Invariant Imbedding, Iterative Linearization, and Multistage Countercurrent Processes:

III. Estimation and the Overdetermined System

E. S. LEE and J. C. NOH

Department of Industrial Engineering
Kansas State University, Manhattan, Kansas 66502

In the design of distillation processes, it is frequently necessary to obtain a specified purity of certain product from a given feed mixture by the use of an existing column. The only variable within the designer's control is the reflux ratio. This design problem cannot be solved easily by existing computational methods. In general a trial-and-error approach is used. To avoid this difficulty, this problem is solved as an estimation problem by the use of the quasilinearization approach. To show the effectiveness of this approach, several problems are solved. In general, a four-digit accuracy is obtained in four iterations with very approximate initial approximations. Furthermore, this approach can treat the overdetermined system in a straightforward manner by the use of least squares criterion and minimization. Only the cases with constant total flow rates of the vapor and liquid streams within each section of the column are considered. The relative volatilities are also taken to be constant throughout the column.

The quasilinearization technique has been shown to be an effective tool for solving countercurrent stagewise diffusional processes in previous papers (*1*, *2*). The purpose of this work is to show that this approach is also useful for certain design problems where the reflux ratio is the unknown variable.

In the design of distillation processes, it is frequently necessary to obtain a specified purity of certain product from a given feed mixture by the use of an existing column. The only variable within the designer's control is the reflux ratio. Since the reflux ratio is the unknown variable, this problem cannot be solved in a straightforward manner using the conventional computational procedure. One approach is using a trial-and-error procedure by guessing the unknown reflux ratio. This trial-and-error approach needs human interference and is not suited for modern high-speed computers.

To avoid this difficulty, the problem is formulated as an estimation problem. This estimation problem is then solved by the quasilinearization or the generalized Newton-Raphson approach (*3*).

The main advantage of the quasilinearization technique is its quadratic convergence rate. In general, only four or five iterations are needed to obtain a four- to five-digit accuracy. As can be seen from the numerical examples, convergence can be obtained even if very approximate initial approximations or initially guessed values for the unknown functions are used.

It should be mentioned that various versions of the Newton-Raphson methods have been applied to countercurrent processes (*4* to *8*). However, all of the approaches cannot solve the problem straightforwardly where the reflux ratio is the unknown variable. By incorporating the concept of estimation into quasilinearization, this problem can generally be solved in a straightforward manner in a few iterations.

It is shown that the distillation problem can be formulated either as a boundary-value problem or as an estimation problem, depending on the number of terminal concentrations specified. Least squares criterion is used in the estimation. It should be noted that any other criterion can also be used in this estimation approach. In order to focus attention on the fundamental principles of the approach, the total flow rates of the vapor and liquid streams are taken to be constant within each section.

THE DESIGN PROBLEM

To illustrate the approach, consider the simple binary distillation process shown in Figure 1 in which the feed enters the column at the bottom. We further assume that the column has a total condenser. To simplify the discussion, constant vapor and liquid molal flow rates will be assumed. This assumption eliminates the need for enthalpy balances. It should be noted that the numbering of the subscripts of the concentrations is different from the literature. Using this numbering system, we replace the one second-order difference equation by two first-order simultaneous difference equations. The material balance equation around stage n is

$$x(n) = x(n-1) + \frac{V}{L}[y(n) - y(n-1)] \qquad (1)$$

Since the streams leaving stage n are in equilibrium, the equilibrium relationship is

$$y(n) = \frac{\alpha x(n-1)}{1 + (\alpha - 1)x(n-1)} \qquad (2)$$

where x and y represent the mole fractions of the more volatile component in the liquid and vapor phases, respectively, L and V represent the molal flow rates of liquid and vapor, respectively, and α is the relative volatility.

One design problem which arises frequently in practice is as follows: A limited quantity of a certain product with

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J. C. Noh is with Foxboro Company, Foxboro, Massachusetts 02035.

a certain purity is needed. This product can be obtained from a given binary mixture. Since this product is not needed in large quantity, an existing distillation column with a given number of plates will be used to obtain the desired product. Since both the compositions of the raw material and the final product are given, and since the distillation column is fixed, the only variable within the designer's control is the reflux ratio. The problem is to find the reflux ratio so that the desired purity is obtained. As has been discussed in the introduction, this design problem cannot be solved easily by available computation methods. This problem will be solved by the quasilinearization technique by treating the problem as a boundary-value problem or as an estimation problem, depending on the specified conditions. It is obvious that in order for this problem to have a solution, the desired purity must be within the capability of the existing column.

A BOUNDARY VALUE PROBLEM

Let the purity of the desired product be

$$x_D = c \tag{3}$$

where the subscript D represents the distillate. The purity of the raw material is given as

$$y(0) = e \tag{4}$$

Since a total condenser is used, we have

$$x(N) = y(N) = x_D = c \tag{5}$$

which can be written as

$$x(N) = c, \quad y(N) = c \tag{6}$$

Equations (1) and (2) are two first-order simultaneous difference equations with x and y as the two unknowns. The total number of plates N and the relative volatility α are given.

In the usual design approach, Equations (1) and (2) are solved by using Equation (4), the given value of N, and $x(N) = y(N)$. Since V/L must be known before the calculation can be started, a certain value of V/L is assumed. The value of c obtained in this calculation is generally not the desired c. Thus a different value of V/L must be assumed and the calculation is repeated. In this way, a series of valued of c, each corresponding to an assumed value of V/L, is obtained. This is essentially a trial-and-error procedure and is apparently very time-consuming.

To overcome this difficulty, let us consider V/L as another variable parallel to x and y, and let

$$z = V/L \tag{7}$$

The following difference equation can be used to represent this variable:

$$z(n) = z(n-1) \tag{8}$$

Equation (1) becomes

$$x(n) = x(n-1) + z[y(n) - y(n-1)] \tag{9}$$

Now, we have three variables, x, y, and z, and three first-order difference equations, Equations (2), (8), and (9). The three boundary conditions for these three equations are represented by Equations (4) and (6). Since the condition in Equation (4) is given at $n = 0$ and the conditions in Equation (6) are given at $n = N$, Equations (2), (4), (6), (8), and (9) constitute a boundary-value problem in difference equations. Since x, y, and z are the unknowns, both Equations (2) and (9) are nonlinear and they cannot be solved easily. The quasilinearization technique which has been shown to be an effective technique for solving nonlinear boundary-value problems in differential equations (3) can also be used to solve nonlinear boundary-value problems in difference equations.

THE GENERALIZED NEWTON-RAPHSON APPROACH

To overcome the nonlinearity difficulty, Equations (2) and (9) can be linearized by the generalized Newton-Raphson formula. Consider the m first-order nonlinear difference equations:

$$\begin{aligned} f_i\,[x_1(n+1), x_2(n+1), \ldots, x_m(n+1);\\ x_1(n), x_2(n), \ldots, x_m(n); n] = 0 \\ i = 1, 2, \ldots, m \end{aligned} \tag{10}$$

Expanding Equation (10) around $\mathbf{x}_k(n+1)$ and $\mathbf{x}_k(n)$ by the use of Taylor series with terms higher than the first order omitted, we have

$$\begin{aligned} \mathbf{f}[\mathbf{x}_k(n+1), \mathbf{x}_k(n), n] + \mathbf{J}_{\mathbf{x}(n+1)}\,[\mathbf{x}_{k+1}(n+1)\\ - \mathbf{x}_k(n+1)] + \mathbf{J}_{\mathbf{x}(n)}\,[\mathbf{x}_{k+1}(n) - \mathbf{x}_k(n)] = 0 \end{aligned} \tag{11}$$

where $\mathbf{x}(n+1)$, $\mathbf{x}(n)$, and $\mathbf{f}$ represent m-dimensional vectors with components $x_1\,(n+1), x_2(n+1), \ldots, x_m(n+1)$; $x_1(n), x_2(n), \ldots, x_m(n)$; and $f_1, f_2, \ldots, f_m$, respectively. The $\mathbf{J}_{\mathbf{x}(n)}$ and $\mathbf{J}_{\mathbf{x}(n+1)}$ are Jacobian matrices with respect to $\mathbf{x}_{(n)}$ and $\mathbf{x}_{(n+1)}$, respectively. The variables with subscript k are known variables and are obtained in the previous k^{th} iteration. Only the variables with subscript $(k+1)$ are unknown and are being calculated at the current $k+1$st iteration. Thus the equations in Equation (11) are linear difference equations.

Linearizing Equations (2), (8), and (9) by using Equation (11) with $m = 3$, we have

$$y_{k+1}(n) = \frac{\alpha x_{k+1}(n-1) + \alpha(\alpha-1)[x_k(n-1)]^2}{[1 + (\alpha-1)x_k(n-1)]^2} \tag{12}$$

$$\begin{aligned} x_{k+1}(n)\\ = x_{k+1}(n-1) + z_k(n)\,[y_{k+1}(n) - y_{k+1}(n-1)]\\ + z_{k+1}(n)[y_k(n) - y_k(n-1)]\\ - z_k(n)[y_k(n) - y_k(n-1)] \end{aligned} \tag{13}$$

$$z_{k+1}(n) = z_{k+1}(n-1) \tag{14}$$

The three boundary conditions can be rewritten as

$$y_{k+1}(0) = e, \quad x_{k+1}(N) = c, \quad y_{k+1}(N) = c \tag{15}$$

Although Equations (12) through (14) are linear difference equations, their coefficients are functions of the stage number n. In general, linear difference equations with variable coefficients cannot be solved in closed form. However, since these equations are linear, their solution must obey the superposition principle. In other words, the solution of the above equations can be represented by (3, 9)

$$y_{k+1}(n) = y_{p,k+1}(n) + \sum_{i=1}^{3} a_{i,k+1}y_{hi,k+1}(n) \tag{16}$$

$$x_{k+1}(n) = x_{p,k+1}(n) + \sum_{i=1}^{3} a_{i,k+1}x_{hi,k+1}(n) \tag{17}$$

$$z_{k+1}(n) = z_{p,k+1}(n) + \sum_{i=1}^{3} a_{i,k+1} z_{hi,k+1}(n) \quad (18)$$

for $1 \leq n \leq N$. The subscript p is used to indicate particular solutions, the subscript h denotes the homogeneous solutions, and a denotes the arbitrary constants which are to be determined from the three given boundary conditions.

The following initial conditions are used to obtain the particular solution:

$$y_{p,k+1}(0) = e, \quad x_{p,k+1}(0) = 0, \quad z_{p,k+1}(0) = 0 \quad (19)$$

If the following two sets of initial conditions are used for the first two homogeneous solutions

$$y_{h1,k+1}(0) = 0, \quad x_{h1,k+1}(0) = 1, \quad z_{h1,k+1}(0) = 0 \quad (20)$$
$$y_{h2,k+1}(0) = 0, \quad x_{h2,k+1}(0) = 0, \quad z_{h2,k+1}(0) = 1$$

it can be shown that the third set of homogeneous solution is not needed. Notice that the above initial conditions are chosen so that the given initial condition in Equation (15) is satisfied. The remaining two arbitrary constants, a_1 and a_2, can be obtained from the remaining two conditions. Instead of Equations (19) and (20), any other sets of initial conditions can also be used as long as the homogeneous solutions form a fundamental set (9).

At $n = N$ and with two sets of homogeneous solutions, Equations (16) and (17) can be written as

$$y_{k+1}(N) = c = y_{p,k+1}(N) + a_{1,k+1} y_{h1,k+1}(N) \\ a_{2,k+1} y_{h2,k+1}(N) \quad (21)$$

$$x_{k+1}(n) = c = x_{p,k+1}(N) + a_{1,k+1} x_{h1,k+1}(N) \\ + a_{2,k+1} x_{h2,k+1}(N) \quad (22)$$

Since the particular and homogeneous solutions are known, the only unknowns in Equations (21) and (22) are $a_{1,k+1}$ and $a_{2,k+1}$. These two constants can now be obtained by solving these two equations. Once $a_{1,k+1}$ and $a_{2,k+1}$ are obtained, the values of $x_{k+1}(n)$, $y_{k+1}(n)$, and $z_{k+1}(n)$ for $1 \leq n \leq N$ can be obtained from Equations (16) through (18) with $i = 1, 2$, in the summation term. Using this newly obtained x, y, and z, an improved x, y, and z can again be obtained by first obtaining the particular and homogeneous solutions by solving Equations (12) through (14) and by using Equations (19) and (20) as the initial conditions. This iterative procedure can be continued until the desired results are obtained. The reflux ratio R can finally be obtained from

$$R = \frac{L}{D} = \frac{1}{\dfrac{V}{L} - 1} = \frac{1}{z - 1} \quad (23)$$

MULTICOMPONENT SEPARATION PROCESS AS A BOUNDARY-VALUE PROBLEM

The above approach can also be used to solve multicomponent design problems. Consider the same problem illustrated in Figure 1 except that there are m components in the mixture. With the other assumptions remaining the same, the problem can again be represented by equations similar to (2), (8), and (9), except that Equations (2) and (9) now represent $2(m - 1)$ equations with x_i, y_i, α_i, $i = 1, 2, \ldots, (m - 1)$.

The design problem con be stated as follows: Given an N-plate distillation column and a raw mixture with fixed composition, we wish to obtain a product with a specified concentration of one of the components. Mathematically, these given conditions form the following boundary conditions:

$$x_{1D} = x_1(N) = c_1, \quad y_i(0) = e_i, \quad i = 1, 2, \ldots, m - 1 \quad (24)$$

Since a total condenser is used, we also have

$$x_i(N) = y_i(N), \quad i = 1, 2, \ldots, m - 1 \quad (25)$$

Equations (24) and (25) constitute $2(m - 1) + 1$ boundary conditions for the $2(m - 1) + 1$ equations. This system of nonlinear boundary-value problems can again be solved by the combined use of quasilinearization and the superposition principle.

To illustrate this approach, let us consider a system with four components. Using the least volatile component as the base component, we find the volatilities for the three more volatile components to be $\alpha_1 = 8.0$, $\alpha_2 = 4.0$, $\alpha_3 = 2.0$. The composition of the feed mixture is assumed as

$$y_1(0) = e_1 = 0.055, \quad y_2(0) = e_2 = 0.102, \\ y_3(0) = e_3 = 0.459 \quad (26)$$

The product must contain the following mole fraction of component 1:

$$x_1(N) = c_1 = 0.182 \quad (27)$$

The distillation column has a total condenser and five plates.

The $2(m - 1) + 1$ equations can be linearized; they are

$$y_{i,k+1}(n) = \frac{\alpha_i x_{i,k+1}(n-1)}{1 + \sum_{i=1}^{3} [(\alpha_i - 1) x_{i,k}(n-1)]} - \frac{\alpha_i x_{i,k}(n-1) \sum_{i=1}^{3} [(\alpha_i - 1)(x_{i,k+1}\{n-1\} - x_{i,k}\{n-1\})]}{\left[1 + \sum_{i=1}^{3} [(\alpha_i - 1) x_{i,k}(n-1)]\right]^2}, \quad i = 1, 2, 3 \quad (28)$$

$$x_{i,k+1}(n) = x_{i,k+1}(n-1) + z_k(n) \\ [y_{i,k+1}(n) - y_{i,k+1}(n-1)] \\ + z_{k+1}(n)\,[y_{i,k}(n) - y_{i,k}(n-1)] \\ - z_k(n)\,[y_{i,k}(n) - y_{i,k}(n-1)] \quad (29)$$

$$z_{k+1}(n) = z_{k+1}(n-1) \quad (30)$$

The seven boundary conditions for the above seven equations are

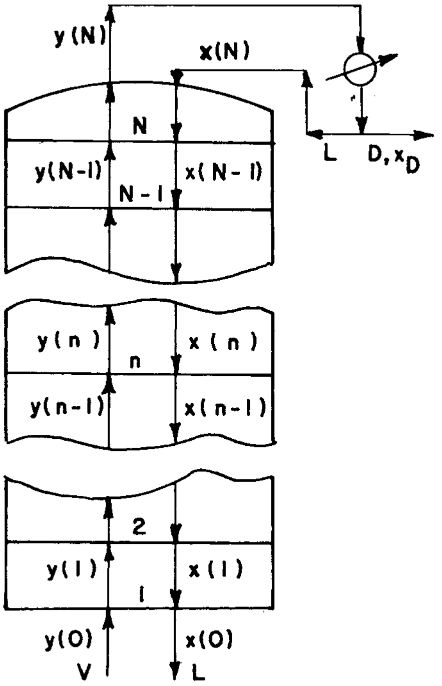

Fig. 1. Diagram for the simple example.

$$\begin{aligned} &x_{1,k+1}(N) = c_1 = 0.182, \quad y_{1,k+1}(0) = 0.055, \\ &y_{2,k+1}(0) = 0.102, \quad y_{3,k+1}(0) = 0.459, \\ &x_{i,k+1}(N) = y_{i,k+1}(N), \quad i = 1, 2, 3 \end{aligned} \tag{31}$$

The initial conditions used for the particular and the homogeneous solutions are

$$\begin{aligned} &y_{1p}(0) = 0.055, \quad y_{2p}(0) = 0.102, \quad y_{3p}(0) = 0.459 \\ &x_{1h1}(0) = x_{2h2}(0) = x_{3h3}(0) = z_{h4}(0) = 1.0 \end{aligned} \tag{32}$$

All the other initial conditions used for the particular and homogeneous solutions are zero.

This problem is solved with the following initial approximations or initially guessed values for the six variables:

$$\begin{aligned} &x_{1,k=0}(n) = 0.055, \quad x_{2,k=0}(n) = y_{2,k=0}(n) = 0.102, \\ &x_{3,k=0}(n) = y_{3,k=0}(n) = 0.459, \\ &y_{1,k=0}(n) = e_1 + \frac{n}{N}(c_1 - e_1) \end{aligned} \tag{33}$$

for all n. Notice that a constant starting value was assumed except for $y_{1,k=0}$. The initial approximation for the variable z is

$$z_{k=0}(n) = \left(\frac{V}{L}\right)_{k=0} = 10$$

This problem was solved on an IBM 360/50 computer. The convergence rate of the reflux ratio is shown in the third column of Table 1. The convergence rate for the concentrations is approximately the same as that shown in Table 1. In other words, four-digit accuracy in concentration is obtained in four iterations. To see the effect of the initial approximation on the convergence rate, the problem with the following initial approximations for z is also solved:

$$z_{k=0} = 1, 5, 20$$

All these three problems have the same fast convergence rate as that shown in Table 1.

OVERDETERMINED SYSTEM AND ESTIMATION

Instead of just requiring one component with a certain concentration in the product, the concentrations of several components may be specified in the product. For example, instead of the first equation in Equation (24), we may have

$$x_i(N) = c_i, \quad i = 1, 2, \ldots, m - 1 \tag{34}$$

with the other required conditions in Equations (24) and (25) remaining the same. The design problem now becomes that, given the complete composition of the feed mixture, we wish to obtain a product with a specified composition by the use of an existing distillation column. Obviously, it is not always possible to obtain the exact specified product. However, we wish to obtain a product which is as near as possible to the desired one.

The boundary conditions are represented by Equations (25), (34), and the last equation in Equation (24). The system is represented by the same $2(m - 1) + 1$ first-order difference equations discussed in the last section, but there are now $3(m - 1)$ boundary conditions. Thus this problem has too many boundary conditions specified. Mathematically, it may be impossible to satisfy all these boundary conditions. Since we wish to obtain the product as near as possible to the specified one, the least squares approach can be used (3). Instead of Equation (34), the following sum of squares is minimized:

$$Q = \sum_{i=1}^{m-1} [x_i(N) - c_i]^2 \tag{35}$$

where $x_i(N)$ is the calculated value and c_i is the specified composition of the product. Equation (25) and the last equation in (24) constitute $2(m - 1)$ boundary conditions. The other boundary condition can be obtained by minimizing Equation (35). Thus we are essentially estimating the best possible product composition if the required product composition cannot be obtained.

Since the difference equations are nonlinear, it is very difficult, if not impossible, to minimize Equation (35). Quasilinearization can be used to overcome this difficulty. To illustrate the approach, consider again the example solved in the previous section. In addition to the seven boundary conditions listed in Equation (31), we also have the following two additional boundary conditions:

$$x_{2,k+1}(N) = c_2 = 0.273, \quad x_{3,k+1}(N) = c_3 = 0.509 \tag{36}$$

Both the feed and the product are completely specified. There are seven first-order difference equations with nine boundary conditions. The three conditions represented by the first equation in Equation (31) and Equation (36)

TABLE 1. CONVERGENCE RATE OF REFLUX RATIO FOR THE BOUNDARY-VALUE PROBLEM

Iteration	Boundary-value problem V/L	R	Estimation problem V/L	R
0	1.0	0.1111	1.0	∞
1	1.4171	2.3974	0.0000	−1.0000
2	1.3504	2.8537	1.8261	1.2106
3	1.3417	2.9263	1.5461	1.8312
4	1.3416	2.9276	1.3672	2.7231
5	1.3416	2.9276	1.3356	2.9800
6	——	——	1.3353	2.9825
7	——	——	1.3353	2.9825

can be reduced to one by minimizing the following least squares expression:

$$Q_{k+1} = \sum_{i=1}^{3} [x_{i,k+1}(N) - c_i]^2 \tag{37}$$

where c_i is the given or desired product composition and $x_{i,k+1}(N)$ represents the calculated values which can be obtained in the following manner.

Using the same initial conditions listed in Equation (32) for the particular and homogeneous solutions and using the superposition principle, we can reduce Equation (37) with $n = N$ to

$$Q_{k+1} = \sum_{i=1}^{3} \left[x_{ip,k+1}(N) + \sum_{j=1}^{4} a_{j,k+1} x_{ihj,k+1}(N) - c_i \right]^2 \tag{38}$$

Since c_i represents the given product composition and the homogeneous and particular solutions are known once the $(k + 1)^{st}$ iteration is calculated, the only unknowns in Equation (38) are the four arbitrary constants a_j, $j = 1, 2, 3, 4$. Furthermore, since the values of three of the constants can be obtained by using the last equation in (31), Equation (38) can be represented symbolically by

$$Q_{k+1} = \sum_{i=1}^{3} [f_i(a_4) - c_i]^2 \tag{39}$$

where f_i is a very complicated function of a_4 and the homogeneous and particular solutions at $n = N$. The problem is to find the value of a_4 so that Equation (39) is minimized. The various search techniques (3) can be used to minimize Equation (39). In this work differentiation is used. The value of a_4 which gives the minimum of Equation (39) is obtained by solving the equation

$$\frac{\partial Q_{k+1}}{\partial a_4} = \frac{\partial}{\partial a_4} \left[\sum_{i=1}^{3} [f_i(a_4) - c]^2 \right] = 0 \tag{40}$$

It should be noted that in general Equation (40) does not guarantee a minimum. The solution of Equation (40) may give the maximum, the minimum, or just the stationary points. However, for the present problem, a minimum is obtained.

This problem is solved on an IBM 360/50 computer with the following initial approximations or initially guessed starting values for the seven variables:

$$x_{1,k=0}(n) = y_{1,k=0}(n) = 0.055,$$

$$x_{2,k=0}(n) = y_{2,k=0}(n) = 0.102,$$

$$x_{3,k=0}(n) = y_{3,k=0}(n) = 0.459,$$

$$z_{k=0}(n) = \left(\frac{V}{L}\right)_{k=0} = 1.0$$

for all n, $0 \leq n \leq N$. In other words, constant functions are used for the initial assumed functions. The values of these constant functions are the given initial conditions for the concentrations. The convergence rate of the reflux ratio is shown in the last column of Table 1. Notice the fast convergence rate in spite of the very approximate starting values used. The convergence rates of the concentrations over the various stages are approximately the same as those shown in Table 1. A five-digit accuracy was obtained in concentration in six iterations.

INTERMEDIATE FEED

The notation used for the problem is illustrated in Figure 2. A total condenser is assumed. A given feed mixture is to be distilled in an existing column with a fixed number of plates. The product distribution for a certain component, say component 1, must have the following concentrations in the overhead and bottom products:

$$x_{1D} = x_1(0) = e_1, \quad x_1(N) = c_1 \tag{41}$$

Since the feed conditions, the compositions, the number of plates in each section of the column, and one component distribution in the overhead and bottom products are completely specified, the only variable within the designer's control is the reflux ratio. The problem is to find the desired reflux ratio so that the specified product distribution is satisfied. Since a total condenser is used, the following equations must be true:

$$x_i(0) = y_i(0), \quad i = 1, 2, \ldots, m - 1 \tag{42}$$

From material balance on each component over the entire column, we have

$$Fx_{if} = Dx_i(0) + Bx_i(N), \quad i = 1, 2, \ldots, m - 1 \tag{43}$$

where D and B denote the flow rates for the overhead and bottom streams, respectively, and F denotes the feed rate. Overall material balance gives

$$F = B + D \tag{44}$$

From Figure 2 the equilibrium relationship for constant relative volatility is

$$x_i(n) = \frac{y_i(n-1)/\alpha_i}{1 + \sum_{i=1}^{m-1} \left[\left(\frac{1}{\alpha_i} - 1 \right) y_i(n-1) \right]}, \quad n = 1, 2, \ldots, N \tag{45}$$

Material balances for the rectifying section, the feed plate, and the stripping section give

$$y_i(n) = y_i(n-1) + u[x_i(n) - x_i(n-1)], \quad n = 1, 2, \ldots, f - 1 \tag{46}$$

$$y_i(f) = \frac{\overline{L}}{\overline{V}} x_i(f) + \frac{V}{\overline{V}} y_i(f-1) - \frac{L}{\overline{V}} x_i(f-1) - \frac{Fx_{if}}{\overline{V}} \tag{47}$$

$$y_i(n) = y_i(n-1) + \frac{\overline{L}}{\overline{V}} [x_i(n) - x_i(n-1)], \quad n = f + 1, f + 2, \ldots, N - 1 \tag{48}$$

where $u = L/V$ and $\overline{L}$ and $\overline{V}$ represent the flow rates of the liquid and vapor streams, respectively, in the stripping section. The rates $\overline{L}$ and $\overline{V}$ in Equations (47) and (48) can be represented by the flow rates of the feed, the distillate, and the vapor and liquid rates in the rectifying section by the use of simple material balances. The following equation can again be established for the variable u:

$$u(n) = u(n-1), \quad n = 1, 2, \ldots, N \tag{49}$$

Equations (45) through (49) constitute the desired difference equations. The unknowns or independent variables

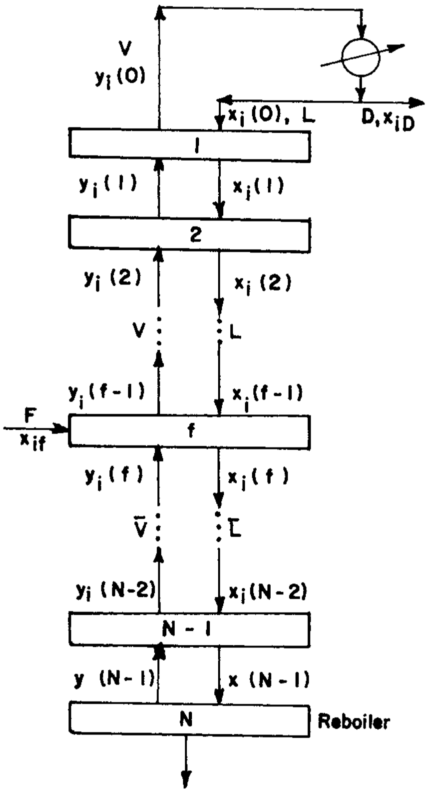

Fig. 2. Schematic diagram of distillation column.

in these difference equations are u, x_i, and y_i, $i = 1, 2, \ldots, m-1$. The problem has a total of $2(m-1)+1$ dependent variables. Equations (45) and (49) constitute $(m-1)+1$ difference equations. The other $(m-1)$ difference equations are represented by the material balance on each component. These material balance equations are different for different sections of the column. Since we have $2(m-1)+1$ first-order difference equations, $2(m-1)+1$ boundary conditions are needed. Equations (41) through (44) furnish $2(m-1)+3$ equations or conditions. However, B and D are unknown values which must be solved for from these equations. Thus Equations (41) through (44) constitute $2(m-1)+1$ conditions. The system represented by Equations (41) through (45) forms a two-point boundary-value problem in nonlinear difference equations.

To illustrate the approach, an example solved by Holland (*5*) will be solved as a boundary-value problem. Holland solved this problem by the Thiele and Geddes method (see Example 3-1 of reference *5*) with a given reflux ratio. In this example, the concentration of one component will be specified in both the overhead and the bottom. The reflux ratio will be assumed unknown. We wish to find the reflux ratio and the distributions of other components. The numerical data used by Holland, and the concentration for component 1 in the overhead and bottom products obtained by Holland, are used in the calculations. Equations (45) through (49) can be linearized. The boundary conditions for these $2(m-1)+1$ first-order linearized difference equations are

$$\begin{gathered} x_{1,k+1}(0) = 0.528, \quad x_{1,k+1}(4) = 0.140, \\ y_{1,k+1}(0) = x_{1,k+1}(0) = 0.528, \\ y_{2,k+1}(0) = x_{2,k+1}(0) \\ Fx_{2f} = 50x_{2,k+1}(0) + 50x_{2,k+1}(4) \end{gathered} \tag{50}$$

Equation (50) represents five boundary conditions which are obtained from Equations (41) through (43). Since Equation (43) with $i = 1$ has already been used to calculate the values of B and D, this equation is not used in Equation (50).

The initial conditions assumed for the particular and homogeneous solutions are

$$\begin{gathered} x_{1p,k+1}(0) = y_{1p,k+1}(0) = 0.528, \\ x_{2h1,k+1}(0) = y_{2h2,k+1}(0) = u_{h2,k+1}(0) = 1 \end{gathered} \tag{51}$$

All other initial conditions used for the particular and homogeneous are zero.

This problem is solved with the following initial approximations for the five unknown discrete functions

$$\begin{gathered} x_{1,k=0}(n) = 0.528/(n+1), \\ x_{x,k=0}(n) = y_{2,k=0}(n) = 0.0, \\ y_{1,k=0}(n) = 0.528, \quad u_{k=0}(n) = \left(\frac{L}{V}\right)_{k=0} = 0.1 \end{gathered}$$

for all n, $0 \leq n \leq N$.

The convergence rates of the reflux ratio and the terminal concentrations of the second component are shown in Table 2. Notice the fast convergence rate. Only four iterations with less than 0.5 min. computation time are needed to obtain a four-digit accuracy. To see the influence of the initial approximation on the convergence rate, the problem is also solved with the following different values for u:

$$u_{k=0}(n) = 0.2, \ 0.4, \ 0.7$$

With all the other numerical values used remaining the same, the convergence rates for these three problems are approximately the same as those shown in Table 2.

DISCUSSION

If the problem solved in the last section were solved by the θ method (*5*) or by the conventional Newton-Raphson methods (*4* to *8*), a series of problems must be solved with different assumed values of the reflux ratios. This is because the value of the reflux ratio must be known or given before computation can be started for the conventional or usual approaches. In this work the problem is solved and the unknown reflux ratio is obtained in one calculation. Furthermore, this approach can solve problems in which too many variables are specified, or the overdetermined system, by the use of minimization and the classical least squares criterion.

Obviously, the problem solved in the last section can also be treated as an estimation problem if more terminal conditions or concentrations are specified. A weighted sum of squares can also be used with the present computational procedure. For example, if a certain component must have a specified concentration in the product while the specified concentrations of the other components are desirable but not necessary, then a very large weight can be put on the

TABLE 2. SOME NUMERICAL RESULTS WITH INTERMEDIATE FEED

Iteration	R	L/V	$x_2(0)$	$x_2(4)$
0	0.1111	0.1000	0.0	0.0
1	0.8235	0.4516	0.3141	0.3519
2	0.9137	0.4775	0.3665	0.2995
3	1.0093	0.5023	0.3616	0.3044
4	1.0086	0.5021	0.3616	0.3045
5	1.0086	0.5021	0.3616	0.3045

concentration of this certain component and relatively small weights are used for the other components. Furthermore, instead of the least squares criterion, any other criterion can also be used in the procedure discussed above.

An estimation problem with multipoint boundary value (3) in difference equations can also be solved by essentially the same approach. For example, it is frequently necessary to have a certain specified purity of a certain side stream. Since this side stream is located at a plate inside the column and not at the terminals, a multipoint boundary-value problem is formulated. Many other specifications of the conditions of a distillation column are possible (5). As we shall see in later papers, the present approach has certain distinct advantages over the conventional procedures for some of the specifications.

It should be emphasized that the problem formulated does not always have solution. For example, the specified purity of the end product must be within the capability of the specified column in order for a solution to exist. The estimation approach avoids this problem. This is because of the fact that the least squares criterion only demands a solution that is as near as possible to the desired one.

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The PVT Behavior of Isopropyl Alcohol at Elevated Temperatures and Pressures

JAMES K. TSENG

Syracuse University, Syracuse, New York

and LEONARD I. STIEL

University of Missouri, Columbia, Missouri 65201

Experimental PVT data have been obtained for isopropyl alcohol by the use of a constant-volume apparatus. Smoothed values of the compressibility factor are presented for temperatures from 200° to 300°C. and pressures from 1,000 to 8,000 lb./sq. in. The experimental data are estimated to be accurate to within 0.4%. The compressibility factor of isopropyl alcohol is also analyzed by the fourth-parameter approach. It is shown that the normal fluid relationship for the compressibility factor can be extended to polar fluids by the inclusion of linear and quadratic terms in the fourth parameter.

Experimental volumetric data are not available for most polar fluids, particularly at elevated temperatures and pressures. In previous studies, PVT data have been obtained for methyl alcohol (3) and ethyl alcohol (*12*) for the dense gaseous and liquid regions. These data are useful for the development of a generalized relationship for the thermodynamic properties of polar fluids by an extended theorem of corresponding states.

No previous volumetric data are available for isopropyl alcohol at elevated temperatures in the dense gaseous and liquid regions. In addition, since this substance has a relatively low critical temperature, experimental PVT data can be obtained for higher reduced temperatures than for most other alcohols of large molecular size.

For isopropyl alcohol, Ambrose and Townsend (*1*) have reported critical constants, vapor pressure data, and densities of the saturated liquid and vapor to the critical point (235.25°C., 47.02 atm.). Moreland, McKetta, and Silberberg (*13*) have presented compressibility factors for gaseous isopropyl alcohol from 100° to 200°C. to pressures slightly below the vapor pressure at each temperature (maximum pressure 24.64 atm.). Smoothed compressibility