Invariant Imbedding, Iterative Linearization, and Multistage Processes:

II. Multicomponent Distillation and Quasilinearization

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The quasilinearization technique has been shown to be an effective tool for solving continuous nonlinear boundary-value problems represented by differential equations (*1*). The purpose of this paper is to apply quasilinearization to discrete nonlinear boundary-value problems in difference equations. The equations representing multicomponent distillation form a class of fairly complicated discrete boundary-value problems. These problems are not only highly nonlinear but they also have complicated boundary conditions. For some complex columns with several feed plates and withdrawn streams, multipoint boundary-value problems can be formulated. It will be seen that quasilinearization is ideally suited for solving those nonlinear boundary-value problems. Because of its fast convergence rate, this technique forms an effective tool for solving the equations representing multicomponent distillation.

In an earlier paper (*2*), discrete invariant imbedding has been used to solve the equations representing countercurrent stagewise diffusional processes. One difficulty in using the invariant imbedding concept is that the resulting equations are fairly complicated partial difference equations. Quasilinearization was used to reduce these partial difference equations into ordinary difference equations. It will be seen that the quasilinearization technique is equally effective when used by itself without the combination with invariant imbedding.

The equations representing multicomponent distillation have been studied extensively by Holland and co-workers (*3*). These authors have shown that the θ method is a useful technique for solving multicomponent distillation problems. For comparison purposes, two of the examples solved by Holland are solved in this work.

MULTICOMPONENT DISTILLATION WITH CONSTANT FLOW RATES

In order to focus attention on the fundamental principles of the approach, multicomponent distillation with constant flow rates within each section of the column will be considered in this section. The basic principles of the quasilinearization approach can be demonstrated clearly by the use of this simplified column. Modifications needed when the flow rates are not constant and are determined by the use of enthalpy balances will be discussed later.

Consider the conventional distillation column shown in Figure 1. The column has a total condenser and a total of N plates, including the reboiler. The plates are numbered from top to bottom. Notice that the numbering of the subscript of the concentration is different from the conventional numbering system in the literature (*3*). This system reduces the one second-order difference equation in each plate into two first-order difference equations (*2*).

Since $x_i(n)$ is in equilibrium with $y_i(n-1)$, we have the equilibrium equations (*3*)

$$x_i(n) = \frac{y_i(n-1)/\alpha_i}{1 + \sum_{j=1}^{m-1} \left[\left(\frac{1}{\alpha_j} - 1 \right) y_j(n-1) \right]} \tag{1}$$

$$i = 1, 2, \ldots, m-1; \quad n = 1, 2, \ldots, N$$

The material balance equations for the rectifying section are

$$y_i(n) = y_i(n-1) + \frac{L}{V}\left[x_i(n) - x_i(n-1)\right] \tag{2}$$

$$i = 1, 2, \ldots, m-1; \quad n = 1, 2, \ldots, f-1$$

At the feed plate, we have

$$y_i(f) = \frac{\bar{L}}{\bar{V}} x_i(f) + \frac{V}{\bar{V}} y_i(f-1) - \frac{L}{\bar{V}} x_i(f-1) - \frac{F x_{if}}{\bar{V}} \tag{3}$$

$$i = 1, 2, \ldots, m-1$$

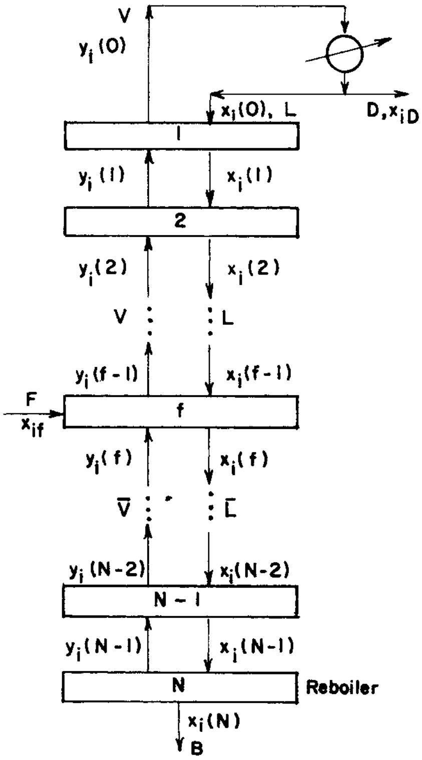

Fig. 1. Schematic diagram of a distillation column.

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The equations for the stripping section are

$$y_i(n) = y_i(n-1) + \frac{\overline{L}}{\overline{V}}\left[x_i(n) - x_i(n-1)\right] \qquad (4)$$

$$i = 1, 2, \ldots, m-1; \quad n = f+1, f+2, \ldots, N-1$$

where α is the relative volatility; L and V are the liquid and vapor rates, respectively, in the rectifying section; $\overline{L}$ and $\overline{V}$ are the liquid and vapor rates in the stripping section; x_i and y_i are the mole fractions of component i in the liquid and vapor phases, respectively; and m is the number of components in the system.

The conditions specified for the column are the number of plates N, the location of the feed plate f, the flow rate as well as the composition and thermal condition of the feed, the distillate rate D, and the reflux rate L. Notice that the above specifications are the specifications needed when the Thiele and Geddes method is used (3).

Equations (2) through (4) are essentially a system of nonlinear first-order difference equations. Equation (1) represents $(m-1)$ first-order difference equations. Equations (2) through (4) represent another $(m-1)$ first-order difference equations for the entire length of the column. Notice that different equations are used for different sections of the column in the material balance equations. Thus there are a total of $2(m-1)$ first-order difference equations. We need $2(m-1)$ boundary or initial conditions to specify the system completely. Since a total condenser is used, we have

$$x_i(0) = y_i(0), \quad i = 1, 2, \ldots, (m-1) \qquad (5)$$

Material balance over the entire column gives

$$Fx_{if} = Dx_i(0) + Bx_i(n), \quad i = 1, 2, \ldots, (m-1) \qquad (6)$$

The above two equations give $2(m-1)$ conditions.

From the specified conditions, we can see that the values of V, $\overline{L}$, $\overline{V}$, and B in the above equations are unknown values. These unknown values can be obtained from the following equations.

$$F = D + B \qquad (7)$$

$$\overline{L} = L + F_L \qquad (8)$$

$$V = \overline{V} + F_V \qquad (9)$$

$$V = D + L \qquad (10)$$

where F_L and F_V are the flow rates of liquid and vapor, respectively, in the feed. A partially vaporized feed condition has been assumed.

Using Equations (7) through (10), the only unknowns in the system represented by Equations (1) through (6) are the $2(m-1)$ unknown functions, x_i and y_i, $i = 1, 2, \ldots, (m-1)$, whose values can be obtained by solving those equations.

The conditions represented by Equations (5) and (6) are not given at one point. They are given at the two terminal points, $n = 0$ and $n = N$. Thus the system represented by Equations (1) through (6) form a two-point or mixed-point nonlinear boundary-value problem which cannot be solved easily. The quasilinearization technique has been shown to be an effective technique for solving nonlinear boundary-value problems in differential equations. It will be shown that this technique is also effective for solving nonlinear boundary-value problems in difference equations.

Numerical Example

To illustrate the approach, a simple example solved by Holland (3) will be solved by the quasilinearization technique. This example (Example 3-1 in reference 3) has been solved by various convergence methods by Holland. Thus a comparison between this approach and other techniques in the literature can be made.

Equations (2), (3), and (4) are linear difference equations in the unknowns x_i and y_i. The nonlinear equation, Equation (1), can be linearized into the following linear equation by the generalized Newton-Raphson formula:

$$\begin{aligned} x_{i,k+1}(n) = {} & \frac{y_{i,k+1}(n-1)/\alpha_i}{1 + \sum_{j=1}^{2}\left[\left(\frac{1}{\alpha_j} - 1\right) y_{j,k}(n-1)\right]} \\ & + \frac{y_{i,k}(n-1)}{\alpha_i} \\ & \frac{\sum_{j=1}^{2}\left(\left(1 - \frac{1}{\alpha_j}\right)\left[y_{j,k+1}(n-1) - y_{j,k}(n-1)\right]\right)}{\left[1 + \sum_{j=1}^{2}\left[\left(\frac{1}{\alpha_j} - 1\right) y_{j,k}(n-1)\right]\right]^2} \end{aligned} \qquad (11)$$

$$i = 1, 2; \quad n = 1, 2, 3, 4$$

where the variables with subscript k are known and are obtained from the previous k^{th} iteration. The variables with subscript $(k+1)$ are the unknowns. The boundary conditions are

$$x_{i,k+1}(0) = y_{i,k+1}(0), \quad i = 1, 2 \qquad (12)$$

$$2x_{if} = x_{i,k+1}(0) + x_{i,k+1}(4), \quad i = 1, 2 \qquad (13)$$

Equations (2), (3), (4), (11), (12), and (13) form a linear two-point boundary-value problem in difference equations. The general solution of this linear problem can be represented by the use of the superposition principle with one set of particular and four sets of homogeneous solutions.

Once the particular and homogeneous solutions are obtained numerically by using the initial conditions listed in Table 1, the four arbitrary constants used in the superposition principle equation can be obtained using the four boundary conditions listed in Equations (12) and (13).

After the values for the arbitrary constants are obtained, the values of x and y at the $(k+1)^{\text{st}}$ iteration can be calculated using the superposition principle equation. Call these newly calculated x and y as the k^{th} iteration, another improved $(k+1)^{\text{st}}$ iteration can be obtained by first obtaining the particular and homogeneous solutions and then obtaining the four arbitrary constants. This iterative procedure can be continued until the desired accuracy on x and y is obtained.

To start the iterations, the following initial approximations or initially guessed values for the four unknown variables are used

$$x_{1,k=0}(n) = x_{2,k=0}(n) = y_{1,k=0}(n) = y_{2,k=0}(n) = c \qquad (14)$$

for all n, $0 \leq n \leq N$, with $c = 0.5$. In other words, a constant function is used for all the four unknown functions. Notice that this initial approximation is very approximate. In practical situations, a much better initial guess can be easily obtained. The convergence rates of the overhead and bottom compositions in the liquid phase are shown in Table 2.* Notice the fast convergence rate in spite of the

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* Tabular material has been deposited as document 01384 with the ASIS National Auxiliary Publications Service.

very approximate initial approximations used. Only four iterations are needed to obtain a five- to six-digit accuracy. Approximately 0.5 min. is needed for 10 iterations on an IBM 360/50 computer. This problem has been solved by Holland using the various iteration methods. The convergence rates are summarized in Table 4-8 of reference 3. The θ method was found to be the best. However, seven to eight iterations are still needed by the θ method. If direct iteration is used, 10 to 11 iterations are needed (3).

To see the influence of the initial approximations on convergence rate, the problem was also solved by using $c = 0.0$ and $c = 0.7$. The convergence rates using these two initial approximations are approximately the same as those shown in Table 2.

TABLE 1. INITIAL CONDITIONS USED FOR OBTAINING THE PARTICULAR AND HOMOGENEOUS SOLUTIONS FOR THE CONSTANT FLOW RATE EXAMPLE

Variable	Particular solution	Homogeneous solutions 1	2	3	4
x_1	1.0	1.0	0.0	0.0	0.0
x_2	0.0	0.0	1.0	0.0	0.0
y_1	0.0	0.0	0.0	1.0	0.0
y_2	0.0	0.0	0.0	0.0	1.0

MULTICOMPONENT DISTILLATION WITH ENTHALPY BALANCE

The quasilinearization approach can also be applied to multicomponent distillation with variable molal rates. The flow rates must now be obtained from the enthalpy balance. Using the conventional nomenclature on distillation column in the literature (3), one can obtain the following well-known overall and individual material balances for the rectifying section:

$$L(n) + D = V(n+1) \quad n = 1, 2, \ldots, f-1 \tag{15}$$

$$L(n)x_i(n) + Dx_{iD} = V(n+1)y_i(n+1) \tag{16}$$

$$i = 1, 2, \ldots, m; \quad n = 1, 2, \ldots, f-1$$

where the plates are numbered consecutively down from the top of the column to the reboiler. The condenser is assigned the number zero, the top plate the number 1, the bottom plate the number N, and the reboiler the number $N + 1$. The symbols $L(n)$ and $V(n)$ denote the total molal rates at which liquid and vapor streams leave plate n, and $x_i(n)$ and $y_i(n)$ denote the mole fraction of component i leaving plate n in the liquid and vapor phases, respectively. The material balance equations for the stripping section are

$$L(n) + D = V(n+1) + F, \quad n = f, f+1, \ldots, N \tag{17}$$

$$L(n)x_i(n) + Dx_{iD} = V(n+1)y_i(n+1) + Fx_{if} \tag{18}$$

$$i = 1, 2, \ldots, m; \quad n = f, f+1, \ldots, N$$

The enthalpy balance for the rectifying section is

$$L(n) \sum_{j=1}^{m} x_j(n)h_j(n) + D \sum_{j=1}^{m} x_{jD}h_{jD} + Q_c = V(n+1) \sum_{j=1}^{m} y_j(n+1)H_j(n+1) \tag{19}$$

$$n = 1, 2, \ldots, f-1$$

where Q_c represents the condenser duty, the net heat removed by the condenser per unit time. The symbols $h_j(n)$ and $H_j(n)$ represent the enthalpies of the pure component j in the vapor and liquid streams, respectively, at the temperature of the n^{th} plate. For the stripping section, the enthalpy balance is

$$L(n) \sum_{j=1}^{m} x_j(n)h_j(n) + D \sum_{j=1}^{m} x_{jD}h_{jD} + Q_c = V(n+1) \sum_{j=1}^{m} y_j(n+1)H_j(n+1) + \sum_{j=1}^{m} Fx_{jf}h_{jf} \tag{20}$$

$$n = f, f+1, \ldots, N$$

where h_{jf} denotes the enthalpy of pure component j in the feed. Using the equilibrium ratio, the equilibrium relationships are

$$y_i(n) = K_i(n)x_i(n), \quad i = 1, 2, \ldots, m; \quad n = 1, 2, \ldots, N+1 \tag{21}$$

The unknowns in the above equations are $L(n)$, $V(n+1)$, $y_i(n+1)$, and $x_i(n)$, $i = 1, 2, \ldots, m$—a total of $(2m + 2)$ unknowns. Notice that the enthalpies h and H and the equilibrium ratio K are not unknowns. The values of these variables can be obtained from the temperature and composition. Furthermore, temperature can also be obtained from the equilibrium composition by the use of bubble point or dew point temperature calculations. Thus h, H, and K are really functions of the composition or mole fraction. Equations (15) through (21) represent $2m + 2$ equations for the entire column. Equation (21) represents m equations and Equations (16) and (18) represent another m equation over the entire length of the column. Equations (15) and (17) give one equation and Equations (19) and (20) give another equation. Assuming that the column has a total condenser, we have the following equation:

$$x_i(0) = y_i(1) = x_{iD} \tag{22}$$

The variables $L(n)$, $V(n+1)$, and $y_i(n+1)$, $i = 1, 2, \ldots, m$, can be eliminated from the above equations. After this elimination, the rectifying section can be represented by

$$F_i(n) = [K_i(n+1)x_i(n+1) - x_i(0)] \sum_{j=1}^{m} x_j(n)h_j(n) + [x_i(0) - x_i(n)] \sum_{j=1}^{m} K_j(n+1)x_j(n+1)H_j(n+1) + [x_i(n) - K_i(n+1)x_i(n+1)]u = 0 \tag{23}$$

$$i = 1, 2, \ldots, m; \quad n = 1, 2, \ldots, f-1$$

where Equation (22) has been used and

$$u = \sum_{j=1}^{m} x_j(0)h_j(0) + \frac{Q_c}{D} \tag{24}$$

and the stripping can be represented by

$$G_i(n) = \left[K_i(n+1)x_i(n+1) - \frac{F}{B}x_{if} + \frac{D}{B}x_i(0) \right] \sum_{j=1}^{m} x_j(n)h_j(n) + \left[\frac{F}{B}x_{if} - \frac{D}{B}x_i(0) - x_i(n) \right] \sum_{j=1}^{m} K_j(n+1)x_j(n+1)H_j(n+1) + [x_i(n) - K_i(n+1)x_i(n+1)]w = 0 \tag{25}$$

$$i = 1, 2, \ldots, m; \quad n = f, f+1, \ldots, N$$

where

$$w = \frac{1}{B}\left[\sum_{j=1}^{m} Fx_{jf}h_{jf} - D\sum_{j=1}^{m} x_j(0)h_j(0) - Q_c\right] \tag{26}$$

Since a total condenser is used, Q_c can be represented by

$$Q_c = V(1)\sum_{j=1}^{m} x_j(0)\,[H_j(1) - h_j(0)] \tag{27}$$

From Equation (21) with $n = 1$ and Equation (22), we obtain

$$x_i(0) = K_i(1)x_i(1), \quad i = 1, 2, \ldots, m \tag{28}$$

Equations (23), (25), and (28) represent m first-order nonlinear difference equations over the entire length of the column. The following conditions are assumed specified: the total number of plates N, the feed plate location, the flow rate as well as the composition and thermal condition of the feed, the distillate rate D, and the reflux ratio $L(0)/D$. The bottom flow rate B can be obtained from the overall material balance

$$B = F - D \tag{29}$$

The temperature on each plate can be obtained as the bubble point temperature by using the following equation

$$\sum_{j=1}^{m} K_j(n)x_j(n) - 1 = 0 \tag{30}$$

Notice that the equilibrium and enthalpy data can be correlated as a polynomial in temperature. Thus once the temperature is obtained, the values of h, H, and K can be calculated easily.

The m unknown variables in the m equations are $x_i(n)$, $i = 1, 2, \ldots, m$. If the initial conditions $x_i(0)$ were given, Equation (28) could be used to obtain $x_i(1)$ by an iterative procedure, Equation (23) could be used to obtain $x_i(n)$ for the rectifying section, and Equation (25) for the stripping section. However, the initial conditions $x_i(0)$ are unknown and the conditions given are the following m overall material balance equations which form the mixed boundary condition of the problem.

$$Fx_{if} = Dx_i(0) + Bx_i(N+1), \quad i = 1, 2, \ldots, m \tag{31}$$

This nonlinear two-point boundary-value problem in difference equations can again be solved by the quasilinearization technique.

Numerical Example

To show the effectiveness of this approach, Example 5-1 of Holland (*3*) is solved by the quasilinearization technique.

In order to linearize Equations (23), (25), and (28), notice that $K_i(n)$, $H_i(n)$, and $h_i(n)$ can be considered as functions of $x_i(n)$ implicitly through the temperature on the n^{th} plate. Thus in the linearization process, all the variables x, H, h, and K should be considered. However, in order to study the influences of the various linearization processes, only x, H, and h will be considered in linearization in this section. The values of K are assumed known and are obtained from the previous iteration. Equation (23) can be linearized as (*1*)

$$\mathbf{F}_k(n) + \underset{\sim}{\mathbf{J}}_{\mathbf{x}(0)}\,[\mathbf{x}_{k+1}(0) - \mathbf{x}_k(0)] + \underset{\sim}{\mathbf{J}}_{\mathbf{x}(n)}\,[\mathbf{x}_{k+1}(n) - \mathbf{x}_k(n)] + \underset{\sim}{\mathbf{J}}_{\mathbf{x}(n+1)}\,[\mathbf{x}_{k+1}(n+1) - \mathbf{x}_k(n+1)] = 0$$

$$n = 1, 2, \ldots, f-1 \tag{32}$$

where $\underset{\sim}{\mathbf{F}_k}$ and $\underset{\sim}{\mathbf{x}_k}$ are m-dimensional vectors. The symbol $\underset{\sim}{\mathbf{J}}_{\mathbf{x}(n)}$ denotes the Jacobian matrix. The elements of $\underset{\sim}{\mathbf{J}}_{\mathbf{x}(0)}$ can be represented by

$$\frac{\partial F_i}{\partial x_l(0)} = \left[\sum_{j=1}^{m} K_{j,k}(n+1)x_{j,k}(n+1)H_{j,k}(n+1) - \sum_{j=1}^{m} x_{j,k}(n)h_{j,k}(n)\right]\delta_{il} + [x_{i,k}(n) - K_{i,k}(n+1)x_{i,k}(n+1)]\,\frac{\partial u}{\partial x_l(0)} \tag{33}$$

$$i,\ l = 1, 2, \ldots, m$$

where

$$\frac{\partial u}{\partial x_l(0)} = h_{l,k}(0) + \sum_{j=1}^{m} x_{j,k}(0)\,\frac{dh_{j,k}(0)}{dT_k(0)}\,\frac{\partial T_k(0)}{\partial x_l(0)} \tag{34}$$

To find an expression for $\partial T/\partial x$, Equation (30) can be used. Differentiating Equation (30) with respect to $x_i(n)$ and rearranging, we have

$$\frac{\partial T(n)}{\partial x_i(n)} = -\frac{K_i(n)}{\sum_{j=1}^{m} x_j(n)\,K_j'(n)} \tag{35}$$

The symbol δ_{il} has the following values:

$$\begin{aligned}\delta_{il} &= 1, \quad i = l\\ &= 0, \quad i \neq l\end{aligned} \tag{36}$$

The elements of $\underset{\sim}{\mathbf{J}}_{\mathbf{x}(n)}$ are

$$\frac{\partial F_i}{\partial x_l(n)} = [K_{i,k}(n+1)x_{i,k}(n+1) - x_{i,k}(0)]\left\{h_{l,k}(n) - \frac{K_{l,k}(n)}{\sum_{j=1}^{m} x_{j,k}(n)K'_{j,k}(n)}\sum_{j=1}^{m} x_{j,k}(n)h'_{j,k}(n)\right\} + \left\{u - \sum_{j=1}^{m} K_{j,k}(n+1)x_{j,k}(n+1)H_{j,k}(n+1)\right\}\delta_{1l} \tag{37}$$

$$i,\ l = 1, 2, \ldots, m$$

The elements of $\underset{\sim}{\mathbf{J}}_{\mathbf{x}(n+1)}$ are

$$\frac{\partial F_i}{\partial x_l(n+1)} = [x_{i,k}(0) - x_{i,k}(n)]\left\{K_{l,k}(n+1)H_{l,k}(n+1) - \frac{K_{l,k}(n+1)}{\sum_{j=1}^{m} x_{j,k}(n+1)K'_{j,k}(n+1)}\sum_{j=1}^{m} K_{j,k}(n+1)x_{j,k}(n+1)H'_{j,k}(n+1)\right]$$

TABLE 3. INITIAL CONDITIONS USED FOR OBTAINING THE PARTICULAR AND HOMOGENEOUS SOLUTIONS FOR THE VARIABLE FLOW RATE EXAMPLE

Variable	Particular solution	Homogeneous solutions 1	2	3	4	5
x_1	0.2	0.3	0.2	0.2	0.2	0.1
x_2	0.2	0.2	0.3	0.2	0.2	0.2
x_3	0.2	0.2	0.2	0.3	0.2	0.2
x_4	0.2	0.2	0.2	0.2	0.3	0.2
x_5	0.2	0.1	0.1	0.1	0.1	0.3

$$+\left[K_{i,k}(n+1)\sum_{j=1}^{m}x_{j,k}(n)h_{j,k}(n)-uK_{i,k}(n+1)\right]\delta_{il} \tag{38}$$

$$i,\ l=1,2,\ldots,m$$

For the stripping section, Equation (25) can be linearized into the following form:

$$\mathbf{G}_k(n)+\underset{\sim}{\mathbf{J}}_{\mathbf{x}(0)}[\mathbf{x}_{k+1}(0)-\mathbf{x}_k(0)]$$
$$+\underset{\sim}{\mathbf{J}}_{\mathbf{x}(n)}[\mathbf{x}_{k+1}(n)-\mathbf{x}_k(n)]$$
$$\underset{\sim}{\mathbf{J}}_{\mathbf{x}(n+1)}[\mathbf{x}_{k+1}(n+1)-\mathbf{x}_k(n+1)]=0,$$
$$n=f,\ f+1,\ldots,N \tag{39}$$

The elements in the Jacobian matrices can be obtained in the same way as that used for the rectifying section.

Equations (28), (31), (32), and (39) form a linear boundary-value problem in $x_{i,k+1}$. The general solution can again be represented by using the superposition principle. The m arbitrary constants can be obtained using the boundary condition, Equation (31).

Since Equation (30) is an implicit equation, some iterative technique is needed to obtain the temperature. Newton's method is used in this work (*1, 3*). The initial conditions used are listed in Table 3. Using the following initial approximations

$$x_{1,k=0}(n)=0.05,\quad x_{2,k=0}(n)=0.15,\quad x_{3,k=0}(n)=0.25,$$
$$x_{4,k=0}(n)=0.20,\quad x_{5,k=0}(n)=0.35 \tag{40}$$

for all n, $1\leq n\leq N+1$, we solve this problem. Notice that the initial approximations used are very approximate and the feed composition is used as the initially assumed functions. The convergence rates of the distillate rate and distillate composition are shown in Table 4.* In 10 iterations the distillate flow rate obtained is 48.88. Holland (Table 5-3 in reference 3) obtained a D value of 48.94 in six iterations. However, a better initial approximation was used by Holland. Notice that the starting temperature profile used in this work is a constant value and is equal to 184.63°F. for all the plates.

MULTICOMPONENT DISTILLATION WITH MORE COMPLETE LINEARIZATION

Many variations can be considered on the problem solved in the previous section. For example, since Equations (28), (32), and (39) are linear equations in $x_{i,k+1}(n)$, these equations can be solved in various ways. In the previous section, the superposition principle is used to obtain the numerical solution. Matrix inversion has been used to avoid stability problems in solving nonlinear boundary-value problems in differential equations by quasilinearization (*1*); matrix inversion will be used in this section. A second point to consider is in linearization. In the previous section, only the variables x, H, and h are considered in the linearization process and K is not considered. It should be expected that this partial linearization would slow down the convergence rate. To see what is the influence when K is neglected in linearization, the variable K will be considered in linearization in this section.

To use the matrix inversion approach, consider Equations (23), (25), (28), and (31) as a system of $m(N+2)$ simultaneous equations with the $m(N+2)$ unknowns $x_i(n)$, $i=1,2,\ldots,m$, $n=0,1,2,\ldots,N+1$. This system of equations can be linearized. Equation (28) can be linearized as

$$x_{i,k+1}(0)-x_{i,k+1}(1)\frac{\partial}{\partial x_i(1)}[K_{i,k}(1)x_{i,k}(1)]$$
$$=K_{i,k}(1)x_{i,k}(1)-x_{i,k}\frac{\partial}{\partial x_i(1)}[K_{i,k}(1)x_{i,k}(1)],$$
$$i=1,2,\ldots,m \tag{41}$$

where the partial differentiation term can be obtained by using Equation (35).

Because of the summation terms in Equations (23) and (25), all the x_j's for $j=1,2,\ldots,m$ appear in all these equations. However, to simplify the linearization, only x_j for $j=i$ in F_i or G_i will be considered, and other x_j's for $j\neq i$ in F_i or G_i will be considered known and are obtained in the previous iteration. Thus Equations (23) and (25) can be linearized into the following equations:

$$x_{i,k+1}(0)\frac{\partial F_i(n)}{\partial x_i(0)}+x_{i,k+1}(n)\frac{\partial F_i(n)}{\partial x_i(n)}$$
$$+x_{i,k+1}(n+1)\frac{\partial F_i(n)}{\partial x_i(n+1)}=x_{i,k}(0)\frac{\partial F_i(n)}{\partial x_i(0)}$$
$$+x_{i,k}(n)\frac{\partial F_i(n)}{\partial x_i(n)}+x_{i,k}(n+1)\frac{\partial F_i(n)}{\partial x_i(n+1)}-F_{i,k}(n); \tag{42}$$
$$i=1,2,\ldots,m;\quad n=1,2,\ldots,f-1$$

$$x_{i,k+1}(0)\frac{\partial G_i(n)}{\partial x_i(0)}+x_{i,k+1}(n)\frac{\partial G_i(n)}{\partial x_i(n)}$$
$$+x_{i,k+1}(n+1)\frac{\partial G_i(n)}{\partial x_i(n+1)}=x_{i,k}(0)\frac{\partial G_i(n)}{\partial x_i(0)}$$
$$+x_{i,k}(n)\frac{\partial G_i(n)}{\partial x_i(n)}+x_{i,k}(n+1)\frac{\partial G_i(n)}{\partial x_i(n+1)}-G_{i,k}(n);$$
$$i=1,2,\ldots,m;\quad n=f,\ f+1,\ldots,N \tag{43}$$

where the partial derivatives can be obtained in the same way as that discussed in the last section, except that K must be considered in carrying this differentiation. The $m(N+2)$ linear equations listed in Equations (31), (41), (42), and (43) can be represented by the matrix equation

$$\mathbf{A}_i\mathbf{x}_{i,k+1}=\mathbf{C}_i \tag{44}$$

where $\mathbf{x}_{i,k+1}$ is an $(N+2)$-dimensional vector with elements $x_{i,k+1}(0)$, $x_{i,k+1}(1)$ $x_{i,k+1}(2)$, …, $x_{i,k+1}(N+1)$. The coefficient matrix $\mathbf{A}_i$ can be represented symbolically

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* See footnote on page 887.

as $\mathbf{A}_i =$

$$\left[\begin{array}{lllllllll} A_{00} & A_{01} & 0 & \cdot & \cdot & \cdot & & & \\ A_{10} & A_{11} & A_{12} & 0 & \cdot & \cdot & \cdot & & \\ A_{20} & 0 & A_{22} & A_{23} & 0 & \cdot & \cdot & \cdot & \\ A_{30} & 0 & 0 & A_{33} & A_{34} & 0 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & & & & \\ A_{N,0} & 0 & \cdot & \cdot & \cdot & 0 & A_{N,N} & & \\ A_{N+1,0} & 0 & \cdot & \cdot & \cdot & 0 & A_{N+,1N} & A_{N+1,N+1} & \end{array}\right] \quad (45)$$

This problem is solved by matrix inversion using the same numerical values used in Example 5-1 of Holland (*3*). The temperature is again obtained by solving Equation (30) using Newton's method. The initial approximations or starting values listed in Equation (40) are again used. The convergence rates of the distillate flow rate and distillate composition are listed in Table 5.[*] In spite of the very approximate starting values used, only seven iterations are needed to obtain a D value of 48.93. Eleven iterations are needed to obtain a D value of 48.90.

DISCUSSION

The quasilinearization technique is a useful tool for solving the equations representing multicomponent distillation. The basic idea is to consider the equations formulated in multicomponent distillation as nonlinear boundary-value problems in difference equations. Thus the various techniques used in solving nonlinear boundary-value problems in differential equations can be used to solve problems in multicomponent distillation.

The decoupling scheme used in obtaining Equations (42) and (43) from Equations (23) and (25) appear to have slowed down the convergence rate. However, the convergence rate in Table 5 is still about the same as the convergence rate given by Holland by the use of the θ method, in spite of the fact that a better initial approximation was used by Holland.

Since the idea of considering the distillation problem as nonlinear boundary-value problem is very general, various approaches or formulations can be used to solve this problem. For example, the formulation represented by Equations (1) through (4), which are obtained by considering material balance around each individual plate, can also be used for solving problems with variable flow rates. The equations used in the Thiele and Geddes method form another starting point for the application of the quasilinearization concept. Perhaps the most important advantage in the nonlinear boundary-value and quasilinearization approach is that it can be used to solve complex columns with several feed plates and withdrawn streams in the same way as that used to solve simple or conventional distillation columns.

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[*] See footnote on page 887.

Kinetics and Deactivation on Large Catalytic Particles

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Solids of ⅛ in. or larger nominal size are often used in chemical reaction processes as either reactant or catalyst particles. If the particle dimensions or geometry of such particles are altered, the overall reaction rate may change owing to the influence of pore diffusion and/or thermal gradients. The latter effect will be most pronounced for highly exothermic reaction rate-controlling situations because of the sensitivity of rate constants to temperature. It has significance regardless of the rate-controlling mechanism, however, and may alter the catalyst behavior as a result of localized degradation at reactor hot spots. For analyzing the kinetics of an exothermic reaction, one would ideally prefer isothermality in the reactor, a condition difficult to achieve because of the poor effective thermal conductivity of packed gas-solid systems. To overcome the temperature problem, many processes have been switched to fluidized-bed operation in which the particles are ground or crushed to a smaller size and suspended by the reactant gases. Although heat transport throughout the bed is improved by this technique, bubble formation and backmixing reduce the overall conversion. The packed-bed reactor has thus remained the mainstay of gas-solid reactive contact. For fairly exothermic reactions an exchanger or a jacketed reactor can maintain the temperature rise within prescribed limits, but are not adequate for obtaining the degree of isothermality required of kinetic analysis for large size particle systems. Fluidizing inerts in a packed-bed reactor

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