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Computer simulation of a batch distillation column with a reflux divider

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ABSTRACT

Title of Thesis:

COMPUTER SIMULATION OF A BATCH DISTILLATION COLUMN WITH A REFLUX DIVIDER

Michael G. Clarke, Master of Science in Chemical Engineering
1985

Thesis directed by:

Dr. E. C. Roche Jr., Professor of Chemical Engineering

The operation of a batch distillation column with a reflux divider has been mathematically simulated to reproduce operational equipment.

The operation of the column consists of one or more product recoveries. During each product recovery period the column alternates between total reflux and total product withdrawal, with the product withdrawal period being 2 - 5 seconds. Between product recoveries the column operating conditions can be reset.

The basic assumption of this batch distillation simulation is that the column completely equilibrates during the period of total reflux. The determination of the total reflux condition is obtained computationally using the iterative Newton-Raphson method. The significant feature of this simulation is the ability to handle a constant volumetric inventory associated with each contact stage.

Two illustrative examples are included to show the capabilities of the batch distillation simulation. The first consists of a four component chlorinated benzene

system.   The second example simulated the recovery of
acetonitrile from the highly non-ideal water - acetonitrile
binary system.

COMPUTER SIMULATION OF A BATCH DISTILLATION COLUMN

WITH A REFLUX DIVIDER

by
Michael Gerard Clarke

Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology in partial fulfillment of
the requirements for the degree of
Master of Science in Chemical Engineering
1985

APPROVAL SHEET

COMPUTER SIMULATION OF A BATCH DISTILLATION COLUMN

WITH A REFLUX DIVIDER

by
Michael Gerard Clarke

BY

FACULTY COMMITTEE

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DEDICATION

I dedicate this thesis to my caring and loving

parents, Mary and Peter.

ACKNOWLEDGEMENT

I wish to express my gratitude to Dr. E. C. Roche for his support and guidance during the course of work on this thesis. I also wish to thank Dr. Roche for the many computer subroutines made available by him for my use.

I also wish to express my thanks to the faculty of the Chemical Engineering Department of the New Jersey Institute of Technology for their assistance during my years at the Institute.

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INTRODUCTION

The following text discusses the computer simulation of a batch distillation column using a reflux divider. The simulation was accomplished using the FORTRAN language.

A batch distillation is inherently an unsteady-state process. Due to its time dependence it is more difficult to model or simulate than the continuous steady-state distillation process. A batch distillation column can be operated in two distinct ways: constant product composition or constant reflux ratio. In a constant product composition mode of operation the reflux ratio is adjusted in order to maintain a product with a constant mole fraction of the key component. A constant reflux ratio operation will have the product composition vary with time. In addition, batch distillation columns may be operated with continuous product withdrawal or intermittent product withdrawal via a reflux splitter. The operation treated in this thesis is the one of intermittent product withdrawal with a fixed reflux ratio.

The intermittent withdrawal type of operation, the Interval Method, consists of a short product withdrawal period followed by a time period in which the column is in total reflux. For example, if the reflux ratio is 10:3, then the product withdrawal period is 3 seconds, followed by a 10 second time interval in which the column would be at total reflux. Normal column operation is with withdrawal periods of the order of 2 to 5 seconds.

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The algorithm for the Interval Method is:

1. Initialize the variables

2. Find the steady-state solution using the Newton-Raphson Method.

3. Withdraw a small amount of material from the column, assuming constant product composition over the withdrawal period.

4. If the product requirements for the cut are not satisfied, go to step 2 and continue the process. (A cut is a product draw-off that meets given amount or compositional specifications.)

5. At this point the column parameters for the next cut, i.e. the reflux ratio, the molar withdrawal rate, heat input, pressure and pressure drop, and the amount or compositional specifications are adjusted ... repeat the product withdrawal cycle starting with step 1.

6. End of simulation.

The following chapters discuss the mathematical model, the procedure used to simulate the column, and the results.

CHAPTER 1

MATHEMATICAL MODEL OF THE STEADY-STATE TOTAL REFLUX CONDITION

OF THE BATCH DISTILLATION COLUMN

The forthcoming material discusses the mathematical model that was used to simulate batch distillation columns at the steady-state total reflux condition. The assumptions and limitations of the model will be discussed also. The problem of material withdrawal will be discussed in a forthcoming chapter. Note that the stages are numbered from the condenser, stage #1, to the reboiler, stage #N and that subscript i stands for the component number and subscript n stands for the stage number. Figure 1 shows a diagram of a batch column.

At total reflux, $D = 0$, the heat input to the reboiler equals the heat removed in the condenser plus the heat losses associated with each stage. In addition it is assumed that the volumetric inventory on each stage is a known constant. Using these specifications a steady-state condition is determined.

The independent variables for each stage are the liquid and vapor mole fractions for each component, ($x_{i,n}$ and $y_{i,n}$); the temperature, (T_n); the liquid and vapor molar flow rates, (L_n and V_n); and the inventory, (U_n) which is the total molar hold-up on a stage. From the above it can be seen that there are a total of $2*NC+4$ variables per stage, thus $2*NC+4$ independent equations are needed to describe a

BATCH DISTILLATION COLUMN
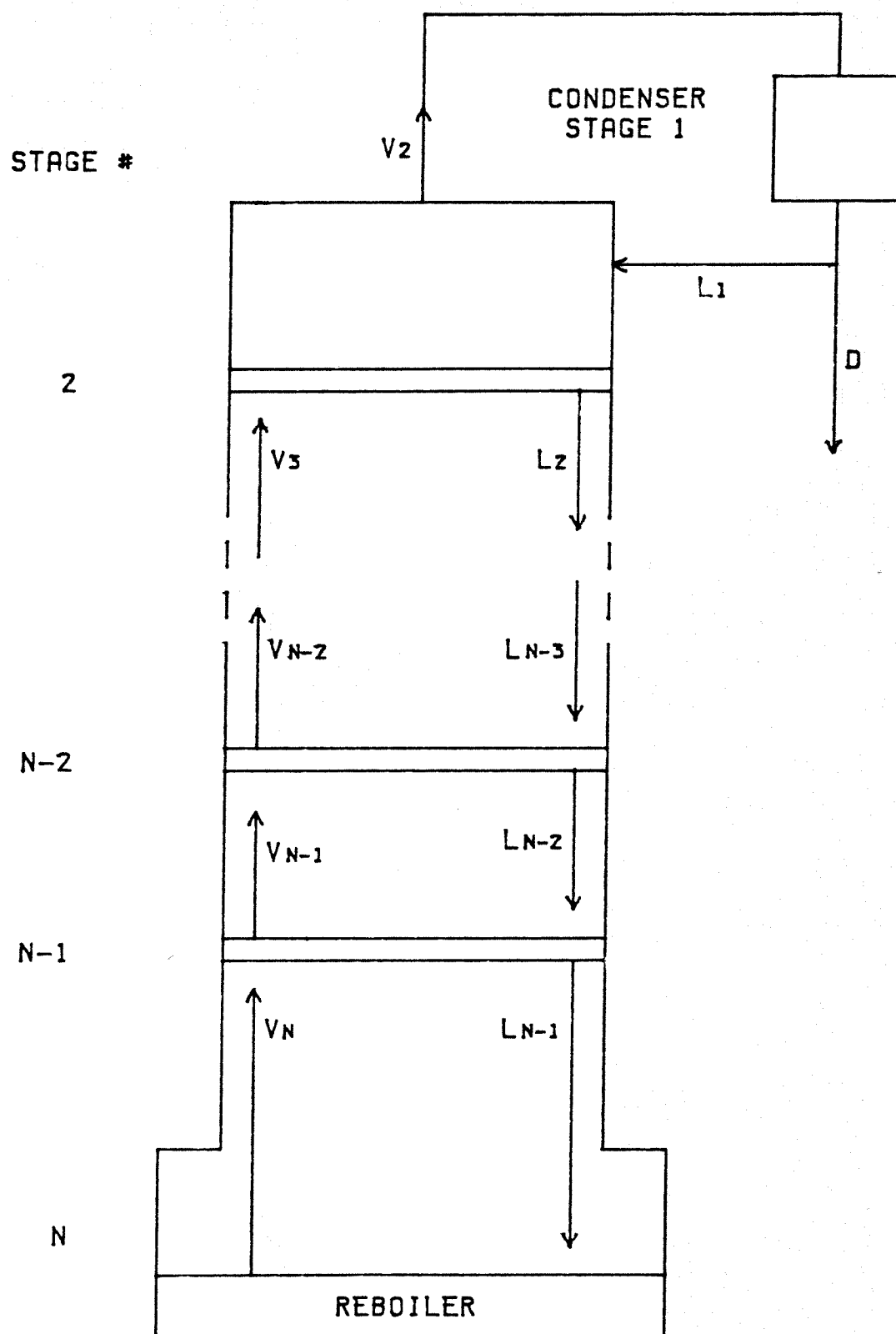
FIG. 1

stage. The equations used to model a typical tray, the condenser, and the reboiler follow.

1.1 General Tray

A tray is any stage in the column except the condenser and the reboiler. The typical tray has a material balance and an equilibrium relationship for each component. Also it has an energy balance, a liquid and vapor flow rate constraint, a vapor mole fraction summation, and an inventory balance.

1.1.1 Componential Material Balance

$$L_{n-1}x_{i,n-1} - L_n x_{i,n} - V_n y_{i,n} + V_{n+1} y_{i,n+1} = 0 \qquad (1-1)$$

This equation is simply a statement of the fact that the componential flow of material entering a stage must equal the componential flow of material leaving a stage at steady-state conditions. There is a componential material balance for each component.

1.1.2 Equilibrium Relationship

$$y_{i,n} - E_{i,n} K_{i,n} x_{i,n} - (1 - E_{i,n}) y_{i,n+1} = 0 \qquad (1-2)$$

This equation provides the relationship between the liquid and vapor mole fractions. There is an equilibrium relationship for each component. $E_{i,n}$ is the Murphree efficiency which is given by the following equation:

$$E_{i,n} = (y_{i,n} - y_{i,n+1})/(y_{i,n}^* - y_{i,n+1}) \qquad (1-3)$$

$K_{i,n}$ is the vapor-liquid equilibrium constant which is given by the relationship:

$$K_{i,n} = y_{i,n}^*/x_{i,n} \qquad (1-4)$$

1.1.3 Energy Balance

$$L_{n-1}h_{n-1} - L_n h_n - V_n H_n + Q_n + V_{n+1}H_{n+1} = 0 \qquad (1-5)$$

The energy balance equation states that there is no net accumulation of energy on a tray at steady-state.

1.1.4 Flow Rate Constraint

$$-L_n + V_{n+1} = 0 \qquad (1-6)$$

At steady-state the flow of liquid from stage n must equal the flow of vapor from stage n+1. The above relationship is obtained by writing a material balance around one end of the column under the condition D = 0.

1.1.5 Summation of the Vapor Mole Fractions

$$\sum_i y_{i,n} - 1 = 0 \qquad (1-7)$$

The summation of the vapor mole fractions must be equal to 1. The companion sum equation is redundant.

1.1.6 Inventory Balance

$$U_n \sum_i x_{i,n}\omega_{i,n} - G_n = 0 \qquad (1-8)$$

In the model a constant volumetric hold-up, G_n, is specified for each tray.

1.2 Condenser

The equations used to describe the condenser are similar in many respects to the equations used to describe the typical tray. The main difference is that there is no liquid flow into the condenser and vapor flow leaving the condenser. A listing of the equations used follows, along with pertinent comments.

1.2.1 Condenser Componential Material Balance (one per component)

$$-L_1 x_{i,1} + V_2 y_{i,2} = 0 \qquad (1-9)$$

1.2.2 Condenser Equilibrium Relationship (one per component)

$$y_{i,1} - K_{i,1} x_{i,1} = 0 \qquad (1-10)$$

1.2.3 Vapor Flow Constraint on Condenser

$$V_1 = 0 \qquad (1-11)$$

The vapor flow constraint replaces the energy balance.

1.2.4 Flow Constraint on Condenser

$$-L_1 + V_2 = 0 \qquad (1-12)$$

1.2.5 Summation of the Vapor Mole Fractions for the Condenser

$$\sum_i y_{i,1} - 1 = 0 \qquad (1-13)$$

1.2.6 Inventory Balance for Condenser

$$U_1 \sum_i x_{i,1} \omega_{i,1} - G_1 = 0 \qquad (1-14)$$

A constant volumetric hold-up, G_1 is specified for the condenser.

1.3 Reboiler

The reboiler is also different from the typical tray. There is no liquid flow from and vapor flow to the reboiler. The equations used to describe the reboiler follow.

1.3.1 Overall Componential Inventory Balance

$$F z_i - \sum_n U_n x_{i,n} = 0 \qquad (1-15)$$

An overall componential inventory balance replaces each componential material balance. It takes into account the

fact that the amount of each component in the column must be a constant at steady-state.

1.3.2 Reboiler Equilibrium Relationship

$$y_{i,N} - K_{i,N}x_{i,N} = 0 \qquad (1-16)$$

1.3.3 Reboiler Energy Balance

$$L_{N-1}h_{N-1} - V_N H_N + Q_N = 0 \qquad (1-17)$$

1.3.4 Summation of the Liquid Mole Fractions for the Reboiler

$$\sum_i x_{i,N} - 1 = 0 \qquad (1-18)$$

1.3.5 Summation of the Vapor Mole Fractions for the Reboiler

$$\sum_i y_{i,N} - 1 = 0 \qquad (1-19)$$

1.3.6 Liquid Flow Constraint on the Reboiler

$$L_n = 0 \qquad (1-20)$$

This constraint replaces the inventory balance for the reboiler.

1.4 Steady-State Model and Variable Assumptions

In the steady-state mathematical model a number of assumptions were made. The first assumption is that of constant heat input to the reboiler. Actually this could vary during the operation of the column. The reasons for this are twofold. The temperature of the material in the sump will rise over time as the column becomes richer in higher boiling components. This will result in reduced heat transfer over time due to the reduced temperature difference between the material in the sump and the heat source. Also the effective heat transfer area may decrease over time as the volume of material in the sump decreases. This is

characteristic of using a jacketed vessel as a still pot or reboiler.

The second assumption is that of constant heat loss from each tray. This parameter would depend on the temperature, flow rates, and composition on the tray. The column characteristics would also play a part. An educated guess must be made of the approximate heat loss or experimental measurements taken on the column in question to generate these values. However, for insulated columns the total heat loss from the trays is usually relatively small and thus does not greatly affect the operation of the column.

The third assumption is that of a constant Murphree efficiency for a component on a particular stage. Column construction and plate type have an effect on the Murphree efficiency. It is also affected by the viscosity of the material on the tray which is strong function of temperature and composition, both which will vary with time. Experimental measurements of the temperature and composition may be needed in order to choose acceptable values for the Murphree efficiencies.

The fourth assumption is that all the hold-up on a stage is in the liquid phase. This is a good assumption at the relatively low pressures a batch column usually operates at. The low density of the vapor makes its hold-up negligible when compared to that of the liquid.

CHAPTER 2

PROCEDURE USED TO SOLVE THE STEADY-STATE SOLUTION

The Newton-Raphson method is used to solve the steady-state solution. First the variables are initialized and then the iterative procedure to solve the linearized equations is employed.

The column variables are initialized before every cut. The initialization procedure provides reasonable estimates of the variables, i.e. $x_{i,n}$, $y_{i,n}$, T_n, L_n, V_n, and U_n. Values of these variables must be close to the actual values in order to assure convergence.

2.1 Initialization Procedure

The initialization procedure assumes no molar hold-up on any tray in the column when calculating the compositional and temperature profiles. In other words, all the material is assumed to be in the sump. This assumption is reasonable since the actual hold-up on the trays and condenser is usually only a small percentage of the total inventory. Using this assumption the initialization procedure generates the mole fractions and temperatures. The initialization procedure for a particular tray is as follows.

1. Bubble point calculations are executed by using subroutine BUBPT. This routine obtains the estimated vapor mole fractions and temperature of the tray. It should be noted that the liquid mole fractions on stage n equal the vapor mole fractions of stage n+1 for a column at the total reflux

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steady-state condition because the passing streams,
L_n and V_{n+1}, must be equal.

2. An energy balance is used to determine L_n and V_{n+1}.
As stated earlier these two flows are equal at
total reflux.

3. At the completion of steps 1 and 2 for all the
stages, an approximate molar inventory is
calculated for each stage using the temperatures
and compositions calculated in step 1.

It should be noted that after the first cut the
initialization procedure does not calculate new mole
fractions or molar inventories, just new temperatures and
flow rates. The reason for this is that a change in the
column parameters should not have a great effect on the
compositional profile and molar inventories in the column.
However a change in the pressure and the heat input can have
a large effect on the temperature profile and the flow
rates.

2.2 Discrepancy Equations

In order to solve the complex set of equations by using
a Newton-Raphson method the equations are put in the form of
discrepancy equations, $f_n = 0$, and then linearized. The
linearized discrepancy equation is really a first order
Taylor series approximation of the function. The following
is an example of an equation with two independent variables
written as a first order Taylor series.

$$f(x,y) = f(x_0,y_0) + (\partial f/\partial x)(x-x_0) + (\partial f/\partial y)(y-y_0) \quad (2-1)$$

All of the equations used to model the total reflux steady-state column are structured so that they equal zero. If this was the case for the above equation it could be written as a discrepancy equation.

$$(\partial f/\partial x)\ \Delta x\ +\ (\partial f/\partial y)\ \Delta y\ =\ -f(x_0, y_0)\ =\ 0 \qquad (2\text{-}2)$$

See Tables 1,2, and 3 for the listing of the equations in this form.

2.3 The Newton-Raphson Method

Shown below is an example of how the discrepancy equations would be set-up in three separate matrices, X, Y, and Z, and how the solution would be arrived at.

Example:

    2 equations: f(x,y) and g(x,y)
    2 unknowns: x and y
    XY = Z

$$
\underset{X}{\begin{vmatrix} (\partial f/\partial x) & (\partial f/\partial y) \\ (\partial g/\partial x) & (\partial g/\partial y) \end{vmatrix}}
\cdot
\underset{Y}{\begin{vmatrix} \Delta x \\ \Delta y \end{vmatrix}}
=
\underset{Z}{\begin{vmatrix} -f \\ -g \end{vmatrix}}
$$

The objective is to solve for the variables x and y. The procedure for the above system is as follows.

1. Make an initial guess of x and y, i.e. x_0 and y_0, (m, trial counter/iteration number, = 0).

2. Calculate the partial derivatives, $f(x_m, y_m)$, and $g(x_m, y_m)$. X, a square matrix, and Z, a columnar matrix, can now be formed.

3. Convert X into an identity matrix. Usually this will be accomplished by multiplying X by its inverse. Also multiply Z by the inverse of X. At

TABLE 1

DISCREPANCY EQUATIONS FOR A TRAY

1. Componential Material Balance

$$L_{n-1}^0 \Delta x_{i,n} + x_{i,n-1}^0 \Delta L_{n-1} \qquad (A-1)$$

$$- L_n^0 \Delta x_{i,n} - x_{i,n}^0 \Delta L_n$$

$$- V_n^0 \Delta y_{i,n} - y_{i,n}^0 \Delta V_n$$

$$+ V_{n+1}^0 \Delta y_{i,n+1} + y_{i,n+1}^0 \Delta V_{n+1}$$

$$= -L_{n-1}^0 x_{i,n-1}^0 + L_n^0 x_{i,n}^0 + V_n^0 y_{i,n}^0 - V_{n+1}^0 y_{i,n+1}^0 = 0$$

2. Componential Equilibrium Relationship

$$-E_{i,n} K_{i,n}^0 \Delta x_{i,n} \qquad (A-2)$$

$$- E_{i,n} x_{i,n}^0 \sum_k (\partial K_{i,n} / \partial x_{k,n}) \Delta x_{k,n}$$

$$+ \Delta y_{i,n} - E_{i,n} x_{i,n}^0 \sum_k (\partial K_{i,n} / \partial y_{k,n}) \Delta y_{k,n}$$

$$- E_{i,n} x_{i,n}^0 (\partial K_{i,n} / \partial T_n) \Delta T_n$$

$$- (1 - E_{i,n}) \Delta y_{i,n+1}$$

$$= -y_{i,n}^0 + (1 - E_{i,n}) y_{i,n+1}^0 + E_{i,n} K_{i,n}^0 x_{i,n}^0 = 0$$

3. Energy Balance

$$L_{n-1}^0 ((\partial h_{n-1} / \partial T_{n-1}) \Delta T_{n-1} \qquad (A-3)$$

$$+ \sum_k (\partial h_{n-1} / \partial x_{k,n-1}) \Delta x_{k,n-1})$$

$$+ h_{n-1}^0 \Delta L_{n-1} - h_n^0 \Delta L_n - H_n^0 \Delta V_n$$

$$+ (-L_n^0 (\partial h_n / \partial T_n) - V_n^0 (\partial H_n / \partial T_n)) \Delta T_n$$

$$- L_n^0 \sum_k (\partial h_n / \partial x_{k,n}) \Delta x_{k,n}$$

$$- V_n^0 \sum_k (\partial H_n / \partial y_{k,n}) \Delta y_{k,n}$$

$$+ V_{n+1}^0 ((\partial H_{n+1} / \partial T_{n+1}) \Delta T_{n+1}$$

$$+ \sum_k (\partial H_{n+1} / \partial y_{k,n+1}) \Delta y_{k,n+1})$$

$$+ H_{n+1}^0 \Delta V_{n+1}$$

$$= -L_{n-1}^0 h_{n-1}^0 + L_n^0 h_n^0 + V_n^0 H_n^0$$

$$- V_{n+1}^0 H_{n+1}^0 - Q_n = 0$$

TABLE 1
(Continued)

4. <u>Liquid and Vapor Flow Constraint</u>

$$-\Delta L_n + \Delta V_{n+1} = 0 \qquad (A-4)$$

5. <u>Summation of the Vapor Mole Fractions</u>

$$\sum_i \Delta y_{i,n} = 1 - \sum_i y_{i,n}^0 = 0 \qquad (A-5)$$

6. <u>Inventory Balance</u>

$$\sum_i x_{i,n}^0 \omega_{i,n}^0 \, \Delta U_n \qquad (A-6)$$

$$+ \sum_i U_n^0 \omega_{i,n}^0 \, \Delta x_{i,n}$$

$$+ U_n^0 \sum_i x_{i,n}^0 (\partial \omega_{i,n}/\partial T_n) \, \Delta T_n$$

$$= G_n - U_n^0 \sum_i x_{i,n}^0 \omega_{i,n}^0 = 0$$

TABLE 2

DISCREPANCY EQUATIONS FOR CONDENSER

1. **Componential Material Balance**

$$-L_1^0 \Delta x_{i,1} - x_{i,1}^0 \Delta L_1 + V_2^0 \Delta y_{i,2} + y_{i,2}^0 \Delta V_2 \qquad (A-7)$$

$$= L_1^0 x_{i,1}^0 - V_2^0 y_{i,2}^0 = 0$$

2. **Componential Equilibrium Relationship**

$$-K_{i,1}^0 \Delta x_{i,1} - x_{i,1}^0 \sum_k (\partial K_{i,1}/\partial x_{k,1}) \Delta x_{k,1} \qquad (A-8)$$

$$+ \Delta y_{i,1} - x_{i,1}^0 \sum_k (\partial K_{i,1}/\partial y_{k,1}) \Delta y_{k,1}$$

$$- x_{i,1}^0 (\partial K_{i,n}/\partial T_1) \Delta T_1$$

$$= -y_{i,1}^0 + K_{i,1}^0 x_{i,1}^0 = 0$$

3. **Vapor Flow Constraint**

$$\Delta V_1 = 0 \qquad (A-9)$$

4. **Liquid and Vapor Flow Constraint**

$$-\Delta L_1 + \Delta V_2 = 0 \qquad (A-10)$$

5. **Summation of the Vapor Mole Fractions**

$$\sum_i \Delta y_{i,1} = 1 - \sum_i y_{i,1}^0 = 0 \qquad (A-11)$$

6. **Inventory Balance**

$$\sum_i x_{i,1}^0 \omega_{i,1}^0 \Delta U_1 \qquad (A-12)$$

$$+ \sum_i U_1^0 \omega_{i,1}^0 \Delta x_{i,1}$$

$$+ U_1^0 \sum_i x_{i,1}^0 (\partial \omega_{i,1}/\partial T_1) \Delta T_1$$

$$= G_1 - U_1^0 \sum_i x_{i,1}^0 \omega_{i,1}^0 = 0$$

TABLE 3

DISCREPANCY EQUATIONS FOR REBOILER

1. **Overall Inventory Balance**

$$-\sum_n U_n^0 \Delta x_{i,N} - \sum_n x_{i,n}^0 \Delta U_N \qquad (A-13)$$

$$= -F^0 z_i^0 + \sum_n U_n^0 x_{i,n}^0 = 0$$

2. **Componential Equilibrium Relationship**

$$-K_{i,N}^0 \Delta x_{i,N} - x_{i,N}^0 \sum_k (\partial K_{i,N}/\partial x_{k,N}) \, \Delta x_{k,N} \qquad (A-14)$$

$$+ \Delta y_{i,N} - x_{i,N}^0 \sum_k (\partial K_{i,N}/\partial y_{k,N}) \, \Delta y_{k,N}$$

$$- x_{i,N}^0 (\partial K_{i,n}/\partial T_N) \, \Delta T_N$$

$$= -y_{i,N}^0 + K_{i,N}^0 x_{i,N}^0 = 0$$

3. **Energy Balance**

$$L_{N-1}^0 ((\partial h_{N-1}/\partial T_{N-1})\Delta T_{N-1} \qquad (A-15)$$

$$+ \sum_i (\partial h_{N-1}/\partial x_{i,N-1})\Delta x_{i,N-1})$$

$$+ h_{N-1}^0 \Delta L_{N-1}$$

$$- V_N^0 ((\partial H_N/\partial T_N)\Delta T_N + \sum_i (\partial H_N/\partial y_{i,N})\Delta y_{i,N})$$

$$- H_N^0 \Delta V_N$$

$$= -Q_N - L_{N-1}^0 h_{N-1}^0 + V_N^0 H_N^0 = 0$$

4. **Summation of the Liquid Mole Fractions**

$$\sum_i \Delta x_{i,N} = 1 - \sum_i x_{i,N}^0 = 0 \qquad (A-16)$$

5. **Summation of the Vapor Mole Fractions**

$$\sum_i \Delta y_{i,N} = 1 - \sum_i y_{i,N}^0 = 0 \qquad (A-17)$$

6. **Liquid Flow Constraint**

$$\Delta L_N = 0 \qquad (A-18)$$

this point Y = Z since X is an identity matrix.
(Note that Y need not be formed since it has
symbolic representation only, nor X multiplied by
its inverse because it yields the identity matrix.)

4.   The Δ's, variable corrections, contained in Z are
added to their respective variables, i.e. $x_{m+1} = x_m$
+ Δx and $y_{m+1} = y_m + \Delta y$. The counter m is then
incremented by one.

5.   If the Δ's have values below the convergence
criteria then the solutions for the variables x and
y are assumed to be found. If the convergence
criteria are not met then the process is repeated
by returning to step 2.

2.4 Structure of Matrix of Derivatives

A diagram of the structures of X, along with Y and Z is
given in Fig 2. X consists of a number of submatrices, A_m,
B_m, C_m, and J_m. Every row of submatrices in matrix X
contains the discrepancy equations used for that stage.
Each submatrix is a square matrix consisting of 2*NC+4 rows
and columns. Matrix X is also a square matrix. The total
number of entries in X is $(N*(2*NC+4))^2$.

2.5 Procedure to Obtain the Steady-State Solution

As the number of trays and components increases the
number of entries in matrix X become very large. To store
matrix X, obtain its inverse, and then multiply its inverse
by matrix Z in order to obtain the Δ's would reflect
inefficient use of memory and a time consuming procedure to

OVERALL STRUCTURE OF LINEARIZED EQUATIONS
(6 STAGES)

STAGE

	X							Y		Z
1	B_1	C_1						$\triangle$'s		R_1
2	A_1	B_2	C_2					$\triangle$'s		R_2
3		A_2	B_3	C_3			$\cdot$	$\triangle$'s	$=$	R_3
4			A_3	B_4	C_4			$\triangle$'s		R_4
5				A_4	B_5	C_5		$\triangle$'s		R_5
6	J_1	J_2	J_3	J_4	J_5	J_6		$\triangle$'s		R_6
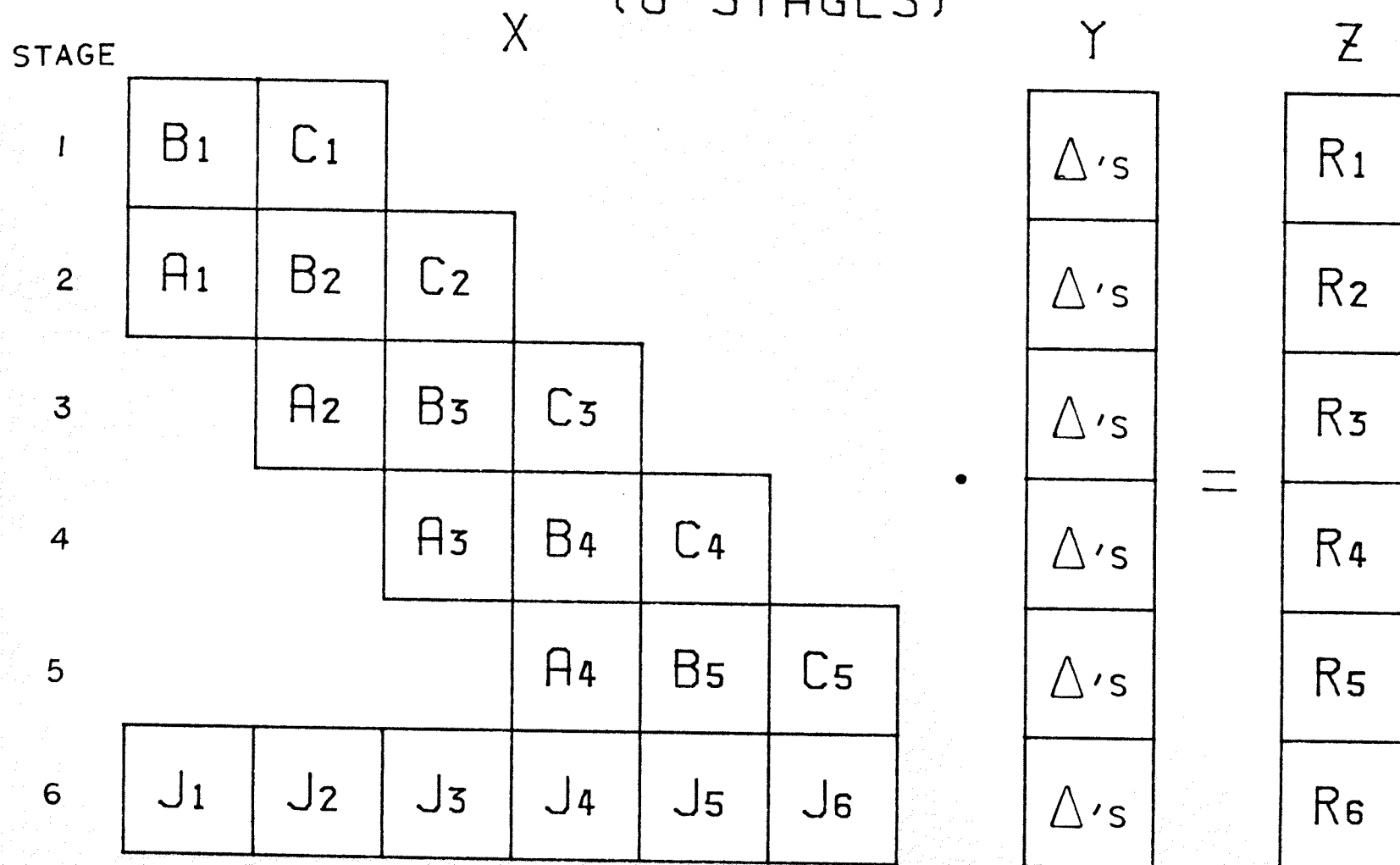
FIG. 2

solve the linear set of equations. Therefore a decomposition procedure is employed.

The problem is to convert X into an identity matrix without inverting X all at once. It can be seen from Fig. 2 that X is a sparse matrix. Any entry that is outside of the defined submatrices is zero. X can be manipulated into an identity matrix in a structured fashion. Z will then contain the variable corrections. Fig. 3 - 9 are the flowcharts of BATCHSTIL of which Fig. 8 contains the process above. (The FORTRAN code for BATCHSTIL can be obtained from Dr. E. C. Roche.) Notice that the procedure needs to store only one A_m, one B_m, and two J_m's along with all of the C_m's and R_m's at any one time.

BATCH DISTILLATION
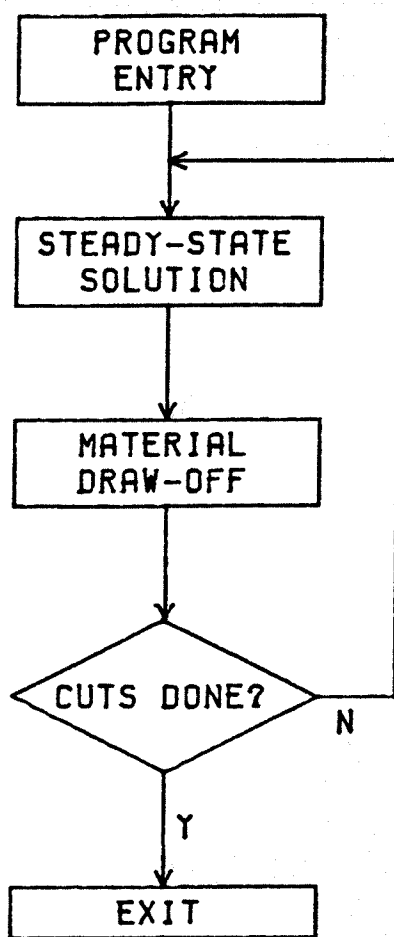
FIG. 3

PROGRAM ENTRY
LEVEL 2

```
          │
          ▼
   ┌──────────────┐
   │    START     │
   └──────────────┘
          │
          ▼
   ┌──────────────┐
   │    INPUT     │
   │ COMPONENTIAL │
   │     DATA     │
   └──────────────┘
          │
          ▼
   ┌──────────────┐
   │ INPUT COLUMN │
   │  PARAMETERS  │
   └──────────────┘
          │
          ▼
```
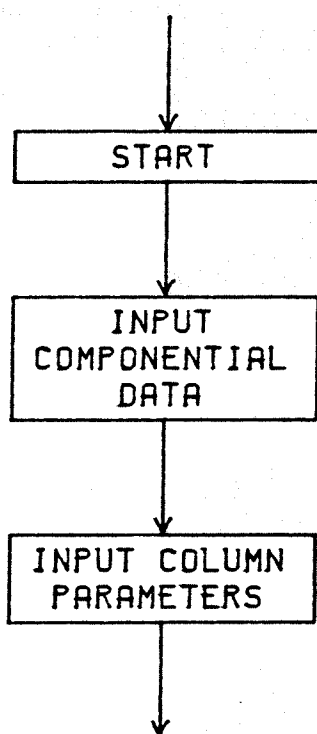
FIG. 4

STEADY-STATE SOLUTION
LEVEL 2

N

NEW CUT?

Y

CHANGE
COLUMN
PARAMETERS

INITIALIZE
VARIABLES

SOLVE FOR
VARIABLES
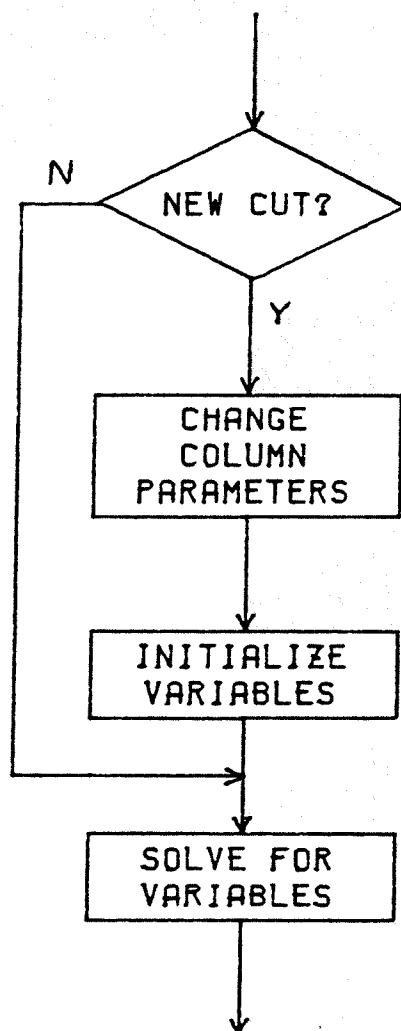
FIG. 5

INITIALIZE VARIABLES
LEVEL 3
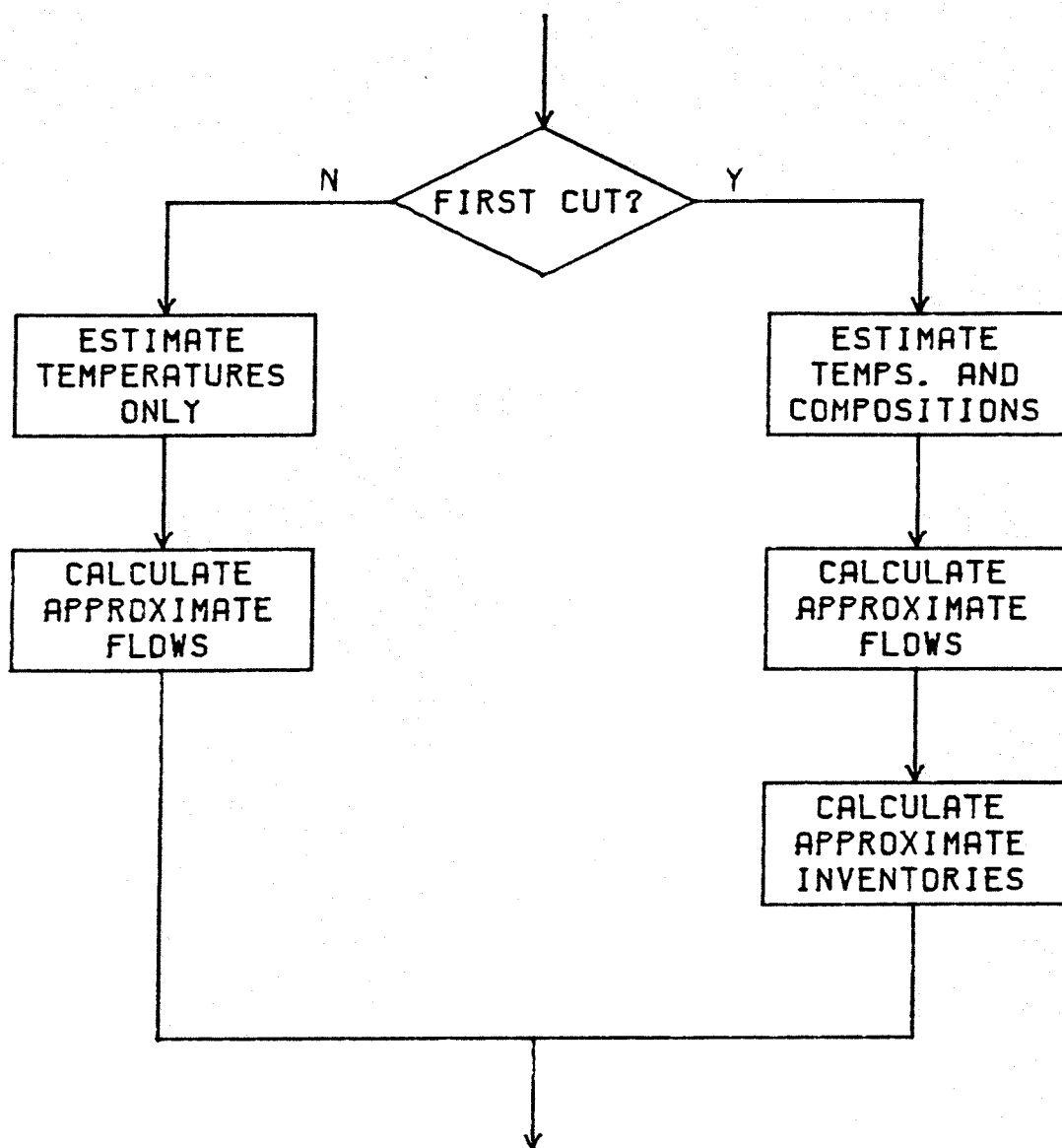
FIG. 6

SOLVE FOR VARIABLES
LEVEL 3
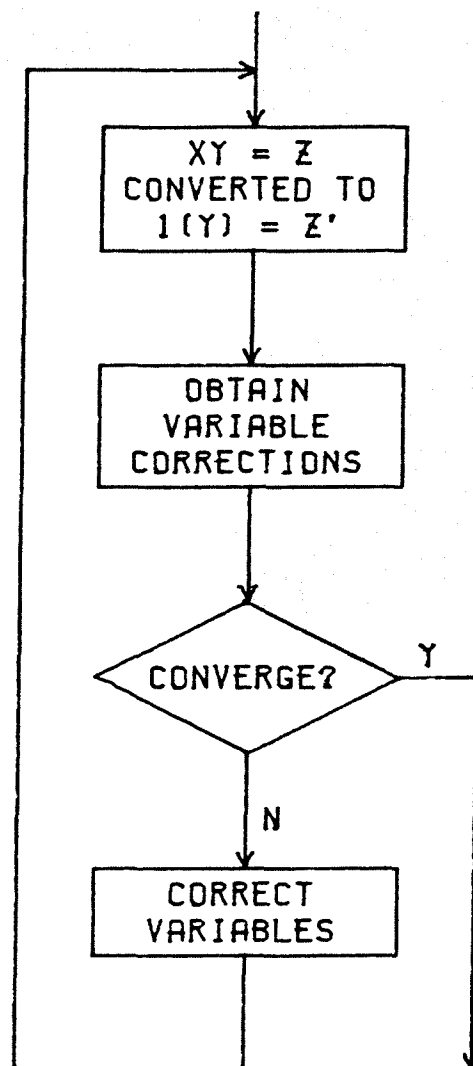
FIG. 7

XY=Z CONVERTED TO 1(Y)=Z'
LEVEL 4
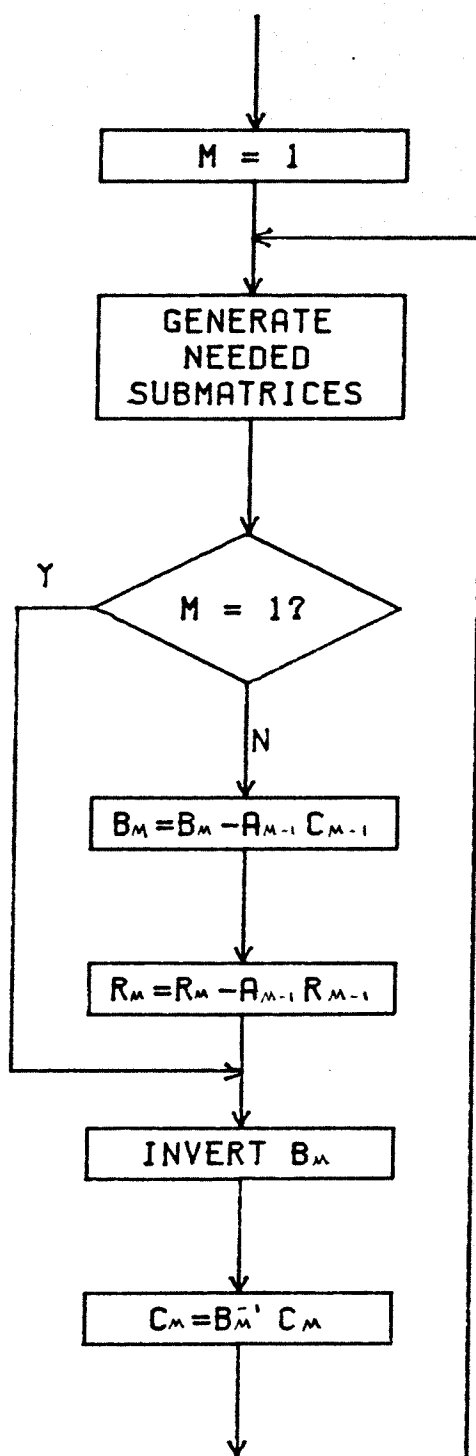
M = 1

GENERATE
NEEDED
SUBMATRICES

M = 1?

Y

N

$B_M = B_M - A_{M-1} C_{M-1}$

$R_M = R_M - A_{M-1} R_{M-1}$

INVERT B_M

$C_M = B_M^{-1} C_M$

FIG.8

XY=Z CONVERTED TO 1(Y)=Z'
(CONTINUED)
LEVEL 4

$$R_M = B_{\bar{M}}^{-1} R_M$$

$$J_{M+1} = J_{M+1} - J_M C_M$$

$$M = N - 1?$$

$$M = M + 1$$

INVERT J_N

$$R_N = J_N^{-1} R_N$$

FIG. 8

XY=Z CONVERTED TO 1(Y)=Z'
(CONTINUED)
LEVEL 4

$$R_M = R_M - C_M R_{M+1}$$

M = 1?

Y

N

M = M − 1
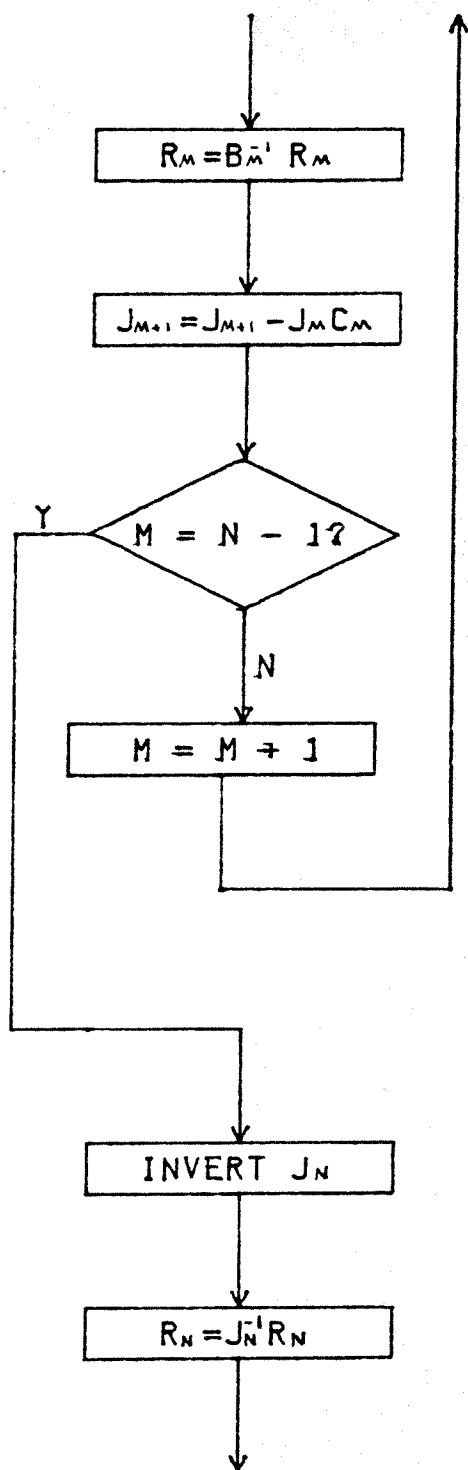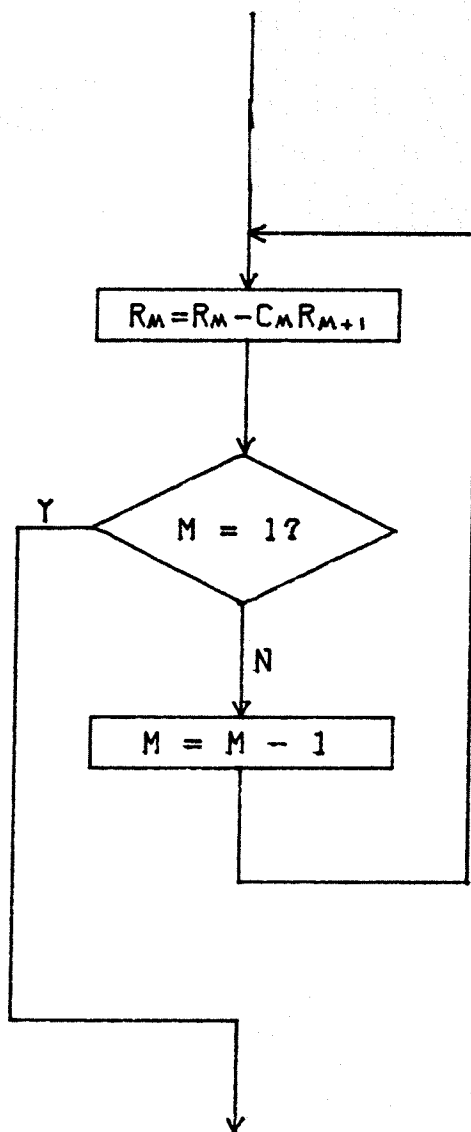
FIG. 8

GENERATE NEEDED SUBMATRICES
LEVEL 5
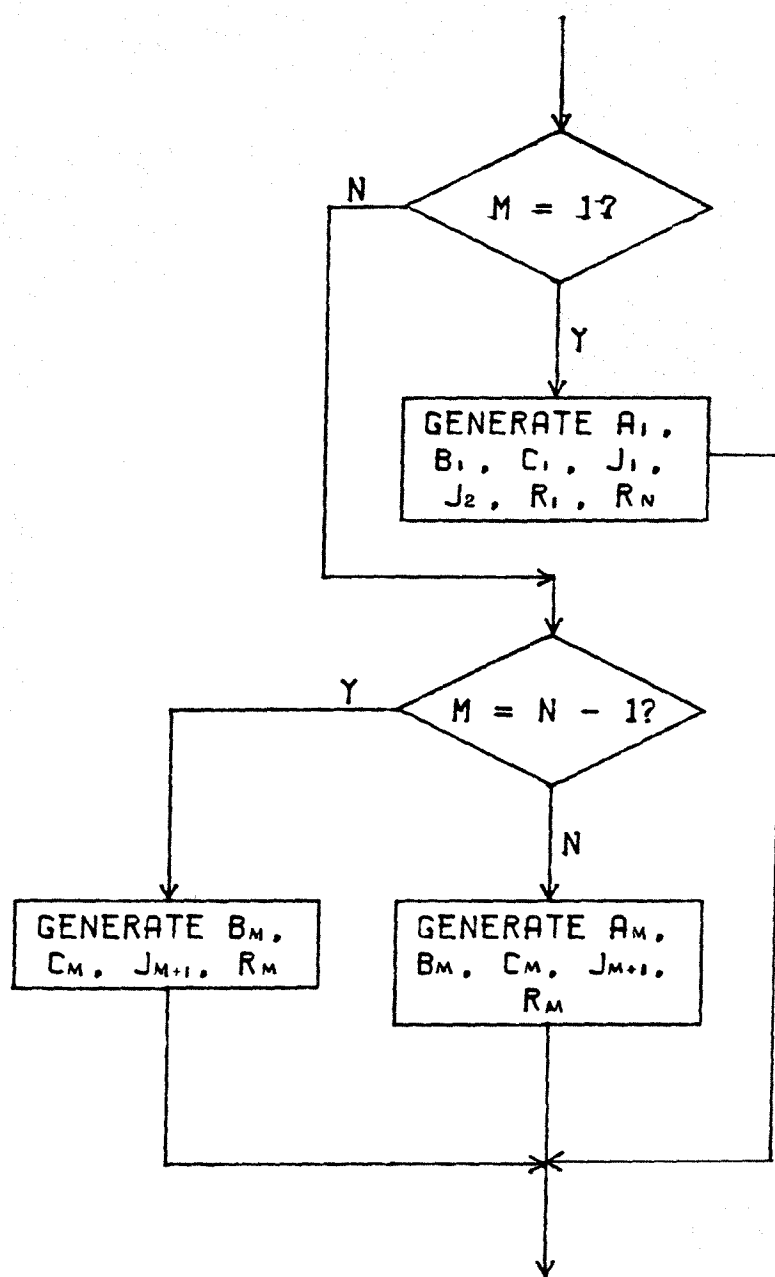
FIG. 9

CHAPTER 3

PRODUCT WITHDRAWAL FROM THE COLUMN

Material is withdrawn from the column as a series of cuts. A cut is defined as a product draw-off from the column at fixed column parameters which include the reflux ratio, the heat input, pressure and pressure drop, and the draw-off rate. It is completed when the product withdrawn has met the specifications for the cut. After a cut has been completed the column conditions and product specifications can be changed for the next cut.

3.1 Specifications for Cuts

There are three types of specifications that are used to determine the end of a cut. The first is a total molar withdrawal specification. The cut is finished when a set molar amount of product has been withdrawn from the column during the cut. The second type of specification possible is that of minimum composition. For example, if the minimum compositional requirement of a specified component is 30 mole %, product will continue to be withdrawn until the mole percent of the total material withdrawal for the cut has reached above 30 mole %. The third type of specification that can be used is the one of maximum composition. For example, if the maximum compositional requirement of a specified component is 5 mole %, product will continue to be withdrawn until the mole percent of the total material withdrawal for that cut has fallen below 5 %.

3.2 Cuts

A single cut is actually made up of a series of small product withdrawals. A small amount of material is taken from the column in each product withdrawal and a new steady-state condition is calculated. The product withdrawn during a product withdrawal is assumed to be at the composition of the condenser reached in the previous steady-state calculation. The time duration of a product withdrawal is only 2 - 5 seconds so the column loadings are not disrupted. This process continues until the cut is completed. The column is not reinitialized after a product withdrawal. Since column parameters such as pressure and heat input are specified as constants during a cut the values for the column variables calculated previous to the product withdrawal are excellent starting points for the Newton-Raphson method used to calculate the steady-state condition. The column typically computationally re-equilibrates in two-three iterations.

The quantity of material taken by and the timing of a product withdrawal is a function of three column parameters that are specified for each cut, the reflux ratio, (RR); the withdrawal rate, (DRATE); and the time increment, (DTIME). The reflux ratio is defined as the time at total reflux : the time on total product withdrawal. The withdrawal rate is defined as the molar flow rate of distillate during a product withdrawal. The time increment is defined as the amount of time that product is withdrawn from the column

during a product withdrawal. Normally the time increment will be from two to five seconds.

The amount of time between the start of product withdrawals, TBLCUTTIME, is given by the following relation.

$$TBLCUTTIME = (RR+1) * DTIME \qquad (3-1)$$

The amount of product withdrawn in a product withdrawal is given by this equation.

$$DMOLE = DRATE * DTIME \qquad (3-2)$$

3.3 Assumptions Used in Material Draw-Off

There are a number of assumptions made in this withdrawal model. The first assumption is that the system actually has enough time to reach a steady-state condition after each product withdrawal. The number of moles removed with a product withdrawal would certainly be a factor here. The more product taken from the column the longer it will take to regain a steady-state condition. Thus the values of RR, DRATE, and DTIME are factors which would effect the validity of this assumption. As seen in equation (3-1) an increase in RR would increase the time between cuts and thus increase the validity of the assumption that the system attains a steady-state total reflux condition between product withdrawals. An increase in DRATE, as seen in equation (3-2), will increase the amount of product withdrawn which makes it more difficult for the column to reach steady-state before the next product withdrawal. The last possible factor is DTIME. Increasing DTIME has two conflicting effects on the ability of the column to reach a

steady-state condition. It increases the length of time between product withdrawal, but also proportionally increases the size of a product withdrawal. Since RR and DRATE are usually specified operating parameters, it is difficult to control the error in this assumption. However, it has been shown that batch stills reach equilibrium in a relatively short time after material draw-off.

Another assumption of the model is that during withdrawal periods the composition of the material withdrawn is assumed to be constant. Actually the composition of the material withdrawn would vary over the withdrawal period. Assuming DRATE to be specified, DTIME can be lowered to a value to make the change in the composition of the product negligible over this period. However, a lower DTIME will mean the computer time used for the cut will be increased. For example, if DTIME is halved, approximately twice as many steady-state solutions will have to be found for that cut. The solving of the steady-state solution is by far the most time consuming procedure in the program. The time taken for a simulation can approximately double.

The fact that the product withdrawn during a product withdrawal is assumed to be a constant at the composition of the condenser calculated in the previous steady-state calculation brings in another problem. It is possible to withdraw more of a component than the total inventory of that component in the column. If the product withdrawn amounts to more material than what is in the condenser the

above can happen. The code takes this into account and adjusts the withdrawal so the amount of that component removed is only the column inventory value of that component.

It is also possible, due to the method of material withdrawal, withdrawing product periodically rather than continuously, that the specifications may not be met exactly on target. For example, suppose each periodic withdrawal size was 1.5 moles. Suppose the specification was for 50 moles total product and 49.5 moles have been taken so far. The next withdrawal would put that value at 51 moles. However, the program adjusts it withdrawal size in order to eliminate this problem.

CHAPTER 4

THERMODYNAMICS

The thermodynamic functions that are important in a distillation process are enthalpies and vapor-liquid equilibrium constants as well their respective derivatives. It is subroutine KFAC which calculates these values.

4.1 Enthalpy

The liquid molar enthalpy of a stage is calculated by the following equation.

$$h_n = \sum_i x_{i,n} \int CPL_i \, dT_n + \Delta h_{mix} \qquad (4-1)$$

This value is obtained by calling subroutine LIQENP. Δh_{mix}, the liquid heat of mixing, is calculated by thermodynamic routines called by LIQENP. The vapor enthalpy of a stage is given by the following equation.

$$H_n = \sum_i y_{i,n} \left(\int CPV_i \, dT_n + \Delta H_{vap,i} \right) + \Delta H_{pres} \qquad (4-2)$$

The value for the vapor enthalpy is obtained in VAPENP. ΔH_{pres}, the vapor enthalpy pressure correction, is obtained by calling thermodynamic routines from VAPENP. The thermodynamic routines chosen to calculate ΔH_{pres} depend on the equation of state chosen to model the vapor phase.

4.2 Enthalpy Derivatives

The enthalpy is a function of three variables, composition, temperature, and pressure.

$$dh_n = (\partial h_n / \partial x_{i,n}) dx_{i,n} + (\partial h_n / \partial T_n) dT_n + (\partial h_n / \partial P_n) dP_n \qquad (4-3)$$

$$dH_n = (\partial H_n / \partial y_{i,n}) dy_{i,n} + (\partial H_n / \partial T_n) dT_n + (\partial H_n / \partial P_n) dP_n \qquad (4-4)$$

The partial derivatives with respect to pressure are zero because each stage operates at a fixed pressure.

$(\partial h_n / \partial x_{i,n})$ and $(\partial H_n / \partial y_{i,n})$ are given by the following two equations.

$$(\partial h_n / \partial x_{i,n}) = \int CPL_i \, dT_n + (\partial \Delta h_{mix} / \partial x_{i,n}) \qquad (4-5)$$

$$(\partial H_n / \partial y_{i,n}) = \int CPV_i \, dT_n + \Delta H_{vap,i} \qquad (4-6)$$
$$+ (\partial \Delta H_{pres} / \partial y_{i,n})$$

$(\partial h_n / \partial T_n)$ and $(\partial H_n / \partial T_n)$ are given by the following relationships.

$$(\partial h_n / \partial T_n) = \sum_i x_{i,n} CPL_i(T_n) + (\partial \Delta h_{mix} / \partial T_n) \qquad (4-7)$$

$$(\partial H_n / \partial T_n) = \sum_i y_{i,n} CPV_i(T_n) + (\partial \Delta H_{pres} / \partial T_n) \qquad (4-8)$$

4.3 Vapor-Liquid Equilibrium Constants

The equilibrium constants are calculated by the following formula.

$$K_{i,n} = \frac{VP_{i,n} \, \gamma_{i,n} \, \sigma^S_{i,n} \, PE_{i,n}}{\sigma_{i,n} \, P_n} \qquad (4-8)$$

The vapor pressure is calculated by a six constant Antoine Equation.

$$VP_{i,n} = \exp(A_i - B_i / (T_n + C_i) + D_i \ln(T_n) + E_i T_n + F_i T_n^2) \qquad (4-10)$$

The activity coefficient, $\gamma_{i,n}$, is calculated by thermodynamic routines according to the liquid phase model that is selected.

The term $PE_{i,n} \, \sigma^S_{i,n} / \sigma_{i,n}$ is calculated as a lumped parameter which is called $FUG_{i,n}$. $FUG_{i,n}$ is evaluated using an equation of state and the definition of the component type.

4.4 Derivatives of Equilibrium Constants

The vapor-liquid equilibrium constant is a function of two parameters: composition and temperature.

$$dK_{i,n} = (\partial K_{i,n}/\partial x_{i,n})dx_{i,n} + (\partial K_{i,n}/\partial y_{i,n})dy_{i,n} \qquad (4-11)$$
$$+ (\partial K_{i,n}/\partial T_n)dT_n$$

Referring to equation (4-9), only $\gamma_{i,n}$ is significantly affected by a change in liquid composition at low pressures. Therefore the partial derivative with respect to $x_{i,n}$ is located in the activity coefficient.

$$(\partial K_{i,n}/\partial x_{j,n}) = \frac{VP_{i,n}\ FUG_{i,n}}{P_n} \qquad (4-12)$$
$$* \frac{(\gamma_{i,n}(x_{j,n}+\Delta x_{j,n}) - \gamma_{i,n}(x_{j,n}))}{\Delta x_{j,n}}$$

A change in the vapor composition only effects the lumped fugacity coefficient, $FUG_{i,n}$, to a significant extent. The forthcoming equation calculates the partial derivative of $K_{i,n}$ with respect to the vapor composition.

$$(\partial K_{i,n}/\partial y_{j,n}) = \frac{VP_{i,n}\ \gamma_{i,n}}{P_n} \qquad (4-13)$$
$$* \frac{(FUG_{i,n}(y_{j,n}+\Delta y_{j,n}) - FUG(y_{j,n}))}{\Delta y_{j,n}}$$

$(\partial K_{i,n}/\partial T_n)$ is obtained from the following equation.

$$(\partial K_{i,n}/\partial T_n) = K_{i,n}(\partial \ln(VP)_{i,n}/\partial T_n) \qquad (4-14)$$
$$+ \frac{VP_{i,n}\ FUG_{i,n}}{P_n} \frac{(\gamma_{i,n}(T_n+\Delta T_n) - \gamma_{i,n}(T_n))}{\Delta T_n}$$
$$+ \frac{VP_{i,n}\ \gamma_{i,n}}{P_n} \frac{(FUG_{i,n}(T_n+\Delta T_n) - FUG_{i,n}(T_n))}{\Delta T_n}$$

CHAPTER 5

INPUT-OUTPUT

5.1 Input

The program data consists of the componential thermodynamic data and the column specifications. Subroutine CDATA handles the bulk of the componential thermodynamic data while INPUT handles the column specifications.

Free format is used for all numeric data. An explanation of the input and the options available are contained in Appendix A.

5.2 Output

The following discusses what output is obtained from the simulation. All of the column parameters are summarized. The flow rates and the liquid composition of each stage are listed before the start of a cut. For every incremental withdrawal the composition and the molar amount are listed. Also, the temperature profile and the accumulation of the withdrawals for a given cut are listed.

The componential data and the maximum errors for every iteration can be displayed if LDBUG is set equal to 1.

CHAPTER 6

RESULTS AND CONCLUSION

6.1 Simulation of a Quaternary System

The results of BATCHSTIL for the quaternary system of para-dichlorobenzene, (p-DCB); ortho-dichlorobenzene, (o-DCB); 1,2,4-trichlorobenzene, (TCB(124)); and 1,2,4,5-tetrachlorobenzene, (TCB(1245)); were compared to the results of an earlier program written by E. C. Roche on the same system. BATCHSTIL specifies a temperature dependent componential liquid density and a constant volumetric hold-up for each tray and the condenser. Roche's program specifies a constant molar hold-up or inventory for each tray and the condenser. This constant molar inventory program was used to verify the newly developed simulation program (BATCHSTIL) where the tray inventory is constant volume.

To accomodate the verification, the input data to BATCHSTIL was structured to give constant molar hold-up. The relationship for constant volumetric hold-up is given in equation (1-8). If $\omega_{i,n}$ is set equal to 1, equation (1-8) reduces to the following:

$$U_n \sum_i x_{i,n} - G_n = 0 \qquad (6-1)$$

If G_n is redefined as the molar hold-up, then equation (6-1) specifies a constant molar hold-up.

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To make $\omega_{i,n}$ equal to 1, both W_i and $\rho_{i,n}$ are set equal to one.

$$\omega_{i,n} = W_i/\rho_{i,n} = 1 \qquad (6-2)$$

Equation (1-8) thus reduces to equation (6-1).

With this input data definition, the programs' are identical, as seen by Table 4 which summarizes the results of the chlorinated benzene simulation.

6.2   Simulation of a Non-Ideal Binary System

Two simulations of the highly non-ideal acetonitrile — water system were also done. This system forms a low boiling azeotrope at an acetonitrile liquid mole fraction of 0.69 at 1 atmosphere. Fig. 10 contains the equilibrium data. The first simulation started off with a charge composition of 36.4 mole % acetonitrile. As expected, the azeotrope was formed at the top of the column. The product remained at the azeotropic composition until the acetonitrile inventory in the column was depleted. When all of the acetonitrile was removed, the column conditions were those of pure water. The second simulation started with a charge compositon of 86.4 mole % acetonitrile. This put the charge on the 'other side' of the azeotrope. Again the product was the azeotrope. After all of the water had been removed, as the azeotrope, the percent of acetonitrile in the product dramatically increased. With all the water removed the column contained only acetonitrile. The results for these two simulations appear in Fig. 11 and 12.

TABLE 4

COMPARISON OF RESULTS OF A QUATERNARY SYSTEM

1st Cut — 48.00 moles total product, 12.66 hr. of operation

Component	(Roche) Mole Fraction	(BATCHSTIL) Mole Fraction
p-DCB	0.1999978	0.2000035
o-DCB	0.8000019	0.7999961
TCB(124)	0.0000000	0.0000000
TCB(1245)	0.0000000	0.0000000

2nd Cut — 137.54 moles total product, 4.20 hr. of operation

Component	(Roche) Mole Fraction	(BATCHSTIL) Mole Fraction
p-DCB	0.0018338	0.0018322
o-DCB	0.9980707	0.9980723
TCB(124)	0.0000953	0.0000953
TCB(1245)	0.0000000	0.0000000

3rd Cut — 38.80 moles total product, 1.34 hr. of operation

Component	(Roche) Mole Fraction	(BATCHSTIL) Mole Fraction
p-DCB	0.0000000	0.0000000
o-DCB	0.0000000	0.0000000
TCB(124)	1.0000000	1.0000000
TCB(1245)	0.0000000	0.0000000

(Note: All compared cuts were under similar operating conditions.)

ACETONITRILE(1) VS. WATER(2)
EQUILIBRIUM DATA
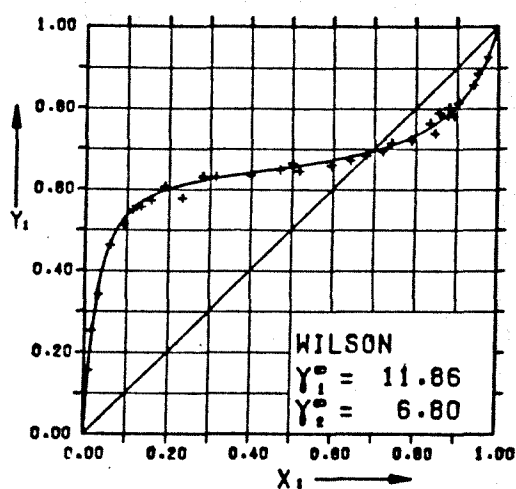
(DECHEMA)

FIG.10

OVERHEAD COMPOSITION AND TEMPERATURE VS. TIME
(CHARGE - 34.6 MOLE% ACETONITRILE)
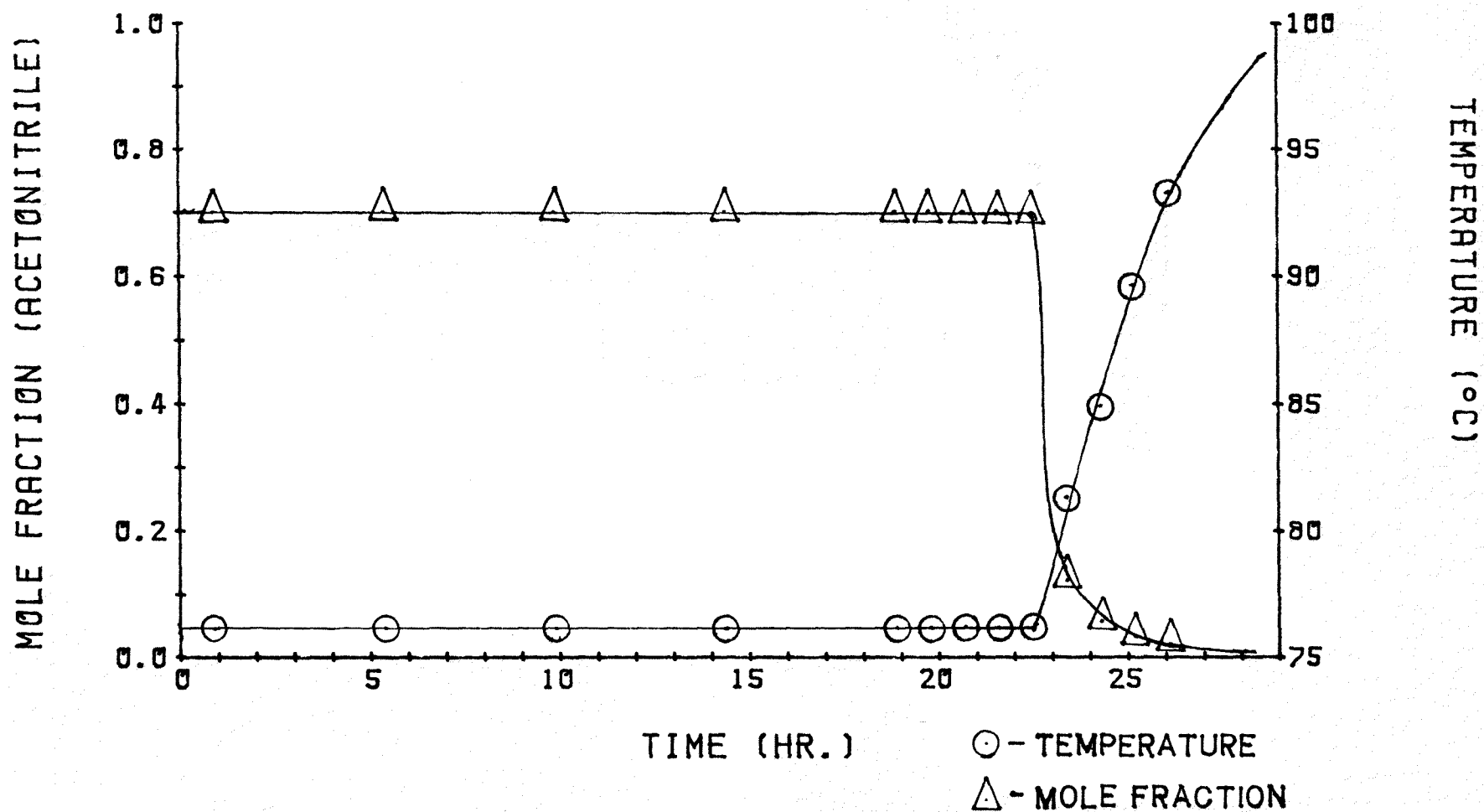
FIG.11

OVERHEAD COMPOSITION AND TEMPERATURE VS. TIME
(CHARGE — 86.4 MOLE% ACETONITRILE)
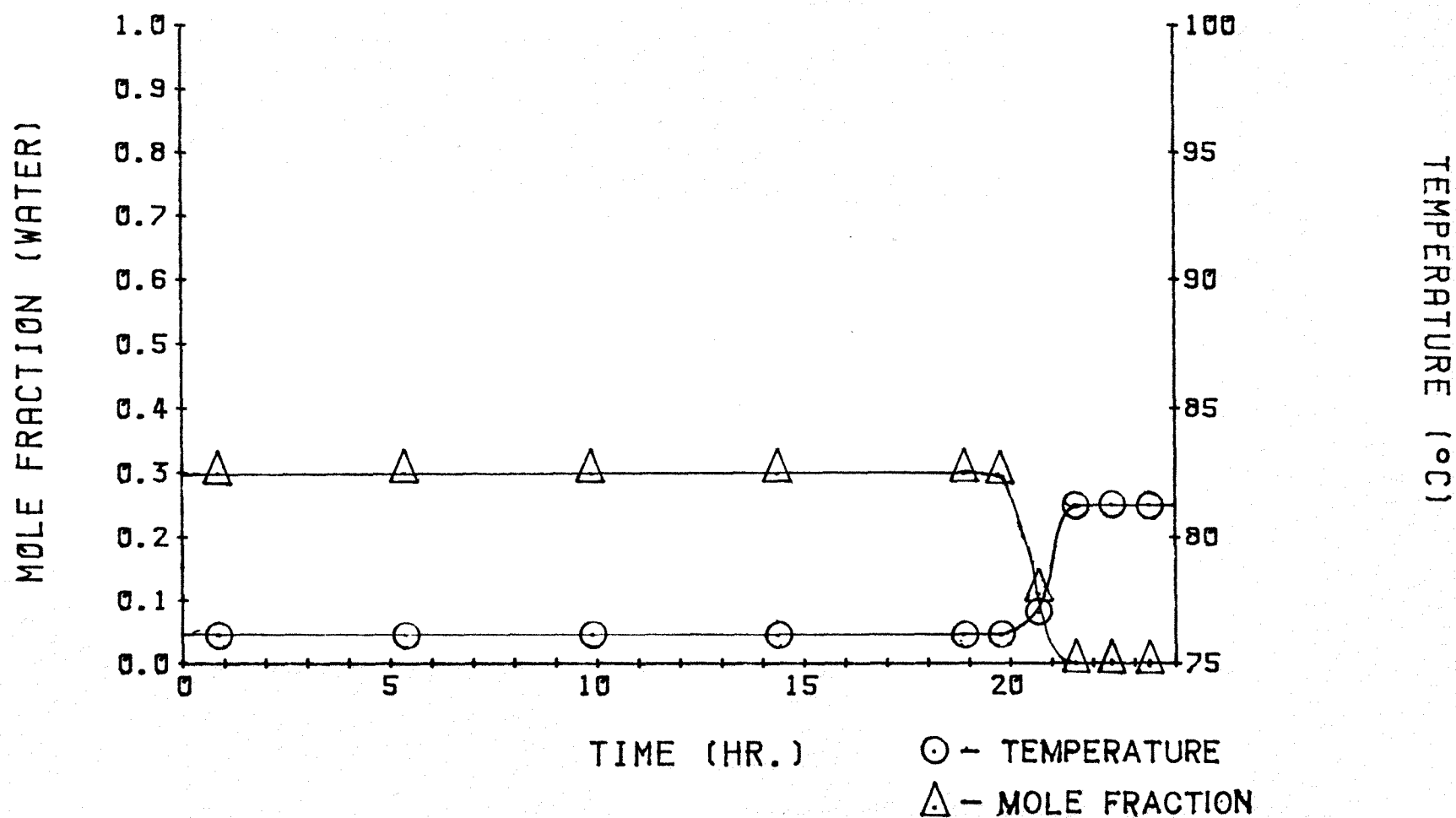
FIG. 12

CHAPTER 7

RECOMMENDATIONS

7.1 Model Assumptions

There are a number of assumptions in the model which can be checked.

7.1.1 Start-up Problem

In BATCHSTIL the start-up problem was ignored. The column was assumed to be at a total reflux steady-state condition at time zero. Obtaining the time the column would need to come to steady-state after the start-up would be valuable in many situations.

7.1.2 Steady-State Condition

In the model it is assumed that before every product withdrawal the column is at a steady-state condition. To check this assumption the transients should be tracked over time.

7.1.3 Product Withdrawal

Every product withdrawal is assumed to have the product withdrawn at the composition of the condenser given by the immediately previous steady-state calculation. Actually the composition would vary over the withdrawal period. The time dependence of the distillate during product withdrawal should be looked into.

7.2 Possible Additions

There are a number of possible additions to BATCHSTIL which would increase its versatility.

7.2.1   Vapor-Liquid-Liquid Equilibria

There are a wide variety of systems which are immiscible in certain concentration ranges. Conditions in which vapor-liquid-liquid equilibria exist can thus appear in the column. The ability to take this into account would increase BATCHSTIL's applicability to a much wider range of systems.

7.2.2   Reactions

The ability to account for vapor phase dimerization as well as liquid phase reactions in the column would also increase BATCHSTIL's versatility.

7.2.3   Lumping Componential Parameters

A number of common systems have a large number of components. Such systems would use a large amount of computer time and memory in a simulation. Lumping componential parameters would help alleviate this problem.

APPENDIX A

DATA INPUT

DATA INPUT

The input to the program is given by the following structure. The data can be viewed as being presented in two segments: Thermodynamic data and Process Data. The components are ordered sequentially in the input data, i.e. component #1, component #2, component #3, ...

I. Title

1. Title of the simulation — upto 80 characters

II. Componential and Thermodynamic Data

2. NC, IDLL, IDLV, IDH, LDBUG, 6*0

(Note that the 0's in the above line reference data for unused variables. The program reads in data using subroutines START and CDATA which were supplied by Dr. E. C. Roche. A number of the input variables were not needed for batch column simulations. In the above line 11 parameters were to be read, but only the first five were needed.) These are all integer values used to specify the options chosen.

NC is the total number of components in the system. It must be a number between 1 and 10 inclusive.

IDLL determines the choice of the activity

coefficient model.

     0 - Ideal

     3 - Wilson

     4 - NRTL

     5 - UNIQUAC

     6 - UNIQUAC ... modified

     7 - UNIFAC

IDLV determines which equation of state is to be used

to describe the vapor phase.

     0 - Ideal

     1 - Virial ... Hayden - O'Connell Correlation

     2 - Virial ... Tsonopoulos' Correlation

     3 - Redlich-Kwong

IDH determines what phases are to be corrected for the

heat of mixing.

     0 - Correct both phases

     1 - Correct vapor phase only

     2 - No Correction

LDBUG determines what is output.

     0 - Printout of initial
        conditions and results

     1 - In addition, the
        componential data is
        printed and the
        maximum errors for
        each iteration.

3.   Pure component data ... one set of 8 records per component. m signifies the component number and n is used to reference polynomial coefficients.

a.   ZNAME(m) contains the names of the components. They are input starting with component #1. A name should be no longer than 8 characters. Each name should be on a separate line and start in column 1.

b.   L(m), W(m), TNBP(m), TC(m), PC(m), VC(m), ZC(m), VOL(m), OMEGA(m)

L(m) is the component type.

-1 - Non-volatile

0 - Non-condensible

1 - Normal

2 - Supercritical

W(m) is the molecular weight ... g per g-mole.

TNBP(m) is the normal boiling point ... deg K.

TC(m) is the critical temperature ... deg K.

PC(m) is the critical pressure ... atm.

VC(m) is the critical volume ... cc per g-mole.

ZC(m) is the critical compressibility factor.

VOL(m) is the molar volume at some reference temperature ... cc per g-mole

OMEGA(m) is the Pitzer accentric factor

c.   OA(m), OB(m), R(m), Q(m), QP(m), AVAL(m), BVAL(m), ZRA(m)

OA(m) and OB(m) are the Redlich-Kwong parameters

R(m), Q(m), and QP(m) are UNIQUAC parameters

R(m) - Volume ... molecular volume

Q(m) - Surface Area ... molecular area

QP(m) - Interaction area ... molecular area

AVAL(m) and BVAL(m) are the Tsonopoulos' parameters for the virial equation.

ZRA(m) is the Racket parameter.

d.   RD(m), DMU(m), ETA(m)

RD(m) is the radius of gyration ... Angstroms

DMU(m) is the dipole moment ... Debyes

ETA(m) is the association parameter

e.   HVAP(m), TREF(m)

HVAP(m) is the heat of vaporization ... cal. per g

TREF(m) is the reference temperature for HVAP(m) ... deg K

f.   CPL(m,n)

> CPL(m,n) are the liquid heat capacity coefficients ... cal per g per deg K. (Note: n = 1 to 4 which corresponds to the coefficients a, b, c, and d for the liquid heat capacity)
> The form of the liquid heat capacity is as follows:

$$CP_i(T) = a + bT + cT^2 + dT^3$$

g.   CPV(m,n)

> CPV(m,n) are the vapor heat capacity coefficients ... cal per g-mole per deg K. (Note: n = 1 to 4 which corresponds to the coefficients a, b, c, and d for the vapor heat capacity.)
> The form of the vapor heat capacity is as follows:

$$CP_i(T) = a + bT + cT^2 + dT^3$$

h.   ANT(m,n)

> ANT(m,n) are the vapor pressure coefficients for a six constant Antoine equation ... atm. (Note: n = 1 to 6 which corresponds to the coefficients a, b, c, d, e, and f for Antoine's equation.)
> The form of Antoine's equation is as follows:

$$ln(P_n) = a - b/(T_n+c) + dln(T_n) + eT_n + fT_n^2$$

4.   Thermodynamic Data/Option

If the Hayden-O'Connell or the Tsonopoulos version of the virial equation is used then the characteristic binary constants must be defined, i.e AK(1,1), AK(1,2), AK(1,3) ... , AK(NC,NC).

5. Activity Coefficient Parameters

The Wilson, NRTL, and UNIQUAC activity coefficient parameters are entered in the temperature dependent form. (Only entered if the above equations are used.)

$$\lambda_{ij} = A_{ij} + B_{ij}T$$

Examples of the input scheme are listed.

a. Binary interaction parameters

    Two component system
    A12 B12 A21 B21

    Three component system
    A12 B12 A21 B21 A13 B13 A31 B31
    A23 B23 A32 B32

    Four component system
    A12 B12 A21 B21 A13 B13 A31 B31
    A14 B14 A41 B41 A23 B23 A32 B32
    A24 B24 A42 B42 A34 B34 A43 B43

    Five component system
    A12 B12 A21 B21 A13 B13 A31 B31
    A14 B14 A41 B41 A15 B15 A51 B51
    A23 B23 A32 B32 A24 B24 A42 B42
    A25 B25 A52 B52 A34 B34 A43 B43
    A35 B35 A53 B53 A45 B45 A54 B54

b. If the NRTL equation is used then α_{ij} must be supplied. (Only enter if the NRTL equation is used.)

    Two component system
    A12

    Three component system
    A12 A13 A23

    Four component system
    A12 A13 A14 A23 A24 A34

    Five component system
    A12 A13 A14 A15 A23 A24 A25 A34
    A35 A45

6. Liquid Density Data ... Temperature Dependent

    The following is additional physical data required by the batch simulation column. This data is defined by subprogram LIQVOL ... accessed directly by the executive program, BATCHSTIL.

    a. NVOL(m) is the number of liquid density versus temperature data points that are available for each component. These are input starting with component #1.

    b. TVOL(m,n) contains the temperature half of the liquid density versus temperature (K) data. Starting with the first component all the temperatures are input for that component. The next component is input next and so on.

        Example

        TVOL(1,1), TVOL(1,2), ... TVOL(1,NVOL(1)), TVOL(2,1), ... , TVOL(NC,NVOL(NC))

    c. CVOL(m,n) contains the liquid density (g/cc.) half of the liquid density versus temperature data. It is input in a similar manner to TVOL.

II.   Process Data

1.   NTT, KODE, NOSET

NTT   is the number of trays. Note that this number excludes the condenser and the reboiler. Also it cannot be greater than 48.

KODE determines whether the condenser heat duty or the reboiler heat duty is specified

1 - condenser duty specified

2 - reboiler duty specified

NOSET is the number of cuts that are made during a run. The maximum number of cuts is 10.

2.   IMURPH and IQSTAGE are code parameters which describe the Murphree efficiency and heat loss variations in the column.

IMURPH = 0, then all the trays are ideal stages and no values are input.

IMURPH = 1, then the Murphree efficiency varies only with the component, not with the tray. NC values of Murphree efficiency are input starting with component #1.

IMURPH = 2, then the Murphree efficiency varies only with the trays. N-2 values are input starting at the first tray, i.e. second stage. Notice that no values are input for the condenser or the reboiler.

IMURPH = 3, then the Murphree efficiency varies with the component and the tray. (N-2)*NC values are input. They are input in the following order.

E(m,n)   m th component

            n th tray

E(1,1), E(2,1), E(3,1), ...

IQSTAGE = 1, the trays are adiabatic, no input.

IQSTAGE = 2, all the trays have the same heat loss, only this value is input.

IQSTAGE = 3, the trays have differing heat losses, a value is input for each tray, i.e. N - 2 values.

3.   The Murphree efficiencies, E(j,i), are next to be input. What is input depends on IMURPH.

4. The following are product withdrawal process operating parameters and product specifications.

ZXP(m), ZXDP(m), ZDRATE(m), ZRR(m), ZTEMP2(m), ZDTIME(m), ZZMU(m), ZTOTCT(m), ZQQ(m), ZNCNC(m), ZUNIT(m), ZVALUE(m), ZMNMX(m)

The above are column parameters and specifications for each cut, where m is the cut number. The number of cuts is given by NOSET.

ZXP(m) - Condenser pressure ... atm

ZXDP(m) - Pressure drop per stage ... atm

ZDRATE(m) - draw-off rate ... moles per hr.

ZRR(m) - reflux ratio, time at total reflux : time on product withdrawal

ZTEMP2(m) - column top temperature limit ... deg K

ZDTIME(m) - numerical time step ... hrs.

ZZMU(m) - predictor corrector weighting factor ... not used

ZTOTCT(m) - total amount of draw-off per cut ... moles

ZQQ(m) - specified heat load ... cal per hr. (Depends on the value of KODE).

Specifications:

ZNCNC(m) - component # of the component that has a minimum or maximum product specification.

ZUNIT(m) - units of the specification

        1 - moles

        2 - weight

        3 - volume

ZVALUE(m) - value of specifications in %

ZMNMX(m) - specification status

        0 - no specification

        1 - minimum specification

        2 - maximum specification

5. QSTAGE(n) is defined depending on the value of IQSTAGE. (n - stage #)

6. TBOT is the initial guess of the reboiler temperature.

7. CHARGE is the initial charge to the still in g-moles.

8. F(m) is the initial componential charge input to the still in g-moles, F(1), F(2), F(3), ..., F(NC).

9. GSTAGE(n) contains the volume inventory of each stage except the reboiler. Its values are input starting with the condenser and continuing down to the last tray.

      GSTAGE(1), GSTAGE(2), ... GSTAGE(N-1)

10. ZCONVT, ZCONVF, ZCONVU, ZCONXY

These are the temperature, flow rate, inventory, and mole fraction convergence criteria respectively.

ZCONVT – temperature convergence tolerance ... deg K
        (default – 0.001)

ZCONVF – flow rate convergence tolerance for internal streams ... delta flow/flow
        (default – 0.001)

ZCONVU – molar inventory convergence tolerance ... delta inventory/inventory
        (default – 0.001)

ZCONXY – mole fraction convergence tolerance
        (default – 0.00001)

APPENDIX B

NOMENCLATURE

NOMENCLATURE

A_m - Submatrix of X

B_m - Submatrix of X

C_m - Submatrix of X

$CPL_{i,n}$ - Liquid heat capacity of component i on stage n ... cal. per g-mole per deg K

$CPV_{i,n}$ - Vapor heat capacity of component i on stage n ... cal. per g-mole per deg K

D   - Distillate flow

DMOLE - G-moles removed during a given product withdrawal

DRATE - Flow rate of distillate during product withdrawal

DTIME - Time lapse of a given product withdrawal

$E_{i,n}$ - Murphree efficiency of component i on stage n.

F_i - Total column inventory of component i at a given time ... g-moles

$FUG_{i,n}$ - Lumped fugacity coefficient

G_n - Volumetric hold-up on stage n ... cc.

h_n - Liquid enthalpy on stage n ... cal/g-mole

Δh_{mix} - Heat of mixing of liquid ... cal/g-mole

H_n - Vapor enthalpy on stage n ... cal/g-mole

ΔH_{pres} - Vapor enthalpy correction for pressure ... cal. per g-mole

$\Delta H_{vap,i}$ - Heat of vaporization of component i

J_m - Submatrix of X

NOMENCLATURE
(Continued)

$K_{i,n}$ — Equilibrium constant of component i on stage n.

L_n — Liquid flow rate on stage n

N — Total number of stages; also the stage number of the reboiler

NC — Number of components in the system

P_n — Pressure on stage n ... atm.

$PE_{i,n}$ — Poynting Effect, component i, stage n

Q_n — Heat input on stage n ... cal/hr.

R_m — Submatrix of Z

RR — Reflux ratio

TBLCUTTIME — Time between product withdrawals

T_n — Temperature of stage n ... deg K

U_n — Inventory on stage n ... g-moles

V_n — Vapor flow rate on stage n ... g-mol/hr.

$VP_{i,n}$ — Vapor pressure of component i on stage n ... atm.

W_i — Molecular weight of component i

$x_{i,n}$ — Liquid mole fraction of component i on stage n

X — Matrix of partial derivatives

$y_{i,n}$ — Vapor mole fraction of component i on stage n

NOMENCLATURE
(Continued)

$y^*_{i,n}$ – Vapor mole fraction of component i on stage n that would be in equilibrium with $x_{i,n}$

Y – Matrix of variable corrections

z_i – Mole fraction of component i in the column

Z – Matrix containing the right hand side of the discrepancy equations

$\gamma_{i,n}$ – Activity coefficient

$\rho_{i,n}$ – Liquid density ... g/cc.

$\sigma_{i,n}$ – Fugacity coefficient, vapor of component i on stage n

$\sigma^S_{i,n}$ – Fugacity coefficient of saturated liquid of component i on stage n

$\omega_{i,n}$ – Volume of component i on stage n ... cc./g-mole

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