



Optimization of the batch distillation of terpenes  
by Paul Ernest Simacek

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering  
Montana State University  
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Abstract:

Optimization of the operating policy of chemical processes has been desired but not easily obtained. The advent of the modern-day computer and new techniques permit optimization of processes previously too complicated. The optimization method chosen for the study of the batch distillation process' was dynamic programming. The process was evaluated for a system of crude sulfate turpentine. The distillation required 52 theoretical plates to separate the four major terpene chemicals: alpha pinene, beta pinene, delta-3-carene, and dipentene. Crude sulfate turpentine from three pulp mills in the West was evaluated. These mills were of interest since they are the only ones in the United States which produce sulfate turpentine containing the terpene delta-3-carene. These turpentines contain varying amounts of eight terpenes (C<sub>10</sub>H<sub>16</sub> isomers) of which only the four mentioned above are obtainable on commercial sized equipment.

The optimization technique was applied to yield the operating policy guaranteeing the maximum profit per run. The optimum policy consisted of the reflux ratio changes and the purity for the product. The technique was based on distillation data in the form of graphs of purity versus percentage distilled. A mathematical model was evaluated as a method for obtaining the necessary distillation data. The method used was that from Holland's "Unsteady State Processes with Application in Multicomponent Distillation". The simulation was attempted on the UNIVAC 1108 and found to require in excess of 24 minutes execution time for each reflux ratio. The method was found to be too costly for determining distillation data.

Experimental data were obtained on one inch laboratory equipment. These data for each reflux ratio were optimized using the IBM 1620. In order to prove the validity of the relationships used in the optimization scheme, the computer predicted operating policy was followed on pilot plant equipment. These verification runs checked within two percent deviation from the predicted values. All the results were within the accuracy of the equipment and the relationships used in optimization were proved to follow with accepted accuracy. Thus it was proven that a batch distillation system too complicated to simulate can be optimized efficiently using experimental data and the method developed.

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## ABSTRACT

Optimization of the operating policy of chemical processes has been desired but not easily obtained. The advent of the modern-day computer and new techniques permit optimization of processes previously too complicated. The optimization method chosen for the study of the batch distillation process was dynamic programming. The process was evaluated for a system of crude sulfate turpentine. The distillation required 52 theoretical plates to separate the four major terpene chemicals: alpha pinene, beta pinene, delta-3-carene, and dipentene. Crude sulfate turpentine from three pulp mills in the West was evaluated. These mills were of interest since they are the only ones in the United States which produce sulfate turpentine containing the terpene delta-3-carene. These turpentines contain varying amounts of eight terpenes ( $C_{10}H_{16}$  isomers) of which only the four mentioned above are obtainable on commercial sized equipment.

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Experimental data were obtained on one inch laboratory equipment. These data for each reflux ratio were optimized using the IBM 1620. In order to prove the validity of the relationships used in the optimization scheme, the computer predicted operating policy was followed on pilot plant equipment. These verification runs checked within two percent deviation from the predicted values. All the results were within the accuracy of the equipment and the relationships used in optimization were proved to follow with accepted accuracy.

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## INTRODUCTION

Most chemical engineering plant operations problems have at least several and possibly an infinite number of solutions. Selection of the "best" answer or optimum solution is not a new concept with the engineer. In order to satisfy his curiosity and desire to produce optimally, he has long sought the best way of doing things. However, optimal solutions very often are based on past experience or on intuition.<sup>3</sup>

Optimization theory has developed in direct proportion to the growth of the electronic computer. Now sophisticated mathematical tools are available for calculation of optimum conditions and values of the decision variables. Mathematical techniques for decision making can be broadly classified as either deterministic or probabilistic.<sup>15</sup> In deterministic methods the return is given by specifying values for the decision variable. There are no uncontrollable or random variables. On the other hand, probabilistic models contain random variables whose values are given by a probability distribution. The definition of the return or net profit for a batch distillation enables only the deterministic approach to be considered.

The most common of the recently developed optimization methods are linear programming, dynamic programming and maximum principle.<sup>4</sup> Linear programming is a technique which was

started during World War II and was well developed in the post-war period. It is specifically applied to a class of problems which are described by a linear objective function and linear non-negative constraints. A fairly universal technique, simplex algorithm, is available for its solution.<sup>8</sup> Dynamic programming was developed by Richard Bellman in the 1950's.<sup>2</sup> This technique converts a multi-decision process into a series of single stage problems, each containing a few variables. It is powerful in treating the optimization of the performance in which the entire procedure can be regarded as a sequence of stages.<sup>4</sup> Maximum principle was first hypothesized by the Russian mathematician Pontryagin in 1956 and like dynamic programming takes advantage of the serial structure of the problem.<sup>8</sup>

Dynamic programming was chosen for this study because it has the ability to handle data (returns and interstage relationships), in either analytical, tabular or graphical form.<sup>14</sup> Thus it is a powerful tool for solution of the optimization of common chemical engineering problems based on either experimental or mathematically modeled data.

Specifically in the application of this technique to batch distillation, a batch of feed stock of given composition and quantity is to be distilled in a given piece of equipment consisting of a reboiler, column and condenser with a reflux unit. Throughout the distillation the reflux ratio can be

varied within the physical limitations of the equipment.<sup>12</sup> When the overhead product stream is collected in a single container the average mole fraction of each component varies with time. The purities or times to empty the contents of the product container are also variables of optimization. The combination of these decision variables were found for a given set of parameters, namely, selling price at various purities.

An important reason for interest in operation optimization is the competition within the chemical process industries that make it necessary to operate at conditions guaranteeing maximum performance. Optimization techniques also enables decisions to be made on firm scientific principles rather than past experience or intuition and thus a better understanding of the process can be obtained.

The feed stock evaluated was crude sulfate turpentine, a by-product from the Kraft sulfate process for pulping wood. This turpentine is the condensed gas from the digesters used in the process. Disposal of turpentine is one of the major problems associated with the Kraft pulp and paper mills. Releasing the gases to the atmosphere results in air pollution. If the turpentine is dumped into rivers or other bodies of water, the sulfur compounds and a mixture of terpene class chemicals have such a high biological oxygen demand that the

water becomes sterile. Increases in pollution restrictions and in interest in individual pure terpene hydro-carbons causes recovery of the crude sulfate turpentine and separation into its individual components to become of greater importance.

The feed stocks evaluated consisted of eight individual terpenes in varying amounts depending on the source of the turpentine. The turpentine was obtained from three pulp mills located in the West.\* These are of interest since their by-product turpentine is the only source within the United States from which the terpene, delta-3-carene can be obtained. There is no commercial facility in the United States for the sole purpose of separating pure delta-3-carene from turpentine mainly because there is no ready market for it, in this country either as a chemical raw material or as an end-product in its pure state. However, there has been considerable research done on the chemistry of delta-3-carene some of which may open the door for commercial utilization in the near future.<sup>5</sup>

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\* Hoerner-Waldorf Paper Products, Co., Missoula, Montana.  
Southwest Forest Industries, Snowflake, Arizona.  
Potlatch Forests, Inc., Lewiston, Idaho.

## RESEARCH OBJECTIVES

The overall objective of this research was to develop a technique in the form of a computer program to determine the optimum operating conditions for the distillation of crude sulfate turpentine. Optimum conditions are defined as those which yield the maximum profit per run for a given set of parameters, selling price at various purities and feed stock composition. The technique was developed in a manner so the operating conditions could be predicted accurately with minimum effort.

The particular turpentines evaluated contain eight individual components and require 52 theoretical plates to obtain the four major terpenes in desirable purities. A mathematical model was evaluated for simulation of this distillation in order to obtain optimization data. Experimentally determined data were also used for this purpose.

The above objectives were realized and optimum conditions were verified on pilot plant equipment.

This research was meant to be both fundamental and applied in nature, with the hope that the technique could be applied in commercial operations.

## EQUIPMENT

### Experimental Distillation Equipment

The distillation column used to obtain the experimental data required for the optimization program was two four-foot sections of glass cylinders of 1.0 inch diameter. To decrease heat loss from the column, the 1.0 inch cylinder was placed inside two glass cylinders of 2.0 and 3.0 inch diameters, respectively. The middle cylinder was wrapped with Nichrome wire as a heating coil. The 1.0 inch inner cylinder was equipped with ground glass joints, ball joints on the bottom and taper joints on the top.

The packing selected for the 1.0 inch inner cylinder was Fenske rings, one-eighth inch stainless steel helices. The column was calibrated with a toluene-methylcyclohexane system and shown to contain 51 theoretical plates.

A Corad head was used to serve the purpose of condensing the overhead product and controlling the desired reflux ratio. A one-liter flask was used for a stillpot for the steam distillation.

Heating equipment for the stillpot and column consisted of heating mantels and Powerstats. A distillation equipment diagram is shown in Figure 1.

### Pilot Plant Distillation Equipment

The distillation column used to verify predicted optimum operating conditions consisted of five ten-foot sections of 8 inch inside diameter mild steel pipe. In order to decrease heat loss from the column, it was insulated with 2 inch Johns-Manville Thermobestos pipe insulation.

The packing selected for this column was one-half inch ceramic Berl saddles. This particular packing was chosen because it has a high-void space (63 percent), resists corrosion and can be readily cleaned by many solvents. Calibration with a toluene-methylcyclohexane system showed that the column contained 52 theoretical plates.

A specially constructed heat exchanger served the dual purpose of condensing the overhead product and establishing the reflux ratio. The condenser consisted of 30, one-and one-half inch tubes within an eighteen inch diameter mild steel shell. The reflux ratio was controlled by the number of tubes from which condensate was collected. Reflux ratios of 30:1, 15:1, 10:1 and 5:1 were used for this study.

The reboiler was constructed in the form of a four-foot diameter stainless tank with a length of four feet. It was heated by a steam coil (24 square feet of heat transfer area). The pressure drop through the column was maintained constant by a Foxboro Stablelog controller.



The sulfur containing compounds<sup>5</sup> in the crude turpentine which pass through the condenser were oxidized in a furnace at a temperature of 2000°F. This method can be used to control the air pollution associated with the distillation of crude sulfate turpentine.

A distillation equipment diagram for the pilot plant is shown in Figure 2.

### Analytical Equipment

The terpene samples taken throughout the entire project were analyzed for percentage composition on an Aerograph gas chromatograph, with a thermal-conductivity detector. This machine was manufactured by the Wilkens Instrument and Research Company. The particular column used for terpene analysis was 20 feet by one-quarter inch stainless steel packed with a stationary phase of 20 percent  $\beta$  -  $\beta'$  oxydiproylnitrite on a 60/80 acid washed chromosorb P support. The chromatograph was operated at 75-80°C with a carrier gas-flow rate of 50-60 cc/min for 1 - 2 microliter samples. Chromatographic peaks were recorded on a Sargent Model SR recorder and the chromatograms were converted into percentage compositions by using a compensating polar planimeter.

### Operating Procedure - Experimental

In obtaining both experimental data for optimization and

data for verification runs, steam distillation of the turpentine charge was used. Since water is immiscible with crude turpentine, the partial pressures of each phase are additive, and the boiling-point of the two phases is less than that of pure water. Therefore, the high-boiling terpenes can be distilled at a boiling point below that of water. Steam distillation prevents decomposition and polymerization of the terpenes.

For the distillations carried out to obtain optimization data, a charge was made up of approximately 500 grams of turpentine plus an equal amount of water. Overhead samples were taken for each two percent by weight of the total charge collected as distillate. These samples were analyzed for composition using the gas chromatograph. This procedure was continued until 85% of the total charge had been distilled. The material remaining in the column was analyzed and denoted as the bottoms product. The data were recorded in graphical form of composition versus percent distilled. These graphs will be referred to as "distillation curves" in the remainder of this report. The values required for the optimization program were the beginnings and ends of each fractionation (percent distilled) which yield the desired average purity. These points are determined by a trial and error procedure with the Planimeter such that the area above the desired purity equals the area below it. This step could have been computerized.

Operating Procedure - Verification Runs

The crude from which the distillation curves had been obtained on the experimental equipment was charged into the pilot plant column. The amount was the same as that used in the optimization program. The pressure drop through the column was maintained at 90 inches of water to insure the constant boil-up rate of 705 pounds per hour-square feet of the 50-50 percent weight mixture of terpene and water.

The column was operated according to the operating schedule which is an output of the optimization program shown in Table XIV, based on the amount of overhead product. The operation of the column consisted of the changing of reflux ratios and product containers. The average purity of each product was determined on the gas chromatograph. This average purity of each fraction was the criterion used for verification of the optimization procedure.

## MATHEMATICAL MODEL

The development of the high speed digital computer has made it practical to determine the dynamic behavior of most industrial processes. In order to determine necessary distillation curves by means other than experimentation, a mathematical model was evaluated for simulation of the system. The first step in determining the dynamic behavior is writing the equations describing the physical phenomena taking place. Most assumptions for continuous columns have been incorporated in batch distillation theory. The complications arising in batch distillations which considerably increase the difficulties in calculations are:

1. Unsteady state -- compositions throughout the column change, as product is withdrawn.
2. Column holdup -- the physical amount of material present in the column has a marked effect on its operation.

In simulation of the packed column, it was broken into the calibrated number of theoretical stages and simulated as a tray column with the efficiency on each plate equal to one. In addition to this assumption, the following well-tested assumptions for continuous columns have been used.<sup>11</sup>

1. The composition of the vapor rising from a given

tray is related to the liquid composition on the tray by a known function.

2. Liquid composition is uniform across a given tray and of the same composition as the liquid flowing to the plate below.
3. Vapor holdup in the column is negligible compared to that of the liquid.
4. The operation is adiabatic, except for heat added to the reboiler and removed by the condenser.
5. A total condenser was used for this distillation.
6. The liquid holdup (molar) on any plate and the condenser is constant (but possibly different for each tray) for the entire distillation.

Under the above assumptions, differential equations for component and total material and an enthalpy balance for each stage (all trays plus reboiler and condenser) are required. These are derived in the following sections.

#### Component Material Balance<sup>9</sup>

$$\int_{t_n}^{t_n + \Delta t} (v_{J+1, i} + l_{J-1, i} - v_{J, i} - l_{J, i}) dt \quad (1)$$

$$= u_{J, i} \Big|_{t_n + \Delta t} - u_{J, i} \Big|_{t_n}$$

This equation can be approximated by the two-point implicit method to yield;

$$[\mu (v_{J+1,i} + l_{J-1,i} - v_{J,i} - l_{J,i}) - (1-\mu)(v_{J+1,i}^0 + l_{J-1,i}^0 - v_{J,i}^0 - l_{J,i}^0)]\Delta t = u_{J,i} - u_{J,i}^0 \quad (2)$$

Holland defines the liquid flow rate in terms of the vapor flow rates by use of the relationship:<sup>6</sup>

$$l_{j,i} = A_{j,i} v_{j,i} \quad (3)$$

where  $A_{j,i}$  is defined as the absorption factor for component  $i$  and plate  $j$ :  $A_{j,i} = L_j / (E_{j,i} K_{j,i} V_j)$  and the liquid hold-ups in terms of vapor flow rates by means

$$u_{j,i} = (U_j / L_j) A_{j,i} v_{j,i} \quad (4)$$

The set of equations describing the entire column is obtained and yields a tri-diagonal matrix:<sup>1</sup> (For definition of terms, see page 150 and Figure 3 for a schematic of a batch distillation system.)

$$\begin{bmatrix} -\rho_{0,i} & 1 & 0 & \cdot & \cdot & 0 \\ A_{0,i} & -\rho_{1,i} & 1 & 0 & \cdot & 0 \\ 0 & A_{1,i} & -\rho_{2,i} & 1 & \cdot & 0 \\ \cdot & & & & & \\ \cdot & & & & & \\ 0 & 0 & 0 & 0 & A_{N,i} & -\rho_{N+1,i} \end{bmatrix} \begin{bmatrix} v_{0,i} \\ v_{1,i} \\ v_{2,i} \\ \cdot \\ \cdot \\ v_{N+1,i} \end{bmatrix} = \begin{bmatrix} -P_{0,i} \\ -P_{1,i} \\ -P_{2,i} \\ \cdot \\ \cdot \\ -P_{N+1,i} \end{bmatrix} \quad (5)$$

or

$$A X = B$$

where

$v_{0,i} = d_i$  (liquid since a total condenser is used);

$\tau_j =$  dimensionless time factor for plate,  $= (U_j/L_j)/\Delta t$ ;

$\mu =$  a weight factor used in evaluation of an integral in terms of the values of a function at times  $t_n$  and  $t_n + \Delta t$ ;

$$\sigma = (1-\mu)/\mu;$$

$$\rho_{j,i} = 1 + A_{j,i} (1+\tau_j/\mu) \quad j = 0, \dots, N;$$

$$\rho_{n+1,i} = 1 + \frac{U_{n+1}/V_{n+1}}{\mu \Delta t K_{n+1,i}} ;$$

$$P_{j,i} = \sigma [v_{j+1,i}^0 + \ell_{j-1,i}^0 - v_{j,i}^0 - \ell_{j,i}^0] + \frac{u_{j,i}^0}{\mu \Delta t} ;$$

$$P_{n+1,i} = \sigma [\ell_{n,i}^0 - v_{n+1,i}^0] + \frac{u_{n+1,i}^0}{\mu \Delta t}$$

For any set values of  $\Delta t$ ,  $\mu$ , temperatures and  $L/V$  profiles, the set of equations can be solved for the  $v_{j,i}$ 's provided the variables at the beginning of the time period are known.

These equations can be solved by a simple recursion algorithm developed by Holland.<sup>6</sup>

$$f_0 = C_0/B_0 \quad g_0 = D_0/B_0$$

$$f_k = \frac{C_k}{B_k - A_k f_{k-1}} \quad k = 1, \dots, N \quad (6)$$

$$g_k = \frac{D_k - A_k g_{k-1}}{B_k - A_k f_{k-1}} \quad k = 1, \dots, N+1 \quad (7)$$

The value of  $v_j$ 's for the  $i^{\text{th}}$  component are given by

$$v_{N+1} = g_{N+1} \quad (8)$$

and

$$v_k = g_k - f_k v_{k+1} \quad k = N, N-1, N-2, \dots, 0 \quad (9)$$

where

$A_j$  = sub-diagonal elements of Matrix A,  $N + 2$  by  $N+2$ .  
( $J = 0 \dots N+1$ )

$B_j$  = diagonal elements of matrix A

$C_j$  = super diagonal elements of matrix A



$D_j$  = elements in the  $N+2$  component vector  $B$  ( $J=0, \dots, N+1$ ).

For each time interval, temperatures at the end of each time period are converged upon so that the component and total material balance and the enthalpy balances are satisfied as well as the column specifications. The  $\theta$  method of convergence is an indirect method for choosing a new set of temperatures based on the calculated results obtained for the last assumed set of temperatures. This method then alters or corrects the mole fraction. On the basis of these mole fractions, new temperatures are computed.

When the molal holdups  $U_0 \dots U_N$  along with the distillation rate  $D$  are specified, the formulas for the  $\theta$  method of convergence are as follows:

$$\frac{u_{n+1,i}}{d_i} \text{ cor} = \theta_{-1} \frac{u_{n+1,i}}{d_i} \text{ cal} \quad (10)$$

$$\frac{u_{j,i}}{d_i} \text{ cor} = \theta_j \frac{u_{j,i}}{d_i} \text{ cal} \quad (11)$$

$$j = 0, \dots, N$$

The desired set of  $\theta$ 's is that set of positive numbers

that make  $g_{-1} = g_0 = \dots = g_N = 0$  simultaneously. Where

$$g_{-1} (\theta_{-1}, \theta_0, \theta_1, \dots, \theta_N) = \sum_{i=1}^c (d_i)_{cor} - D \quad (12)$$

$$g_j (\theta_{-1}, \theta_0, \theta_1, \dots, \theta_N) = \sum_{i=1}^c (u_{j,i})_{cor} - U_j \quad (13)$$

$$j = 0, \dots, N$$

The desired set of  $\theta$ 's is found by use of the Newton Raphson method solving for  $\Delta\theta_{-1}, \dots, \Delta\theta_N$ .

$$\begin{bmatrix} \frac{\partial g_{-1}}{\partial \theta_{-1}} & \dots & \dots & \dots & \frac{\partial g_{-1}}{\partial \theta_N} \\ \vdots & & & & \vdots \\ \frac{\partial g_N}{\partial \theta_{-1}} & \dots & \dots & \dots & \frac{\partial g_N}{\partial \theta_N} \end{bmatrix} \begin{bmatrix} \Delta\theta_{-1} \\ \vdots \\ \Delta\theta_N \end{bmatrix} = \begin{bmatrix} -g_{-1} \\ \vdots \\ -g_N \end{bmatrix} \quad (14)$$

where

$$\theta_{j,n+1} = \theta_{j,n} + \Delta\theta_j$$

This process is repeated until a set of  $\theta$ 's within the desired accuracy are found.

The equations for determining the calculated ratio of component hold-up to component distillation rate is given by the following relationship.

$$\frac{u_{j,i}}{d_i} \text{ cal} = \frac{(U_j/L_j) A_{j,i} v_{j,i}}{d_i} \quad (15)$$

$$j = 0, \dots, N+1$$

and

$$(d_i)_{\text{cor}} = \frac{-\sigma d_i^0 + (1/\mu\Delta t) \sum_{j=0}^{N+1} u_{j,i}^0}{1 + (1/\mu\Delta t) \left[ \sum_{j=0}^N \theta_n \frac{u_{j,i}}{d_i} \text{ cal} + \theta_{-1} \frac{u_{n+1,i}}{d_i} \text{ cal} \right]} \quad (16)$$

After the  $\theta$ 's are found by the Newton Raphson method, the corrected  $u_{0,1} \dots u_{n+1,1}$  are found by equations 10 and 11. The mole fractions on each stage are determined by the following expression:

$$x_{j,i} = \frac{u_{j,i}}{U_j} \quad (17)$$

The temperatures are found by a technique which Holland refers to as the  $k_B$  method. These expressions can be developed using the vapor-liquid relationship:

$$y_{j,i} = E_{j,i} K_{j,i} x_{j,i} \quad (18)$$

and defining

$$\alpha_{j,i} = K_{j,i}/K_{j,B} \quad (19)$$

where subscript B refers to a base compound which is usually a mid-boiling material. Thus

$$y_{j,i} = E_{j,i} K_{j,B} \alpha_{j,i} x_{j,i} \quad (20)$$

The  $K_{j,B}$  at temperature  $T_{j,n+1}$  is obtained as follows:

$$K_{j,B} \Big|_{T_{j,n+1}} = \frac{1}{\sum_{i=1}^c E_{j,i} \alpha_{j,i} \Big|_{T_{j,n}} x_{j,i}} \quad (21)$$

where  $K_{j,i}$  is defined by the ideal vapor/liquid relationship

$$K_{j,i} = \frac{P_{j,i}}{\pi} \quad (22)$$

The vapor pressure of the pure component ( $P_{j,i}$ ) is established by the Antoine Equation

$$\text{Log } P_{j,i} = A_i + B_i / T_j \quad (23)$$

where  $T_j$  is the temperature on plate  $j$  plus a constant to yield an effective absolute temperature.

These temperatures and compositions are used in the enthalpy and total material balance to determine the flow rates.

Enthalpy Balance:  $j^{\text{th}}$  plate

$$\int_{t_n}^{t_n + \Delta t} [V_{j+1}H_{j+1} + L_{j-1}h_{j-1} - V_jH_j - L_jh_j] dt$$

$$= U_j h_j \Big|_{t_n + \Delta t} - U_j h_j \Big|_{t_n} \quad (24)$$

Condensor duty

$$\int_{t_n}^{t_n + \Delta t} [V_1H_1 - L_0h_0 - DH_0 - Q_C] dt$$

$$= U_0 h_0 \Big|_{t_n + \Delta t} - U_0 h_0 \Big|_{t_n} \quad (25)$$

By use of the two point implicit method this equation may be reduced to

$$[V_1H_1 - L_0h_0 - DH_D - Q_C] + (\sigma)[V_1^0H_1^0 - L_0^0h_0^0 - D^0H_D^0 - Q_C^0]$$

$$= (1/\mu \Delta t)[U_0h_0 - U_0^0h_0^0] \quad (26)$$

In the constant-composition method, the quantity  $V_1H_1$  is replaced by its equivalent,

$$\begin{aligned}
 V_1 H_1 &= \sum_{i=1}^c H_{1,i} V_{1,i} \\
 &= \sum_{i=1}^c H_{1i} [\ell_{oi} + d_i + \sigma(\ell_{oi}^0 + d_i^0 - v_{1i}^0) + (1/\mu\Delta t)(u_{oi} - u_{oi}^0)]
 \end{aligned} \tag{27}$$

Thus,

$$\begin{aligned}
 V_1 H_1 &= L_o H(x_o)_1 + D H(x_D)_1 + \sigma[L_o^0 H(x_o^0)_1 + D^0 H(x_D^0)_1 \\
 &- V_1^0 H(y_1^0)_1] + (1/\mu\Delta t)[U_o H(x_o)_1 - U_o^0 H(x_o^0)_1]
 \end{aligned} \tag{28}$$

where

$$H(x_o)_1 = \sum_{i=1}^c H_{1i} x_{oi} \tag{29}$$

$$H(x_D)_1 = \sum_{i=1}^c H_{1i} x_{Di} \tag{30}$$

$$H(y_1^0)_1 = \sum_{L=1}^c H_{1i} y_{1L}^0 \tag{31}$$

Elimination of  $V_1 H_1$  from Equation 27 followed by rearrangement yields the following for condenser heat duty

$$\begin{aligned}
 Q_c &= L_o [H(x_o)_1 - h_o] + D [H(x_D)_1 - H_D] + \sigma[L_o^0 (H(x_o^0)_1 - h_o^0) \\
 &+ D^0 (H(x_D^0)_1 - H_D^0) - V_1^0 (H(y_1^0)_1 - H_1^0) - Q_c^0] \\
 &+ (U_o/\mu\Delta t)[H(x_o)_1 - h_o] - (U_o^0/\mu\Delta t)[H(x_o^0)_1 - h_o^0]
 \end{aligned} \tag{32}$$

The equations for the flow rates throughout the column are developed in a manner similar to that shown for the heat condenser duty. These relationships are as follows:

$$\begin{aligned}
 L_j = & \frac{-D[H(x_D)_{j+1} - H_D] + Q_c + \sigma(V_{j+1}^0)[H(y_{j+1}^0)_{j+1} - H_{j+1}^0]}{(H(x_j)_{j+1} - h_j)} \\
 + & \frac{-L_j^0[H(x_j^0)_{j+1} - h_j^0] - D^0[H(x_D^0)_{j+1} - H_D^0] + Q_c^0}{(H(x_j)_{j+1} - h_j)} \quad (33) \\
 + & \frac{-\sum_{k=0}^j [U_k[H(x_k)_{j+1} - h_k] - U_k^0[H(x_k^0)_{j+1} - h_k^0]]}{\mu\Delta t[H(x_j)_{j+1} - h_j]}
 \end{aligned}$$

Total Material Balance

$$\int_{t_n}^{t_n + \Delta t} (V_{j+1} - L_j - D) dt = \sum_{k=0}^j [U_k \Big|_{t_n + \Delta t} - U_k \Big|_{t_n}] \quad (34)$$

By use of the implicit method, these equations are reduced to the following:

$$V_{j+1} - L_j - D + \sigma(V_{j+1}^0 - L_j^0 - D^0) = (1/\mu\Delta t) \sum_{k=0}^j [U_k - U_k^0] \quad (35)$$

Since all variables are known at this time, the total vapor flow rates can be determined.

After the flow rates have been calculated, by use of the Enthalpy and Total Material Balances using corrected

mole fractions and temperatures, these flow rates are used for the next trial for the given time period, until the calculated temperatures do not change from trial to trial. Then the procedure is repeated for the next time period.

### Description of Computer Program for Mathematical Model

The Mathematical Model was written in Fortran II and modified to enable use on the UNIVAC 1108 system. (Input/output and library routines.) The program consists of three routines. The mainline routine reads the data and does all the calculations with the exception of inversion of the matrix (subroutine MTRIX) and calculation of the enthalpy of a mixture (subroutine ENTHPY).

The calculation procedure is as follows:

1. Assume a temperature profile and L/V's at time  $t_n + \Delta t$ . Initial values are read as data, and the converged values at time  $t_n$  are used for future guesses.

2. Component material balances are solved for the component flow rates.

3.  $\theta$  method of convergence is used to find a set of components. Distillate rates and component balances in agreement with specified values for the hold-ups at time  $t_n + \Delta t$ .

4. On the basis of the corrected rates, corrected













































































































































































































































































































