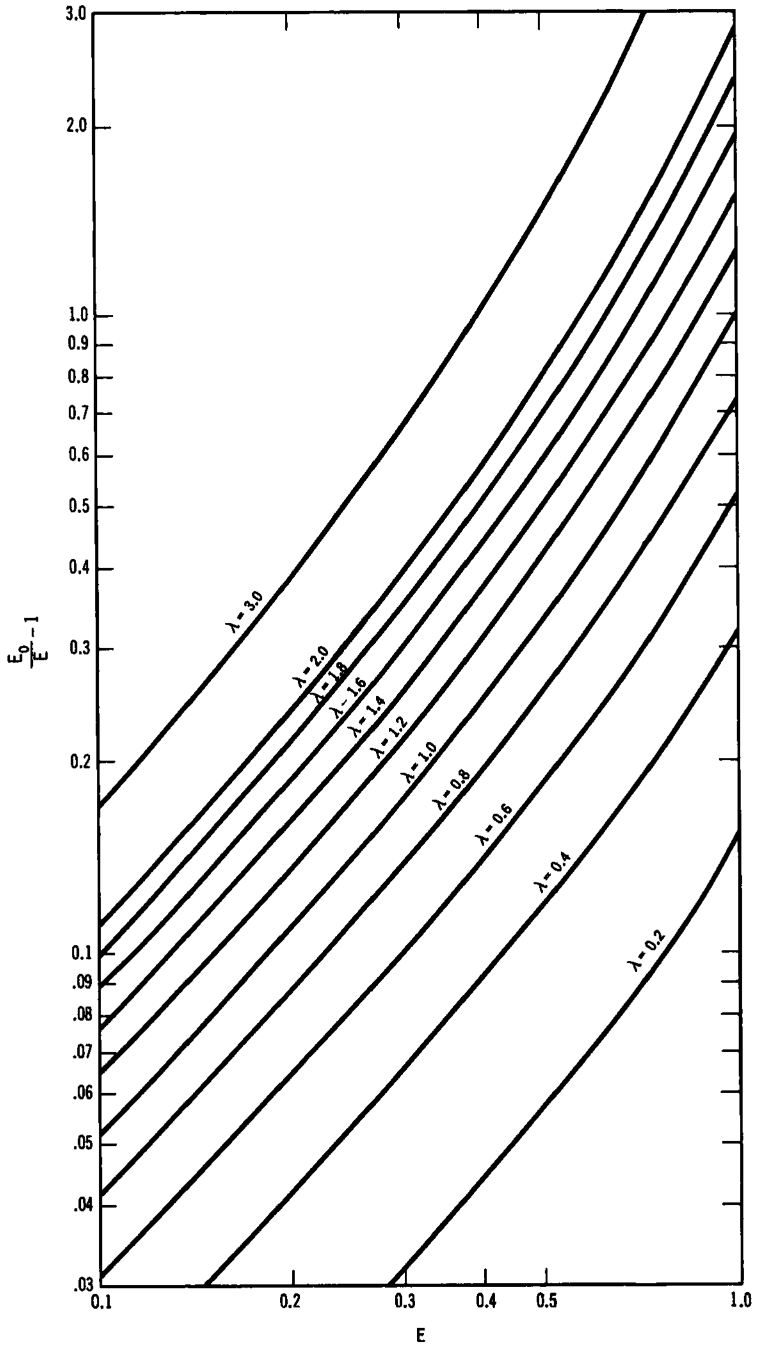

FIG. 6. Effective plate efficiency (E_0) as a function of Murphree point efficiency.

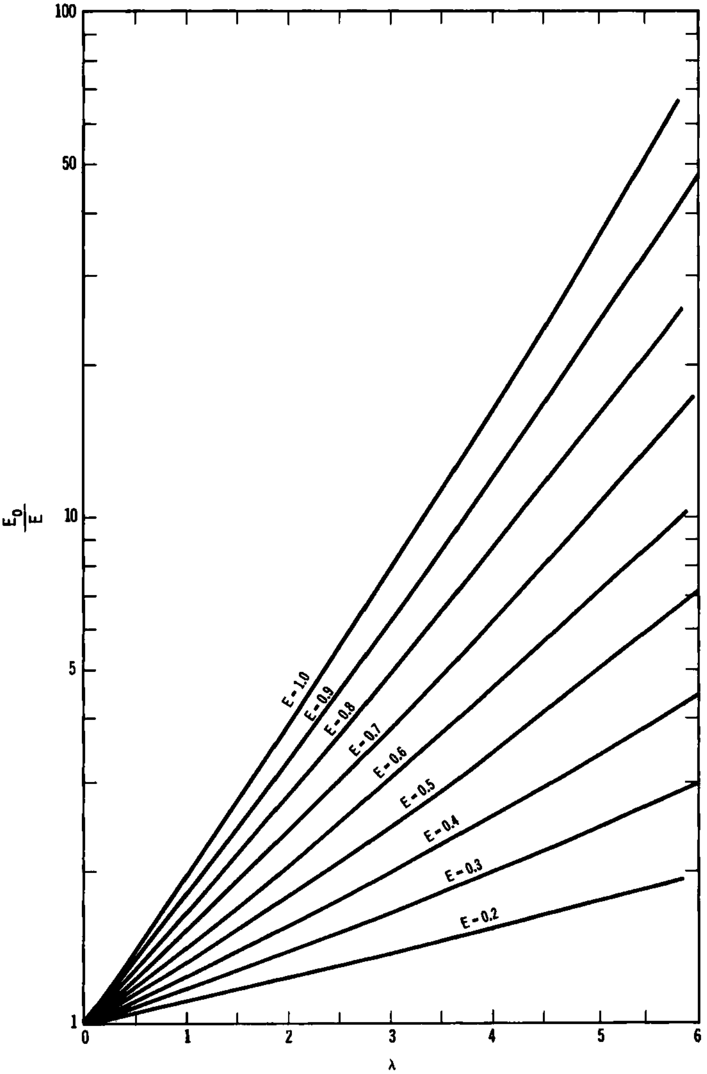

FIG. 7. Ratio of effective plate efficiency (E_0) to Murphree point efficiency (E) as a function of the stripping factor (λ).

reflux). Looking at these comparisons, they are seen to be in extremely good agreement, even though Eq. (59) is derived assuming $k_i = k_j$ and $E_{0,i} = E_{0,j}$.

COMPUTATIONAL METHOD FOR OBTAINING THE THEORETICAL NUMBER OF STAGES

Having obtained the expressions for effective plate efficiencies of a controlled cycling distillation column, an outline of the procedure for calculating the number of actual stages required for a given separation will now be discussed. The idea of this procedure is a natural extension of the Murphree efficiency concept. The effective plate efficiencies, $E_{0,i}$'s, are calculated from the given local stripping factor and instantaneous plate efficiency and then used to construct pseudo equilibrium curves on a McCabe-Thiele diagram. The remainder of the procedure is identical to that for conventional design.

The major difference between the two, however, is that in controlled cyclic distillation the effective plate efficiency also becomes a function of the stage number. Hence, not one but two pseudo equilibrium curves should be used. However, if the number of stages in the column is large, say more than 10, one may assume that all the stages have the same asymptotic efficiency and only one pseudo equilibrium curve need be used. Methods employing an over-all column efficiency can also be used, if the assumption that all $E_{0,i}$ are the same is valid, i.e., for a large number of stages in the column.

The procedure is as follows:

1. Construct a $y^*(x)$ curve and operating lines as in the conventional case.
2. Construct $y^{**}(x) = g(x)$, where

$$g(x) = \frac{H}{V_T}\left[\Psi x + (1 - E_0)\frac{D}{H}x_n\right] + E_0 b$$

in the rectification section and

$$g(x) = \frac{H}{V_T}\left[\Psi x - (1 - E_0)\frac{W}{H}x_1\right] + E_0 b$$

in the stripping section. E_0 is defined by

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

where E, λ, and b are also functions of x. Here $k(x)$ in the expression for λ and $b(x)$ are defined by

$$y^*(x) = k(x)x + b(x)$$

3. Construct $y^{***} = g(x)$, except that E_0 is calculated from

$$e^{E\lambda} = \Psi \exp\left(\frac{E^2\lambda}{\Psi - 1 + E}\right)$$

which is plotted in Fig. 7. The expression for $g(x)$ is derived from Eq. (49) and the material-balance equation for the appropriate section (rectification or stripping) of the column; that is,

$$y_i = \frac{H}{V_T} x_{i+1} + \frac{D}{V_T} x_n$$

or

$$y_i = \frac{H}{V_T} x_{i+1} - \frac{W}{V_T} x_1$$

4. Follow the procedure of the conventional McCabe-Thiele method, except that the first-stage vapor composition is obtained from y^*, the second-stage vapor composition from y^{**}, and the rest of the stage compositions from y^{***}.

Figure 8 shows the modified McCabe-Thiele diagram for the

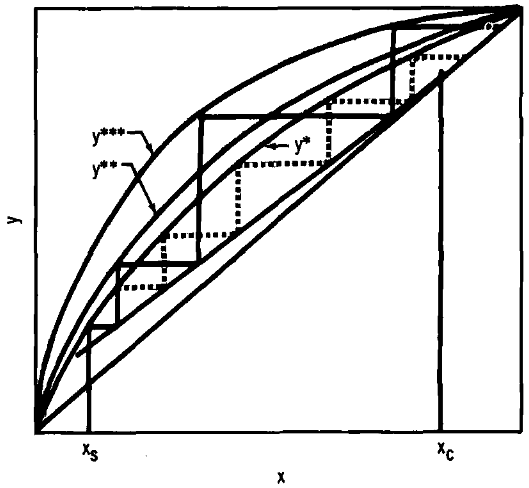

FIG. 8. Design of a rectification still. Three trays are required for a cycling column, whereas five trays are needed in a conventional column ($E = 100\%$).

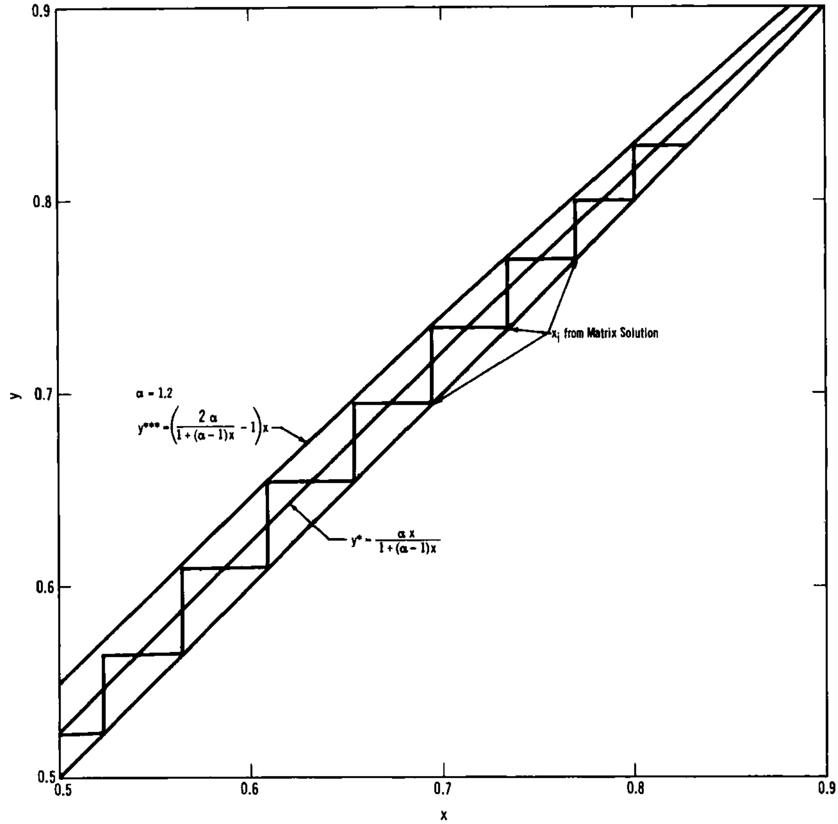

FIG. 9. Plot of the matrix solution on the McCabe-Thiele diagram.

design of a rectification column operating in controlled cyclic fashion. Because of the fact that y^{***} now is a function of x_n (or x_1) and λ, any change in the operating conditions requires a new calculation of y^{**} and y^{***}.

As an example of this method, we chose the problem previously solved on the digital computer using the matrix method. Here at total reflux the equation for y^{***} simplifies to

$$y^{***} = \Psi x + E_0 b$$

Because the operating line (total reflux) and the equilibrium curve are almost parallel, the plate efficiency may be assumed to be 2, or

$\Psi = 2\lambda - 1$. The equilibrium curve is defined as

$$y^* = \frac{\alpha x}{1 + (\alpha - 1)x}$$

The approximate equation for y^{***} is

$$y^{***} = (2k - 1)x + E_0 b = \left[\frac{2\alpha}{1 + (\alpha - 1)x} - 1\right] x$$

Figure 9 shows the curve defined above, where the compositions of the stages are obtained from the result of the iterative-matrix method. The agreement is good for the accuracy of a graphical method. y^{**} is not calculated here.

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