Multicomponent Separation Calculations by Linearization

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A new approach to separation calculations has been developed which has many practical advantages. The equations of conservation of mass and energy and of equilibrium are grouped by stage and then linearized. The resulting set of equations has a block-tridiagonal structure which permits solution by a simple technique. Thus a new way to apply the Newton-Raphson technique to separation calculations is devised. The method has been tried on a number of problems chosen to exhibit characteristics which cause other solution technique to fail. Most problems are solved with ten iterations or less.

While there are many methods available for calculating multicomponent distillation, their performances leave much to be desired in many instances. In this paper a new technique is presented which has the following advantages:

1. Component volatility ranges do not affect the convergence. Absorbers, strippers, and reboiled absorbers can be calculated with the same algorithm used for distillation problems with no modifications.
2. The presence of nonideal solutions is accounted for rigorously and simply with no change in the method.
3. Temperature, key component composition or rate, reflux ratio, recovery, or any other function of condenser or reboiler flows can be used as specifications.
4. Murphree plate efficiencies are taken into account in a rigorous manner.
5. The allowable number of feeds and sidestreams is unlimited. No difficulties are caused by negative flows or rounding errors in multifeed problems.
6. The method is based on a linearization of the distillation equations so that convergence accelerates as the solution is approached. This is also true of the Wang-Oleson (*23*), Greenstadt-Bard (*9*), and Tierney-Bruno (*26*) algorithms. It is not true of methods based upon the Thiele-Geddes method (*5, 7, 11, 22*) or unsteady state approach (*2, 20*).
7. No difficulties or complications arise from component flows being very small, hence seeding procedures are unnecessary.

The primary disadvantage of the new method is its requirement of storage space which necessitates the use of secondary storage media for medium to large size problems, unless a rather large immediate access memory is available. However, recent trends in the computing industry are toward multiprogramming or time-sharing computers, on one hand, and toward small low cost, disk-oriented computers, on the other. Time-sharing would allow this distillation program to retrieve its data from secondary storage while another program was being run. Thus no penalty would need be paid for the relatively slow access time of secondary storage. The small computers rely on disk storage for most problems, so that both these schemes tend to reduce the penalty incurred by requiring a large amount of storage. When a large computer is used the penalty is eliminated.

The equations which describe continuous, multicomponent distillation are well known (*8, 11, 12, 14, 21, 22*). Consider the case of an *n* plate column separating *c* components where plate 1 is a condenser and plate *n* is a reboiler. Furthermore, let sidestreams be specified by the ratio of the sidestream to the stream which remains after they are withdrawn. Figure 1 shows a schematic representation of one such plate. L_{ij}, V_{ij}, and T_i are the variables and Li and Vi will represent the total phase flows. We shall assume that the pressure is known and the plate is adiabatic.

Let us examine three types of functions which describe the physical processes on plate *i*.

Enthalpy balance:

$$E_i = (1 + S_i)H_i + (1 + s_i)h_i - H_{i+1} - h_{i-1} - h_{fi} \tag{1}$$

Component material balances:

$$M_{ij} = (1 + S_i)V_{ij} + (1 + s_i)L_{ij} - V_{i+1,j} - L_{i-1,j} - f_{ij} \tag{2}$$

Equilibrium relationships:

$$Q_{ij} = \frac{\eta_i K_{ij} V_i L_{ij}}{L_i} - V_{ij} + \frac{(1 - \eta_i)V_{i+1,j} V_i}{V_{i+1}} \tag{3}$$

Q_{ij} is derived from the definitions of the vapor phase Murphree plate efficiency. That is

$$\eta_i = \frac{y_{ij} - y_{i+1,j}}{K_{ij} x_{ij} - y_{i+1,j}}$$

or

$$\eta_i K_{ij} x_{ij} - y_{ij} + (1 - \eta_i)\, y_{i+1,j} = 0$$

x and *y* represent component mole fractions. In terms of our variables this equation becomes

$$\frac{\eta_i K_{ij} L_{ij}}{L_i} - \frac{V_{ij}}{V_i} + \frac{(1 - \eta_i)\, V_{i+1,j}}{V_{i+1}} = 0$$

By multiplying each term by V_i we arrive at Equation (3).

These functions* (or equations) apply to all interior plates of the column. They also apply to a partial condenser or reboiler if the heat duty is known and is treated as feed enthalpy. This is the case for absorber and stripper columns where the heat duties are zero (that is, the condenser and reboiler are ordinary trays). Later we shall see how to make specifications other than these.

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* Functions (1), (2), and (3) are discrepancy functions, that is, they are a quantitative measure of the failure of the values of L_{ij}, V_{ij}, and T_i to satisfy the physical relationships. The value of E_i is the number of heat units/time by which the enthalpy balance is unsatisfied, whereas in M_{ij} and Q_{ij} the discrepancy is measured in moles/time. A solution to the problem has been obtained when one has values of the variables which make E_i, M_{ij}, and O_{ij} zero. (1), (2), and (3) can be considered equations if we replaced E_i, M_{ij}, and Q_{ij} by zero. We would then say we are looking for the values of the variables which satisfy the equations.

METHOD OF SOLUTION

There are $2c + 1$ equations and variables on each plate or a total of $n(2c + 1)$ of each. Most methods divide the equations into groups and solve one set as the overall problem, with the other sets being solved as inner subproblems. Friday and Smith (*8*) have analyzed the methods which arise from the different groupings of Equations (1), (2), and (3). Briefly, they report that each grouping of these equations enables one to obtain solutions for some types of problems (that is, wide as opposed to narrow boiling components), but no one grouping will work for all types.

The remaining alternative is to solve all the equations simultaneously. A modified Newton-Raphson procedure was chosen to solve these nonlinear equations because that method is based on a linearization of the equations which becomes more correct as the solution is approached. Thus, as the values of the unknowns become more correct, the convergence to the final values accelerates. This behavior contrasts with distillation methods (that is, nonsteady state and Thiele-Geddes) in which convergence actually decelerates as the solution is approached. Naphtali (*17*) found that if the equations and variables are grouped according to plate, the matrix of partial derivatives needed in the Newton-Raphson method assumes a form which is easy to solve and drastically reduces the amount of storage and number of calculations required. It is this economy which makes the method feasible.

$$\text{Let}\quad \bar{x} = \begin{bmatrix} \bar{x}_1 \\ \bar{x}_2 \\ \cdot \\ \cdot \\ \cdot \\ \bar{x}_n \end{bmatrix} \quad \text{and} \quad \bar{F} = \begin{bmatrix} \bar{F}_1 \\ \bar{F}_2 \\ \cdot \\ \cdot \\ \cdot \\ \bar{F}_n \end{bmatrix}$$

where $\bar{x}_i$ is the vector of variables on plate i, and $\bar{F}_i$ is the vector of functions on that plate. Thus

$$\bar{x}_i = \begin{bmatrix} V_{i1} \\ V_{i2} \\ V_{i3} \\ \cdot \\ \cdot \\ \cdot \\ V_{ic} \\ T_i \\ L_{i1} \\ L_{i2} \\ L_{i3} \\ \cdot \\ \cdot \\ \cdot \\ L_{ic} \end{bmatrix} = \begin{bmatrix} x_{i1} \\ x_{i2} \\ \cdot \\ \cdot \\ \cdot \\ \\ x_{ic} \\ x_{i,c+1} \\ x_{i,c+2} \\ \cdot \\ \cdot \\ \cdot \\ \\ \\ x_{i,2c+1} \end{bmatrix} \quad \text{and} \quad \bar{F}_i = \begin{bmatrix} E_i \\ M_{i,1} \\ M_{i2} \\ \cdot \\ \cdot \\ \cdot \\ M_{ic} \\ Q_{i1} \\ Q_{i2} \\ \cdot \\ \cdot \\ \cdot \\ \\ \\ Q_{ic} \end{bmatrix} = \begin{bmatrix} F_{i1} \\ F_{i2} \\ \cdot \\ \cdot \\ \cdot \\ \\ F_{i,c+1} \\ F_{i,c+2} \\ \cdot \\ \cdot \\ \cdot \\ \\ \\ \\ F_{i,2c+1} \end{bmatrix}$$

Using this notation, the Newton-Raphson method becomes

$$\overline{\Delta x}^{m+1} = -\left(\frac{\overline{\overline{dF}}}{dx}\right)^{-1} \bar{F}_m \quad \text{and} \quad \bar{x}^{m+1} = \bar{x}^m + \overline{\Delta x}^{m+1}$$

where $\overline{\Delta x}^{m+1}$ is the calculated correction, which is added to $\bar{x}^m$ to obtain the new values of the variables $\bar{x}^{m+1}$. If the functions $\bar{F}^m$ were linear this correction would make the value of each of the functions zero. Since they are not $\overline{\Delta x}^{m+1}$ is just an approximation to the needed correction. $\left(\frac{\overline{\overline{dF}}}{dx}\right)$ is the matrix of partial derivatives of all the functions with respect to all of the variables at the present value of the variables $\bar{x}^m$. Hence

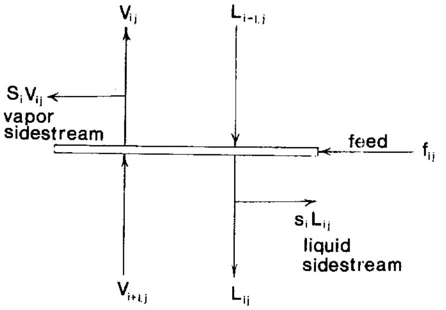

Fig. 1. Schematic representation of one plate.

$$\left(\frac{\overline{\overline{dF}}}{dx}\right) = \begin{bmatrix} \left(\frac{\overline{\overline{dF_1}}}{dx_1}\right) & \left(\frac{\overline{\overline{dF_1}}}{dx_2}\right) & \cdots & \left(\frac{\overline{\overline{dF_1}}}{dx_n}\right) \\ \left(\frac{\overline{\overline{dF_2}}}{dx_1}\right) & \left(\frac{\overline{\overline{dF_2}}}{dx_2}\right) & \cdots & \left(\frac{\overline{\overline{dF_2}}}{dx_n}\right) \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \left(\frac{\overline{\overline{dF_n}}}{dx_1}\right) & \left(\frac{\overline{\overline{dF_n}}}{dx_2}\right) & \cdots & \left(\frac{\overline{\overline{dF_n}}}{dx_n}\right) \end{bmatrix} \tag{4}$$

where

$$\left(\frac{dF_i}{dx_j}\right) = \begin{bmatrix} \frac{dF_{i1}}{dx_{j1}} & \frac{dF_{i1}}{dx_{j2}} & \cdots & \frac{dF_{i1}}{dx_{j,2c+1}} \\ \frac{dF_{i2}}{dx_{j1}} & \cdots & \cdots & \frac{dF_{i2}}{dx_{j,2c+1}} \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \frac{dF_{i,2c+1}}{dx_{j1}} & \cdots & & \frac{dF_{i,2c+1}}{dx_{j,2c+1}} \end{bmatrix} \tag{5}$$

It will be noted that the functions for plate i [Equations (1), (2), and (3)] involve only the variables on plates $i - 1$, i, and $i + 1$. Thus the partial derivatives of the functions on this plate with respect to the variables on all plates other than these three are zero. Thus from (4) we see that

$$\left(\frac{\overline{\overline{dF}}}{dx}\right) =$$

$$\begin{bmatrix} \bar{\bar{B}}_1 & \bar{\bar{C}}_1 & 0 & 0 & \ldots & & & & \ldots 0 \\ \bar{\bar{A}}_2 & \bar{\bar{B}}_2 & \bar{\bar{C}}_2 & 0 & 0 \ldots & & & & \ldots 0 \\ 0 & \bar{\bar{A}}_3 & \bar{\bar{B}}_3 & \bar{\bar{C}}_3 & 0 \ldots & & & & \ldots 0 \\ \cdot & & & & & & & & \cdot \\ \cdot & & & & & & & & \cdot \\ \cdot & & & & & & & & \cdot \\ & & & \ldots & 0 & \bar{\bar{A}}_{n-2} & \bar{\bar{B}}_{n-2} & \bar{\bar{C}}_{n-2} & 0 \\ & & & & 0 & 0 & \bar{\bar{A}}_{n-1} & \bar{\bar{B}}_{n-1} & \bar{\bar{C}}_{n-1} \\ 0 & 0 & 0 & \ldots & 0 & 0 & 0 & \bar{\bar{A}}_n & \bar{\bar{B}}_n \end{bmatrix}$$

where

$$\overline{\overline{A_i}} = \left(\overline{\overline{\frac{dF_i}{dx_{i-1}}}}\right); \quad \overline{\overline{B_i}} = \left(\overline{\overline{\frac{dF_i}{dx_i}}}\right); \quad \text{and} \quad \overline{\overline{C_i}} = \left(\overline{\overline{\frac{dF_i}{\quad_{1}}}}\right)$$

The actual elements of these arrays are shown in the Appendix.

The form of $\left(\overline{\overline{\frac{dF}{dx}}}\right)$ is called block tridiagonal or quasi-tridiagonal, and the simple structure greatly simplifies the solution. The solution can be accomplished by a Gaussian elimination scheme in which only the $\overline{\overline{C}}$ matrices need be stored. (As can be seen in the Appendix, each of the elements in the last c columns of each $\overline{\overline{C}}$ matrix is zero and therefore need not be stored.)

Experience has shown that used by itself the Newton-Raphson method is sometimes unstable. This statement is especially true if the present values of the variables are far from correct. For this reason some method of improving the convergence characteristics of the method must be used. The overall measure of convergence used is the sum of the squares of the discrepancy functions. This value ($\epsilon = \overline{F}^T \overline{F}$) was chosen for two reasons: (1) it is a quantitative measure of the goodness of the solution, and (2) the Newton-Raphson method will produce a set of corrections $\overline{\Delta x}$ whose direction will decrease the sum of the squares (*16*) at least initially. Naphtali (*16*) found that if either the calculated corrections are halved until a smaller sum of the squares was obtained or the values of α from $\alpha = 0$ to $\alpha > 1$ used in defining $x^{m+1} = x^m + \alpha\overline{\Delta x}^{m+1}$ were searched to find the smallest value of the sum of the squares, the linearization method became more stable. This is the solution procedure which was reduced to a computer program.

In order to use this algorithm, one must supply initial estimates of all the variables. This can be done either by guessing all the values or by using some other method to generate the needed numbers. One such generating procedure (*1*) requires only that temperature and liquid over vapor ratio profiles be estimated to generate all component flows. This initialization procedure requires that the vaporization coefficient K be independent of composition, a restriction that the convergence algorithm does not have. Even with this restriction, this procedure is useful because it greatly reduces the number of variables that must be guessed. Of course other methods may be used. Since the Newton-Raphson method is based on linearization of the equations, the closer to the solution one starts the better off he is. Wild initial guesses can make the Newton-Raphson linearization approximation invalid to such an extent that the method will fail to converge.

OTHER END SPECIFICATIONS

We have previously shown that if the end specifications are condenser and reboiler heat duties the functions for an interior plate can be used for the (partial) condenser and (partial) reboiler also. If other specifications are made, then the first and last plate functions may be modified. The new specification function replaces the enthalpy balance function. E_1 or E_n no longer applies because the heat load is unknown. In fact the heat load can be calculated by an enthalpy balance around the condenser or reboiler.

Table 1 gives specification functions which would replace E_1 or E_n. In some situations (that is, reboiled absorbers), it is desirable to control the temperature profile by inserting heat exchangers at various points in the column. The temperature on a specific tray can be fixed by replacing the enthalpy balance on that tray by the equation $T = T_{\text{spec}}$.

A program using the new algorithm has been written in FORTRAN IV. It has been run successfully with many different types of volatility ranges and end specifications. Experience has shown that the method lives up to expectations with regard to convergence on both narrow and wide boiling problems.

PROGRAM DETAILS

Some of the details of the program strategy are presented below. A Fibonacci search was incorporated into the program to find the best fractional part of the Newton-Raphson corrections to use. This procedure, which is described clearly by Wilde (*25*), was chosen because of its high efficiency in locating the minimum value of a function. The values of the liquid and vapor flow rates are never allowed to become negative because of the addition of a negative Newton-Raphson correction. Instead, if a liquid or vapor rate would become negative upon the addition of the correction, a negative exponential correction, as described by Naphtali (*16*), is used to decrease the value of the rate. This strategy keeps the values of the variables in a physically meaningful region. The storage of the variables $\overline{x}$, functional values $\overline{F}$, corrections $\overline{\Delta x}$, and partial derivative matrices $\overline{\overline{C}}$, as well as other problem variables (that is, plate efficiencies and pressures), can be either in the computer's memory or on disk or tape, depending on the memory available and problem size. The storage required for these arrays is $n\{(2c+1)(c+4)+2\} = n(2c^2+9c+6)$ words. For example, for a 10-component, 20-plate problem the requirement is 5,290 words, while for a 20-component, 100-plate problem the requirement is 98,600 words.

TEST OF PROGRAM

The number of different types of problems which potentially can be set up by various combinations of problem specifications is vast. Therefore, looking for the limitations on the capability of the algorithm we set up critical experiments to determine whether it solved problems which stopped other algorithms. Passing these tests is a limited kind of circumstantial evidence that the algorithm will work on a wide variety of problems. (As of this writing the algorithm is in use in industry and has solved hundreds of "live" industrial problems, ranging from reboiled absorbers to alcohol dehydration columns.)

One of the most difficult types of problems to solve for many distillation programs is an absorber problem. This is true because this kind of problem contains both multiple feeds and wide boiling mixtures. As an example we considered a 20-plate column with four hypothetical components with a very wide boiling range. As can be seen

TABLE 1.

Specification	Condenser E_1	Reboiler E_n
Reflux (reboil) ratio	$L_1 - V_1\left(\frac{L}{D}\right)$	$V_n - L_n\left(\frac{V}{B}\right)$
Temperature	$T_1 - T_D$	$T_n - T_B$
Overall product rate	$V_1 - D$	$L_n - B$
Key component rate	$V_{1j} - D$	$L_{nj} - B$
Key component mole fraction	$V_{1j} - V_1 X_D$	$L_{nj} - B_n X_B$

TABLE 2.
K Values

Material	Temperature, 100°F.	200°F.
A	500.0	550.0
B	1.50	1.80
C	0.90	1.00
D	1.0×10^{-6}	1.5×10^{-6}
	Molar liquid enthalpies, 10^3 B.t.u./mole	
A	0.01	0.013
B	0.30	0.33
C	0.40	0.44
D	1.50	1.90
	Molar vapor enthalpies, 10^3 B.t.u./mole	
A	1.00	1.002
B	1.80	1.82
C	2.00	2.03
D	5.75	5.95

from the data in Table 2 the volatility range is extreme.

For the absorber problem, the feeds are listed below as are the initial temperature and *L/V* profiles.

Liquid feed No. 1 to top plate, temperature = 125°F.

Material	Moles
A	0.0
B	0.0
C	0.0
D	100.0

Vapor feed No. 2 to plate 20, temperature = 200°F.

Material	Moles
A	75.0
B	15.0
C	10.0
D	0.0

Plate temperature, initial estimates: linearly interpolated from 145.0 at top to 200.0 at bottom. *L/V* values, initial estimates: linearly interpolated from 1.30 at top to 1.25 at bottom.

This problem converged in four iterations to a sum of the squares of 2.4×10^{-10}. The final values of the top and bottom products are shown below.

Material	Top product	Bottom product
A	74.88	0.12
B	4.68	10.32
C	0.021	9.979
D	0.0000899	100.0

At the other end of the volatility range is the following distillation problem. The components were *n*-butane, *i*-pentane, and *n*-pentane at 1 atm. pressure. The data were taken from tables and graphs in Brown's "Unit Operations" (*6*). The problem was specified as having a reflux ratio of 1,000 while recovering 80% of the feed in the bottoms product. A sidestream on the first plate (condenser) withdrew a liquid product equal to 30% of the reflux liquid. Many programs converge with difficulty if the sidestream has a significant volume. The column contained 20 plates with a liquid feed, $T = 30$°F., flow = 500 moles of each component, on the tenth plate. The initial guesses follow.

Plate	Temp., °F.	*L/V*
1	50.0	1,000.0
2-9	51.5 to 53.0	0.77
10-19	53.0 to 57.0	1.92
20	60	0.92

The initial value of the sum of the squares was 1.7×10^5 and this was reduced to 2.3×10^{-8} in six iterations. The final product streams and temperature profiles are shown as listed.

Moles

Component	Top product	Sidestream	Bottom product
n-C4	0.9966	298.9	200.1
i-C5	1.042×10^{-4}	0.09425	499.9
n-C5	4.371×10^{-6}	5.935×10^{-3}	500.0

Temperature profile

1	29.7	6	31.2	11	56.0	16	57.6
2	29.7	7	33.4	12	56.1	17	59.4
3	29.8	8	37.9	13	56.2	18	62.8
4	29.9	9	45.7	14	56.3	19	68.7
5	30.3	10	56.0	15	56.7	20	77.0

Another type of problem which was tested involved nonideal solutions. The components to be separated were *n*-hexane and ethanol. For simplicity, we assumed that there is no heat of mixing (although the method does not require this). Let $K_i = \frac{\gamma_i P_i^*}{P}$ where γ_i is the activity coefficient, P_i^* the vapor pressure, and P the total pressure. The activity coefficients were calculated using the Van Laar equation data from Perry's Handbook (*18*) and the enthalpy data were taken from Weber (*29*) and Reid and Smith (*19*). The feed was a vapor at 200°F. consisting of 50 moles of each component. The column contained ten plates with the feed entering the sixth. The reflux ratio was specified as being 5.0 and the column was to recover 70% of the feed in the bottoms product. This problem converged in ten iterations to a sum of the squares of 7.4×10^{-7}. The results are shown below.

	n-Hexane	Ethanol	Total
D	22.59	7.413	30.00
B	72.41	42.59	70.00
Total products	50.00	50.00	100.00

Plate temperature

1.	151.4	6.	153.4
2.	151.4	7.	153.4
3.	151.5	8.	153.5
4.	151.7	9.	153.9
5.	152.2	10.	155.4

These three problems represent only a small portion of the problems run, but they illustrate the flexibility and convergence of the method.

ACKNOWLEDGMENT

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NOTATION

$\overline{A}_i$ = partial derivative of equations on plate i with respect to variables on plate $i-1$
$\overline{B}_i$ = partial derivative of equations on plate i with respect to variables on plate i
$\overline{C}_i$ = partial derivative of equations on plate i with respect to variables on plate $i+1$
c = number of components
D = distillate rate
E_i = enthalpy balance on plate i
F_i = feed to plate i
$\overline{F}$ = vector of all functional values
$\overline{F}_i$ = vector of functional values on plate i
$F_{i,j}$ = function value of equation j on plate i
h = liquid enthalpy
H = vapor enthalpy
$K_{i,j}$ = equilibrium vaporization constant on plate i for component j
$L_{i,j}$ = molar liquid flow of component j on plate i
L_i = total liquid molar flow on plate i
$M_{i,j}$ = material balance equation for component j on plate i
n = number of plates
$Q_{i,j}$ = equilibrium equation for component j on plate i
s_i = liquid sidestream on plate i
S_i = vapor sidestream on plate i
SS = value of sum of the squares
T_i = temperature on plate i
$v_{i,j}$ = vapor molar flow of component j on plate i
V_i = total vapor flow on plate i
$\overline{X}$ = vector of all variables
$\overline{X}_i$ = vector of variables on plate i
$X_{i,j}$ = j^{th} variable on plate i
$x_{i,j}$ = liquid mole fraction of component j on plate i
$Y_{i,j}$ = vapor mole fraction of component j on plate i
$\overline{x}$ = vector of generated Newton-Raphson correction
ϵ = convergence criteria (small number)
η_i = vapor-based Murphree efficiency on plate i

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APPENDIX. CONSTRUCTION OF THE PARTIAL DERIVATIVE MATRICES.

A_i Matrix

This is the matrix of partial derivatives of the functions of plate i with respect to the variables of plate i-1.

Enthalpy balance = $F_{i,1}$

$$\frac{dF_{i1}}{dv_{i-1,j}} = \frac{dF_{i1}}{dx_{i-1,j}} = 0 \qquad j = 1, 2, \ldots c$$

$$\frac{dF_{i1}}{dT_{i-1}} = \frac{dF_{i1}}{dx_{i-1,c+1}} = \frac{dh_{i-1}}{dT_{i-1}}$$

$$\frac{dF_{i1}}{dL_{i-1,j}} = \frac{dF_{i1}}{dx_{i-1,c+j+1}} = \frac{dh_{i-1}}{dL_{i-1,j}} \qquad j = 1, 2, \ldots c$$

In all following work we shall omit the x notation, remembering that $\overline{x}_i = [v_{ij}; T_i; L_{ij}]$.

Material balance functions = $F_{i,j+1}$ $\quad j = 1, 2, \ldots c$

$$\frac{dF_{i,j+1}}{dv_{i-1,k}} = 0 \qquad k = 1, 2, \ldots c$$

$$\frac{dF_{i,j+1}}{dT_{i-1}} = 0$$

$$\frac{dF_{i,j+1}}{dL_{i-1,k}} = -\delta_{jk} \qquad k = 1, 2, \ldots c$$

$$\text{where } \delta_{jk} = \begin{cases} 1 \text{ if } j = k \\ 0 \text{ if } j \neq k \end{cases}$$

Equilibrium functions = $F_{i,c+1+j}$; $j = 1, 2, \ldots c$

$$\frac{dF_{i,c+1+j}}{dv_{i-1,k}} = \frac{dF_{i,c+1+j}}{dT_{i-1}} = \frac{dF_{i,c+1+j}}{dL_{i-1,k}} = 0; \quad k = 1, 2, \ldots c$$

Thus the A matrix has the following structure:

$$\begin{bmatrix} 0 & X & X \\ 0 & 0 & -I \\ 0 & 0 & 0 \end{bmatrix}$$

0 represents an all-zero submatrix
X represents a nonzero submatrix
I represents a submatrix which is the identity matrix of appropriate size

B_i Matrix

This is the matrix of partial derivatives of the functions of plate i with respect to the variables on that plate.

Enthalpy balance = $F_{i,1}$

$$\frac{dF_{i,1}}{dv_{ij}} = (1 + S_i)\frac{dH_i}{dv_{ij}}; \qquad j = 1, 2, \ldots c$$

$$\frac{dF_{i,1}}{dT_i} = (1 + S_i)\frac{dH_i}{dT_i} + (1 + s_i)\frac{dh_i}{dT_i}$$

$$\frac{dF_{i,1}}{dL_{ij}} = (1 + s_i)\frac{dh_i}{dL_{ij}}; \qquad j = 1, 2, \ldots c$$

Material balance functions $= F_{i,j+1}$; $\qquad j = 1, 2, \ldots c$

$$\frac{dF_{i,j+1}}{dv_{ik}} = (1 + S_i)\,\delta_{jk}; \qquad k = 1, 2, \ldots c$$

$$\frac{dF_{i,j+1}}{dT_i} = 0$$

$$\frac{dF_{i,j+1}}{dL_{ik}} = (1 + s_i)\,\delta_{jk}; \qquad k = 1, 2, \ldots c$$

Equilibrium functions $= F_{i,c+1+j}$; $\qquad j = 1, 2, \ldots c$

$$\frac{dF_{i,c+1+j}}{dv_{ik}} = \frac{\eta_i L_{ij}}{L_i}\left(K_{ij} + V_i\left(\frac{dK_{ij}}{dv_{ik}}\right)\right) - \delta_{jk} + (1 - \eta_i)\frac{v_{i+1,j}}{V_{i+1}}$$

where

$$\left(\frac{dK_{ij}}{dv_{ik}}\right) = \sum_{p=1}^{c}\left(\frac{dK_{ij}}{dy_{ip}}\right)\left(\frac{dy_{ip}}{dv_{ik}}\right)$$

and

$$\frac{dF_{i,c+1+j}}{dT_i} = \frac{\eta_i L_{ij} V_i}{L_i}\left(\frac{dK_{ij}}{dT_i}\right)$$

$$\frac{dF_{i,c+1+j}}{dL_{ik}} = \frac{\eta_i V_i}{L_i}\left(K_{ij}\,\delta_{jk} + L_{ij}\left(\frac{dK_{ij}}{dL_{ij}}\right) - \frac{L_{ij}}{L_i}K_{ij}\right)$$

where

$$\frac{dK_{ij}}{dL_{ik}} = \sum_{p=1}^{c}\left(\frac{dK_{ij}}{dx_{ip}}\right)\left(\frac{dx_{ip}}{dL_{ik}}\right)$$

and

$$\frac{dx_{ip}}{dL_{ik}} = \frac{1}{L_i}\left(\delta_{kp} - \frac{L_{ip}}{L_i}\right)$$

Thus the B_i matrix has the following structure:

$$\begin{bmatrix} X & X & X \\ (1 + S_i)\bar{\bar{I}} & 0 & (1 + s_i)\bar{\bar{I}} \\ X & X & X \end{bmatrix}$$

C Matrix

This is the matrix of partial derivatives of the functions on plate i with respect to the variables on the plate below.

Enthalpy balance $= F_{i,1}$

$$\frac{dF_{i1}}{dv_{i+1,j}} = -\frac{dH_{i+1}}{dv_{i+1,j}}; \qquad j = 1, 2, \ldots c$$

$$\frac{dF_{i1}}{dT_{i+1}} = -\frac{dH_{i+1}}{dT_{i+1}}$$

$$\frac{dF_{i1}}{dL_{i+1,j}} = 0$$

Material balance functions $= F_{i,j+1}$; $\qquad j = 1, 2, \ldots c$

$$\frac{dF_{i,j+1}}{dv_{i+1,k}} = -\,\delta_{jk}; \qquad k = 1, 2, \ldots c$$

$$\frac{dF_{i,j+1}}{dT_{i+1}} = 0$$

$$\frac{dF_{i,j+1}}{dL_{i+1,k}} = 0; \qquad k = 1, 2, \ldots c$$

Equilibrium functions $= F_{i,c+1+j}$; $j = 1, 2, \ldots c$

$$\frac{dF_{i,c+1+j}}{dv_{i+1,k}} = \frac{(1 - \eta_i)V_i}{V_{i+1}}\left(\delta_{jk} - \frac{V_{i+1,j}}{V_{i+1}}\right); \; k = 1, 2, \ldots c$$

$$\frac{dF_{i,c+1+j}}{dT_{i+1}} = 0$$

$$\frac{dF_{i,c+1+j}}{dL_{i+1,k}} = 0; \qquad k = 1, 2, \ldots c$$

Thus the C matrix looks like

$$\begin{bmatrix} X & X & 0 \\ -I & 0 & 0 \\ X & 0 & 0 \end{bmatrix}$$

EQUATIONS USED FOR SPECIFICATIONS OTHER THAN HEAT DUTIES

Replacing condenser duty specification. Equation $F_{1,1}$ changed

Type of equation	
Reflux ratio	$L_1 - V_1\left(\frac{L}{D}\right)_{\text{spec}}$
Condenser temperature	$T_1 - T_{d\ \text{spec}}$
Distillate rate	$V_1 - D_{\text{spec}}$
Key component flow	$V_{1,\ \text{key}} - D_{\text{spec}}$
Key component mole fraction	$V_{1,\ \text{key}} - V_1 X_{\text{spec}}$

Replacing reboiler duty $\qquad F_{n,i}$ changed

Type of Equation	
Reboil ratio	$V_n - L_n\left(\frac{V}{B}\right)_{\text{spec}}$
Reboiler temperature	$T_n - T_{B\ \text{spec}}$
Bottoms rate	$L_n - B_{\text{spec}}$
Key component flow	$L_{n,\text{key}} - B_{n\ \text{spec}}$
Key component mole fraction	$L_{n,\text{key}} - L_n X_{\text{spec}}$

The partial derivatives of these equations must replace partials of the enthalpy balance equations when they are used. Of course, any other feasible end specification might be used instead.

The functions which describe the phenomena occurring in a total condenser are different from the functions of an equilibrium stage. Of course, the materials balance functions must still hold and E_1 may be modified to describe the desired end specification. The equilibrium relationships however no longer are applicable because we no longer have two phases. In place of these c functions we must use c other functions which describe the process. $(c - 1)$ of these functions must express the restriction that both leaving streams (distillate and reflux) have the same composition. The remaining function is a bubble point function in which the temperature used to calculate K is the actual condenser temperature plus a specified number of degrees of subcooling.

If the precision of the numbers used in calculations were infinite, it would make no difference which component was not used in the $(c - 1)$ composition functions. With limited precision arithmetic, however, it becomes more important that the component omitted is not a trace component.

The functions which replace the equilibrium function Q_{ij} for a total condenser are shown below.

Bubble point function $F_{i,c+2} = Q_i$,

$$F_{1,c+2} = 1 - \sum_{i=1}^{c} K_{1i}\,(T + T_{\text{subcool}})\,x_{1i}$$

Composition functions (This assumes that component 1 is left out of the calculation. Usually, if it is the lightest component, it will be present in the distillate in nontrace amounts. If it is only a trace component in the feed, it could be switched with another nontrace component.)

$$x_{1j} = y_{1j}$$

or

$$F_{1,c+1+j} = L_{1,j} - \frac{L_1 v_{1j}}{V_1} \qquad j = 2, 3, \ldots c$$

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