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-crene. These turpentina contain varying amounts of eight terpenes (C10H16 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.

Thus it was proven that a batch distillation system too complicated to simulate can be optimized efficiently using experimental data and the method developed.
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.3

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.15 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.4 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. Dynamic programming was developed by Richard Bellman in the 1950's. 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. 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.

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. 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.\textsuperscript{12} 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 Stated 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.⁵

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.
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 Stabilog controller.
The sulfur containing compounds 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 β-β' oxydiproynitrite 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 turpen­
tine 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.¹¹

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

\[
\left. \int_{t_n}^{t_n+\Delta t} \left( v_{J+1,i} + l_{J-1,i} - v_{J,i} - l_{J,i} \right) \, dt \right|_n^{n+1} = u_{J,i} \left|_{t_n}^{t_n+\Delta t} \right. - u_{J,i} \left|_n \right.
\]
This equation can be approximated by the two-point implicit method to yield:

\[
[\mu (v_{j+1,i} + \xi_{j-1,i} - v_{j,i} - \xi_{j,i}) - (1-\mu)(v_{j+1,i} + \\
+ \xi_{j-1,i} - v_{j,i} - \xi_{j,i})] \Delta t = u_{j,i} - u_{j,i}^0
\]  

(2)

Holland defines the liquid flow rate in terms of the vapor flow rates by use of the relationship:  

\[
\xi_{j,i} = A_{j,i} v_{j,i}
\]  

(3)

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

\[
u_{j,i} = (U_j/L_j) A_{j,i} v_{j,i}
\]  

(4)

The set of equations describing the entire column is obtained and yields a tri-diagonal matrix:  

(For definition of terms, see page 150 and Figure 3 for a schematic of a batch distillation system.)
\[
\begin{bmatrix}
-\rho_{0,i} & 1 & 0 & \ldots & 0 \\
A_{0,i} & -\rho_{1,i} & 1 & \ldots & 0 \\
0 & A_{1,i} & -\rho_{2,i} & \ldots & 0 \\
\vdots & \vdots & \ddots & \ddots & \vdots \\
0 & 0 & 0 & \ldots & A_{N,i} - \rho_{N+1,i}
\end{bmatrix}
\begin{bmatrix}
v_{0,i} \\
v_{1,i} \\
v_{2,i} \\
\vdots \\
v_{N+1,i}
\end{bmatrix}
= \begin{bmatrix}
-P_{0,i} \\
P_{1,i} \\
P_{2,i} \\
\vdots \\
P_{N+1,i}
\end{bmatrix}
\] (5)

or

\[AX = B\]

where

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

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

\(\mu = \text{a weight factor used in evaluation of an integral in terms of the values of a function at times } t_n \text{ and } t_{n+\Delta t};\)

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

\(\rho_j,i = 1 + A_j,i (1+\tau_j / \mu) \quad j = 0, \ldots, N;\)

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

\(p_{j,i} = \sigma[v^0_{j+1,i} + \lambda^0_{j-1,i} - v^0_{j,i} - \lambda^0_{j,i}] + \frac{u^0_{j,i}}{\mu \Delta t};\)

\(P_{n+1,i} = \sigma[\lambda^0_{n,i} - v^0_{n+1,i}] + \frac{u^0_{n+1,i}}{\mu \Delta t}.\)
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.\(^6\)

\[
f_0 = \frac{C_j}{B_j - A_j F_{k-1}} \quad k = 1, \ldots, N \tag{6}
\]

\[
g_k = \frac{D_j - A_j}{B_j - A_j} \frac{g_{k-1}}{f_{k-1}} \quad k = 1, \ldots, N+1 \tag{7}
\]

The value of \( v_j \)'s for the \( i \)th component are given by

\[
v_{N+1} = g_{N+1} \tag{8}
\]

and

\[
v_k = g_k - f_k v_{k+1} \quad k = N, N-1, N-2, \ldots, 0 \tag{9}
\]

where

\[
A_j = \text{sub-diagonal elements of Matrix } A, N + 2 \text{by } N+2 \quad (J = 0 \ldots N+1)
\]

\[
B_j = \text{diagonal elements of matrix } A
\]

\[
C_j = \text{super diagonal elements of matrix } A
\]
D_j = elements in the N+2 component vector B(J=0, ..., 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 θ 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, ..., U_N along with the distillation rate D are specified, the formulas for the θ method of convergence are as follows:

\[
\frac{u_{n+1,i}}{d_i} \text{ cor} = \theta - 1 \frac{u_{n+1,i}}{d_i} \text{ cal}
\]

\[
\frac{u_{j,i}}{d_i} \text{ cor} = \theta_j \frac{u_{j,i}}{d_i} \text{ cal}
\]

\[j = 0, \ldots, N\]

The desired set of θ's is that set of positive numbers
that make \( g_{-1} = g_0 = \ldots = g_N = 0 \) simultaneously. Where

\[
g_{-1} (\theta_{-1}, \theta_0, \theta_1, \ldots, \theta_N) = \sum_{i=1}^c (d_{i})_{\text{cor}} - D \tag{12}
\]

\[
g_j (\theta_{-1}, \theta_0, \theta_1, \ldots, \theta_N) = \sum_{i=1}^c (u_{j,i})_{\text{cor}} - U_j \tag{13}
\]

\( j = 0, \ldots, N \).

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

\[
\begin{bmatrix}
\frac{\partial g_{-1}}{\partial \theta_{-1}} & \ldots & \frac{\partial g_{-1}}{\partial \theta_N}
\end{bmatrix}
\begin{bmatrix}
\Delta \theta_{-1}
\vdots
\Delta \theta_N
\end{bmatrix}
= \begin{bmatrix}
-g_{-1}
\vdots
\vdots
\end{bmatrix}
\tag{14}
\]

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.

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

\[ j = 0, \ldots, N+1 \]

and

\[
(d_i)_{cor} = -\sigma q^0_{i,j} + \frac{(1/\mu \Delta t)}{1 + (1/\mu \Delta t) \left[ \sum_{j=0}^{N} \frac{u_{j,i}^0}{d_i} + \theta_1 \frac{u_{n+1,i}}{d_i} \right]} \quad (16)
\]

After the \( \theta \)'s are found by the Newton Raphson method, the corrected \( u_0,1 \ldots u_{n+1,1} \) 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:
\[ y_{j,i} = E_{j,i} K_{j,i} x_{j,i} \]  \hspace{1cm} (18) 

and defining
\[ \alpha_{j,i} = \frac{K_{j,i}}{K_{j,B}} \]  \hspace{1cm} (19) 

where subscript \( B \) refers to a base compound which is usually a mid-boiling material. Thus
\[ y_{j,i} = E_{j,i} K_{j,B} \alpha_{j,i} x_{j,i} \]  \hspace{1cm} (20) 

The \( K_{j,B} \) at temperature \( T_{j,n+1} \) is obtained as follows:
\[ k_{j,B} \bigg|_{T_{j,n+1}} = \frac{1}{\sum_{1=1}^c E_{j,i} \alpha_{j,i} x_{j,i}} \]  \hspace{1cm} (21) 

where \( K_{j,i} \) is defined by the ideal vapor/liquid relationship
\[ K_{j,i} = \frac{P_{j,i}}{\pi} \]  \hspace{1cm} (22) 

The vapor pressure of the pure component \( (P_{j,i}) \) is established by the Antoine Equation
\[ \log P_{j,i} = A_i + B_i / T_j \]  \hspace{1cm} (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: jth plate**

\[
\int_{t_n}^{t_{n+\Delta t}} \left[ V_{j+1}^{H_{j+1}} + L_{j-1}^{h_{j-1}} - V_j^{H_j} - L_j^{h_j} \right] dt
\]

\[= U_j^{h_j} \left| t_{n+\Delta t} - U_j^{h_j} \right|_{t_n} \]  \hspace{1cm} (24)

**Condensor duty**

\[
\int_{t_n}^{t_{n+\Delta t}} \left[ V_1^{H_1} - L_0^{h_0} - D_{H_0}^D - Q_C \right] dt
\]

\[= U_0^{h_0} \left| t_{n+\Delta t} - U_0^{h_0} \right|_{t_n} \]  \hspace{1cm} (25)

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

\[
[V_1^{H_1} - L_0^{h_0} - D_{H_0}^D - Q_C] + \sigma [V_1^0^{H_1} - L_0^0^{h_0} - D^0_{H_0}^D - Q_0^C]
\]

\[= \left( \frac{1}{\mu \Delta t} \right) [U_0^{h_0} - U_0^0^{h_0}] \]  \hspace{1cm} (26)

In the constant-composition method, the quantity \( V_1^{H_1} \) is replaced by its equivalent,
Thus,

\[ V_1 H_1 = L_0 H(x_0)_1 + DH(x_D)_1 + \sigma [L_0^0 H(x_0^0)_1 + D^0 H(x_D^0)_1
\]

\[ - V_1^0 H(y_1^0)_1] + (1/\mu \Delta t)[U_0 H(x_0)_1 - U_0^0 H(x_0^0)_1] \]  

where

\[ H(x_0)_1 = \sum_{i=1}^{c} H_{ii} x_{oi} \]  

\[ H(x_D)_1 = \sum_{i=1}^{c} H_{ii} x_{Di} \]  

\[ H(y_1)_1 = \sum_{L=1}^{c} H_{ii} y_{11i} \]  

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

\[ Q_c = L_0 [H(x_0)_1 - h_o] + DH(x_D)_1 - H_D] + \sigma [L_0^0 H(x_0^0)_1 - h^0_o]
\]

\[ + D^0 [H(x_D^0)_1 - H_D^0] - V_1^0 [H(y_1^0)_1 - H_1^0] - Q_c^0]
\]

\[ + (U_0/\mu \Delta t)[H(x_0)_1 - h_o] - (U_0^0/\mu \Delta t)[H(x_0^0)_1 - h^0_o] \]  

(27)
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:

\[
L_j = \frac{-D[H(x_D)_{j+1} - H_D] + Q_c + \sigma(V^0_{j+1})[H(y^0_{j+1})_{j+1} - H^0_{j+1}]}{(H(x_j)_{j+1} - h_j)}
\]

\[
+ \frac{-L^0_j[H(x^0_j)_{j+1} - h^0_j] - D^0[H(x^0_D)_{j+1} - H^0_D] + Q^0_c}{(H(x_j)_{j+1} - h_j)}
\]

\[
+ \sum_{k=0}^{j} \frac{U_k[H(x^0_k)_{j+1} - h_k] - U^0_k[H(x^0_k)_{j+1} - h^0_k]}{\mu \Delta t[H(x_j)_{j+1} - h_j]}
\]

\[
\text{Total Material Balance}
\]

\[
\begin{align*}
t_n & \quad \int_{t_n}^{t_n+\Delta t} (V_{j+1} - L_j - D) \, dt = \sum_{k=0}^{j} \left[ U_k \Big|_{t_n+\Delta t} - U_k \Big|_{t_n} \right]
\end{align*}
\]

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

\[
V_{j+1} - L_j - D + \sigma(V^0_{j+1} - L^0_j - D^0) = (1/\mu \Delta t) \sum_{k=0}^{j} \left[ U_k - U^0_k \right]
\]

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
mole fractions are used to determine a new temperature profile.

5. Corrected compositions and corresponding temperatures are used in enthalpy and total material balances to determine the liquid and vapor rates for the next trial.

6. Steps 2-5 are continued until the assumed temperature and calculated temperature do not change from trial to trial. Then the procedure is repeated for the next time period.

Subroutine MTRIX solves the matrix problem of \( AX = B \) for \( X \) by Gaussian elimination.

Subroutine ENTHPY calculates the enthalpy of a mixture at any temperature by summing the enthalpies of the pure components times their respective mole fractions.

A complete documented program listing is shown in Table VI and the definition of program variables is listed in Table VII.

Input Requirements for the Mathematical Model

The input for the mathematical model consists of a sequence of the type shown in Figure 4. A description of each card type is as follows:

<table>
<thead>
<tr>
<th>CARD TYPE</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Number of Plates and Component Card</td>
</tr>
<tr>
<td></td>
<td>The integer number of plates in</td>
</tr>
</tbody>
</table>
2

Initial Charge

Columns 1-10, total moles charged to column. Columns 11-20-71-80, etc., weight fraction of each component in original charge.

3

Assumed Holdup and Temperature Cards

The assumed molar holdup and temperature at plate preceding from the condenser to the reboiler. Columns 1-10 for the holdup, 11-20 for the temperature with decimal included, temperature is in degrees K.

4

Vapor Pressure Equation Cards

The constants in the vapor pressure equation \( \log P = B + A/T \) for each compound, \( B \) in columns 1-10, \( A \) in columns 11-20 with decimal included, pressure is in mm of Hg.

5

Initial Constant Card


6

Enthalpy Equation Card

Constants for enthalpy equations in form \( h = A + BT \).

columns 1-10 \( A \) for liquid

columns 11-20 \( B \) for liquid

columns 21-30 \( A \) for vapor

columns 31-40 \( B \) for vapor

columns 41-50 = constant for
calculation of latent heat of vaporization
columns 51-60 = critical temperature degrees K
One card per compound in the same order as vapor pressure cards.

Pressure on Each Plate
Columns 1-10 . . . 71-80 contains the pressure on each plate in sequence of condenser down to reboiler.

A list of the typical input for simulation of a batch distillation column is shown in Table VIII.
Richard Bellman, who is undoubtedly the father of dynamic programming, invented a rather misleading name for this technique. The names of "recursive optimization" or "mathematical theory of multi-stage processes" are more representative of this optimization technique. Basically, dynamic programming takes a sequential or multistage decision process containing many inter-dependent variables and converts it into a series of single stage problems, each containing only a few variables. Therefore, it can be applied to any process which can be broken down into stages. The transformation is based on the "Principal of Optimality" which states:

An optimal policy has the property that whatever the initial state and initial decisions, the remaining decision must constitute an optimal policy with respect to the state resulting from the first decision.

This intuitively obvious principle has been proven by a simple contradiction proof presented by Fan. Figure 6 is used to illustrate this procedure. Suppose ACDFG is the shortest path going from A to G. If DFG is longer than DEG, then there is a shorter path namely ACDEG going from A to G. This contradicts the proposition that ACDFG is the shortest path. In other words, for ACDFG to be truly the shortest path, DFG must be shorter than DEG.

The mathematical statement of "the principle of
-28-

optimality", is shown in the following equation of the objective function for additive returns.

\[ F_n(X_n) = \max_{D_n} \left[ R_n(X_n, D_n) + F_{n-1}(X_{n-1}) \right] \] (36)

where \( n \) = number of stages remaining in the process.

\( F_n(X_n) \) = the cumulative value of \( F \) over the \( n \) remaining stages of the process.

\( D_n \) = the decision at the \( n \)th stage.

\( R_n(X_n, D_n) \) = the gain to be made during stage \( n \) by optimal choice of \( D_n \).

\( X_n \) = input to stage number \( n \).

\( X_{n-1} \) = output of stage number \( n \).

\( X_n \) is related to \( X_{n-1} \) by the stage transformation.

\[ X_{n-1} = T_n(X_n, D_n) \] (37)

where \( T_n \) is the transformation function of stage \( n \).

This equation shows that every component in a serial structure influences every downstream component. Stage \( n \) can be shown to be independent of downstream decision. Figure 5 shows each stage has associated with it the following:

1. Input state \( X_n \)
2. Output state \( X_{n-1} \)
3. Decision variable \( D_n \)
4. Return \( R_n \).
The output for stage $n$ is the input to stage $n-1$ for a multi-stage process. The output and return are dependent on the input and the decision. For most chemical engineering problems the transformation property is

$$X_{n-1} = T_n(X_n, D_n)$$

and the returns from each stage is

$$R_n = R_n(X_n, D_n)$$  \hspace{1cm} (38)

From the transformation, it follows that $X_n$ depends only on the decisions prior to stage $n$ ($D_{n+1}, \ldots, D_N$) and $X_N$.

$$X_n = T_{n+1}(X_{n+1}, D_{n+1}) = T_{n+1}(T_{n+2}(X_{n+2}, D_{n+2})D_{n+2})$$

$$= T_{n+1}(X_{n+2}, D_{n+2}, D_{n+1})$$

$$\vdots$$

$$= T_{n+1}(X_N, D_N, \ldots, D_{n+1})$$

Similarly the return from stage $n$ is dependent only on $X_N$ and $D_N, D_{n+1}, \ldots, D_n$. 
or in other words, \( D_n \) only affects the decisions from stages one through \( n \). Thus stage 1 is shown to be independent of all down stream decisions and can be suboptimized for all possible input stages. Once this has been accomplished the final two stages can be grouped and optimized independently. This technique is continued until the entire process has been optimized for an initial input state of \( X_N \). This can be stated mathematically as follows for additive returns:

\[
\begin{align*}
    f_n(X_n) &= \max_{D_n \ldots D_1} [R_n(X_n, D_n) + R_{n-1}(X_{n-1}, D_{n-1})] \\
             & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \vdots \ \\
             &= R(X_1, D_1) \\
\end{align*}
\]  

(39)

Since stage \( n \) return does not depend on decisions \( n-1 \ldots n \), and since the for-real valued functions the maximum of a sum equals the sum of the maximums, the functional equation can be broken up as follows:

\[
\begin{align*}
    f_n(X_n) &= \max_{D_n} [R_n(X_n, D_n)] + \max_{D_{n-1} \ldots D_1} [R_{n-1}(X_{n-1}, D_{n-1}) + \ldots + R_1(X_1, D_1)] \\
\end{align*}
\]

But by definition of \( f_n(X_n) \), it follows that
Thus the result is the objective function

\[ f_{n-1}(X_{n-1}) = \max_{D_{n-1}, \ldots, D_1} \left[ R_{n-1}(X_{n-1}, D_{n-1}) + \ldots + R_1(X_1, D_1) \right]. \]

Application of this principle guarantees that the decision made at each stage is the best one in light of the entire process. Solution of the functional equation yields the value of the maximum return (a global maximum) and the corresponding optimal policy which belongs to the set of \((D_n)\).

The effort expended for this computation is just that of considering every decision for every input for every stage. The number of computations required for this optimization method is \((2N-1)M^2\), where \(N\) is the number of stages and \(M\) the number of decision variables. For comparison, an exhaustive search would require \(N(M)^N\) computations. This reduction in effort required is the chief advantage of dynamic programming.
APPLICATION OF DYNAMIC PROGRAMMING TO THE
BATCH DISTILLATION PROCESS

The breaking into stages to fit a dynamic programming model requires individual analysis for each problem application. The method used for defining stages for the batch distillation is each fraction of product obtainable at the desired purity. This includes the product fraction plus the succeeding midfraction. This method breaks the running time down into a series of stages. For the separation of crude sulfate turpentine the stages are defined by the time required to produce the following terpenes:

<table>
<thead>
<tr>
<th>Stage Number</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dipentene</td>
</tr>
<tr>
<td>2</td>
<td>delta-3-carene</td>
</tr>
<tr>
<td>3</td>
<td>beta-pinene</td>
</tr>
<tr>
<td>4</td>
<td>alpha-pinene</td>
</tr>
</tbody>
</table>

In the general case, stage number 1 is the least volatile major component as is dipentene in this case. Associated with dipentene stage is the bottoms or the material left in the reboiler at the end of the distillation. The stage numbering proceeds in number in order of the lowest volatility to the most volatile compound. Associated with each stage is the mid-fraction between the specific stage in question and the
succeeding fraction or next lower number stage.

The unit for measuring the return is net profit or cost for producing the product of that particular stage. The equations defining the return for each stage are as follows:

Stage 1:

\[ R_1(X_1, D_1) = \text{PRICE} (X_1) \cdot \text{AMOUNT} (X_1, D_1) - \text{COST/BOIL-UP-RATE} \cdot \text{AMOUNT} (X_1, D_1) \cdot (\text{RR}(X_1, D_1) + 1) \cdot \text{AVERAGE} \cdot \text{BOTTOMS} (X_1, D_1) \cdot \text{(COST OF BOTTOM)} \] (41)

Stage 2 . . . N:

\[ R_n(X_n, D_n) = \text{PRICE} (X_n) \cdot \text{AMOUNT} (X_n, D_n) - \text{COST/BOIL-UP-RATE} \cdot \text{AMOUNT} (X_n, D_n) \cdot (\text{RR}(X_n, D_n) + 1) \cdot \text{AVERAGE} \cdot \text{MIDFRACTION} (X_n, D_n) \cdot \text{COST/BOIL-UP-RATE} \cdot (\text{RR}(X_n, D_n) + 1) \] (42)

where the subscript AVERAGE denotes the average value over the entire stage. The return for the entire process is the cumulative sum of return from each stage.

The inputs for each stage are all the possible combinations of reflux ratios and purities to start the stage. The decisions for each stage are that reflux ratio
and purity at which the stage ends. The reflux ratio can be varied from the input to the decision or final reflux ratio. Thus, the value by time averaging is used in the return equations. The output for each stage is the final reflux change for the product that is to be obtained, this is the same as the decision variable since the mid-fraction is taken overhead at that rate. The output or decision on purity is that which is used for the input to the lower sequentially numbered stage. This determines the amount in pounds of mid-fraction between the two products associated with the decision in question.

The variables in the return equation which are functions of the decision variables are AMOUNT and MID-FRACTION. The equations describing these relationships are based on a simplifying assumption that at the time of a reflux change the composition in the column is the same as that for the separate distillation curves. This can be explained by an example: Suppose that desired purity is 95% and this is reached at a reflux ratio of 10:1. Then after operating for a period of time at this reflux ratio a purity of 95% can be reached at 5:1. The assumption that the composition in the column is identical at this point in time for both the reflux ratios, permits use of a linear equation for calculation of the amount of product with a purity higher than
95% obtainable at a reflux ratio 10:1 for this reflux ratio change. It is simply a subtraction of the percent distilled for each reflux ratio.

This assumption would be valid for a continuous change in reflux ratio but leaves some doubt for incremental changes such as used in this study, 30:1, 15:1, 10:1 and 5:1. However, this assumption was found to be valid by verification runs on pilot plant equipment.

The equation describing the AMOUNT and MID-FRACTION at stage n are as follows:

$$\text{AMOUNT} (X_n, D_n) = (\text{PERCENT DISTILLED AT RR}_X^{X_n}, \text{PURITY}_X^{X_n} - \text{PERCENT DISTILLED at RR}_D^{D_n}, \text{PURITY}_X^{X_n}) \cdot \text{TOTAL}$$ \hspace{1cm} (43)

$$\text{MID-FRACTION} (X_n, D_n) = (\text{PERCENT DISTILLED at RR}_D^{D_n}, \text{PURITY}_X^{X_n} - \text{PERCENT DISTILLED at RR}_D^{D_n}, \text{PURITY}_D^{D_n}) \cdot \text{TOTAL}$$ \hspace{1cm} (44)

With the interstage and return defined for each stage, the recursive functional equation (Eq. 36) is applied to obtain a global maximum profit for the entire run. The objective function is maximized for each input to stage 1. Once this has been accomplished the final two stages are
grouped and optimized independently. This technique is continued until the entire process has been optimized.

Description of Optimization Computer Program

The flow chart (computation sequence) of the optimization technique is shown in Figure 8. The program consisted of an executive routine (mainline) and five subroutines all written in Fortran II. Fortran II is acceptable on most modern-day computers with minor modifications to the input/output statements and the library routines. The program was written for the IBM 1620, Model 2, with 60,000 digit storage. The complete documented program listing is shown in Table X and the definitions of program variables is listed in Table XI.

The mainline routine reads in the necessary parameters and basic data required (distillation). It also serves as an executive routine by calling the other routines when they are required. The dynamic programming routine follows the general scheme of computation presented by Nemhauser,\textsuperscript{15} as shown in the flow chart (Fig. 7). The subroutines called DPMOD and SORT follow this general algorithm for optimization of any multistage decision system. The characteristics that distinguish problems are:

1. The return function and transformation.
2. The interpretation as to how $F_n$ and $F_{n-1}$ are to
be combined in the objective equation.

3. Method of maximization of the objective equation. The equations describing both the return and the transformation from stage to stage have been described in the previous section along with the combination of the objective equation. The method of a "one-at-a-time" routine was used for maximization. More sophisticated search routines such as Fibonace Search would reduce the amount of computations required at the expense of a more complicated program. Subroutine DPMOD does the calculations concerned with the return, transformation and maximization. For each input variable \( x_n \), the array of decision variables is cycled through by use of DO loops. The cycling proceeds through all the stages in an outer DO loop.

The dotted lines in Figure 7 shows the use of auxiliary memory to store the optimum decision for each input to the stage. The use of auxiliary memory and storage of only optimum decisions decrease the principal drawback of high dimensionality associated with the dynamic programming procedure. The instructions for using these storage devices are dependent on the equipment employed. In this study, the 1311 IBM Disk Packs were used. After subroutine SORT retrieves the optimum decisions from mass memory and stores them in interval memory, they are printed in suitable form by subroutine EDIT. (Tables XIII - XXIV)
Input Requirements for Optimization Program

The data needed for each optimization run is read in the mainline routine. These data are edited as a portion of the output for the optimization run. This permits the user to have an edited version of the input data from which the optimization was based. A description of each card type as shown in the schematic arrangement of data (Figure 9) is as follows:

<table>
<thead>
<tr>
<th>TYPE</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td><strong>Sentinel Card</strong></td>
</tr>
<tr>
<td></td>
<td>Positive number in column 1-3 indicates a new job. Blank is sentinel for the end of job.</td>
</tr>
<tr>
<td>No. 2</td>
<td><strong>Input Data Description Card or Cards</strong></td>
</tr>
<tr>
<td></td>
<td>1-80 columns per card to be printed describing the following input data. Final card in this group must have a 1 in column 1 and there must be at least one card of this type.</td>
</tr>
<tr>
<td>No. 3</td>
<td><strong>Index Card</strong></td>
</tr>
<tr>
<td></td>
<td>Columns 1-3 contains the number of stages. In three column field the number of purities per stage are placed with the number of reflux ratios in the next three column field. All numbers must be integer and right justified.</td>
</tr>
<tr>
<td>No. 4</td>
<td><strong>Input Data Description Card or Cards</strong></td>
</tr>
<tr>
<td></td>
<td>Same as card type No. 2.</td>
</tr>
<tr>
<td>No. 5</td>
<td><strong>Total Charge Card</strong></td>
</tr>
<tr>
<td></td>
<td>Total charge of turpentine in pounds. Columns 1-10 with decimal.</td>
</tr>
</tbody>
</table>
(TYPE)                                (DESCRIPTION)
No. 6      Input Data Description Card or Cards
            Same as card type No. 2.
No. 7      Distillation Data Preceding the
            Fraction Cards
            Weight fraction distilled preceding cut in order of highest reflux ratio down to lowest on each card. Cards are read in order of stage numbering and purity per stage. 10 columns are used for each data point and decimal must be included.
No. 8      Input Data Description Card or Cards
            Same as card type No. 2.
No. 9      Distillation Data Following the
            Fraction Cards
            Weight fraction distilled following cut in order of highest reflux ratio down to lowest on each card. Cards are read in order of stage numbering and purity per stage. 10 columns are used for each data point and decimal must be included.
No. 10     Input Data Description Card or Cards
            Same as card type No. 2.
No. 11     Reflux Ratio Cards
            Reflux ratios used for each separation in order of highest down. 10 columns are allowed for each reflux ratio and decimal must be included.
No. 12     Input Data Description Card or Cards
            Same as card type No. 2.
No. 13     Price Data Cards
            Selling price in dollars per pound for each component in order of stage number and purity per stage. 10
(TYPE) columns are allowed for each price and decimal must be included.

No. 14 Input Data Description Card or Cards
Same as card type No. 2.

No. 15 Purity Data Cards
Purities evaluated for each stage in order of stage number. 10 columns are allowed for each purity and decimal must be included.

No. 16 Input Data Description Card or Cards
Same as card type No. 2.

No. 17 Cost Data Card
The cost data includes operating cost $/hr, boil-up rate, lbs/hr, cost of Bottoms, $/lbs, and number of runs per year. 10 columns are allowed per item including decimal.

No. 18 Heading Cards
The title for each mid-fraction and stage used in editing of optimum operating conditions order is as shown:
  bottoms
  stage 1
  mid-fraction between stage 1 and 2
  stage 2
  .
  .
  mid-fraction between stage n and n-1
  stage n
Columns 2-40 are allowed for alphanumeric characters with 2N cards required. N is the number of stages considered.

No. 19 Sentinel Card
Same as card type No. 1.
A list of sample input containing sentinels is shown in Table XII, and the edited input in Tables XIII, XVII, and XXI.
DISCUSSION AND RESULTS

Mathematical Model

The mathematical model was written in Fortran II and "debugged" on the IBM 1620. In order to simulate the entire column (52 theoretical plates), the program was modified slightly to enable use of the UNIVAC 1108 system. Changing computers gained a speed factor of 1000-1200.

The program was used to simulate the distillation of Potlatch crude sulfate turpentine which contains eight individual terpene chemicals. This, by the nature of batch distillation, results in four hundred and sixteen simultaneous differential equations (52 x 8) for the component material balance on each plate. There are also 52 simultaneous differential equations resulting from the enthalpy balance and 52 simultaneous differential equations from the total material balance on each plate. In addition to the balancing of these equations, the temperature on each plate must satisfy the column specifications.

The simultaneous differential equations were solved by a two-point implicit method with a weight factor of 0.6. This weight factor was varied from 0.6 to 0.9 and found to have very little effect on the rate of solution. This method is known classically as the modified Euler's method for a
weight factor of 0.5. The simultaneous differential equations from the component material balance were grouped into a tri-diagonal matrix which easily lends itself to inversion by the algorithm described in the Mathematical Model section. The method of convergence is known as the \( \Theta \) method and was developed by Holland.\(^6\) This method requires the inversion of a 52x52 matrix for each step in convergence of temperatures.

The time required to simulate the distillation of Potlatch crude was in excess of 24 minutes on the UNIVAC 1108. The amount of computer time required to gain enough data to establish an optimization output would be greater than one-hour for the four reflux ratios. This would be uneconomical as a method for acquiring the desired data as simulation cost would range from five-hundred to one-thousand dollars per optimization compared to two-hundred to three-hundred dollars for obtaining data in the laboratory. It was concluded that Meadows\(^11\) was correct in stating that simulation of batch distillations are still limited to very simple cases.

Approximations could have been made with the intent of gaining speed of solution, if the accuracy of the solution would permit it. However, the accuracy of the simulation using this complex model leaves something to be desired as shown in Figure 10. This graph of simulated results shows oscillating action due to large tolerances on the convergence criterions. These oscillations could be eliminated by decreas-
The running time required for this simulation of a 17 plate column was 9.42 minutes on the UNIVAC 1108 system. The program itself was known to be properly "debugged" by comparison of results with an existing simulation program on a cut-down version of the column and also by hand checks on the steady-state solution.

Optimum Policy

The optimum policy for each of the crude sulfate turpentine evaluated (Potlatch Industries, Southwest Forest and Hoerner Waldorf) is shown in Tables XIII through XXIV. This consists of the amount of each product at the optimum purity and the reflux ratio changes in obtaining these fractions.

The optimization is based on the maximum profit per run which is calculated from the selling price, operating cost, and distillation data for a particular charge. The selling price of the individual terpenes at different purities is shown in Table V, and the input data for each run in Tables XIII, XVII and XXI.

The operating cost is calculated from the yearly operating cost and placed on a basis of per hour of actual operation time. A low operating cost was chosen (arbitrarily) to yield decisions to use a large number of reflux ratio changes. This insured a true test for the pilot plant verification of the procedure. Using this low operating cost the optimum policy was to secure the most product possible.
at the lower reflux ratios and incrementally increase the reflux ratio to recover all the product possible. This policy will of course, change as the operating cost increases. It was not the objective of this study to determine the optimum conditions of a hypothetical plant but to develop a method in the form of a computer program that would determine optimum operating conditions for a turpentine charge on any batch distillation column. Thus, the effect of this parameter is of little interest for the particular cases studied. This is not the case when the optimum operating policy of a particular plant is desired. Then the operating cost becomes a very important parameter. The calculation of this parameter is based on cost for the actual hourly operation which is readily derived from the yearly operating cost that includes the following:

1. Raw materials
2. Labor
3. Labor benefits
4. Superintendents
5. Steam
6. Cooling water
7. Marketing
8. Maintenance
9. Depreciation

Once the number of runs per year and the approximate running time per charge are known the hourly cost is easily obtained. A trial run with the program using an initial guess on operating cost would yield an approximate running time per charge.

The optimal policy is also based on the distillation curves obtained for each reflux ratio and purity of each product to be evaluated. As shown in the input data (Table XII), this consists of the total percentage distilled preceding the product fraction and the total percentage distilled including the product fraction. These simplified data can be obtained from any reliable source (experimental or mathematical). (See Figures 11-22 for an example of the calculations of these points.) In this particular study the complexity of the distillation eliminates mathematical modeling as a possible choice of data generation. (See discussion in the previous section.) Experimentally determined distillation curves can be obtained from one-inch laboratory distillation columns. The time required for each distillation for the various reflux ratios 5 to 1, 10 to 1, 15 to 1, and 30 to 1, averaged twenty-four hours. This method of obtaining data is much more economical than mathematical modeling and has been shown to be valid for
predicting optimum operating conditions.

**Experimental Verification of Optimization Program**

Verification runs were made following the optimum operating schedule generated by the dynamic programming model. Tables XVI, XX and XXIV describe the results obtained for Potlatch Industry, Southwest Forest Industries and Hoerner Waldorf, crude turpentine, respectively. Changes of both reflux ratios and product fractions were made on the basis of the amount of product collected. The amount of product was weighed to within one-half pound of the predicted value. The average reflux ratio was calculated as a weighted average of the incremental reflux ratios used. The comparison of the average reflux ratios (calculated and indicated by computer) for each product fraction was used as a criterion of the accuracy with which verification runs followed the computer prescribed operating conditions.

Average purity was calculated by a chromatographic analysis of each product fraction collected. The comparison of this value with the computer predicted value was used as a criterion for the validity of assumptions made in developing the interstage and return relationships of the optimization program.

The accuracy with which purities can be analyzed by measuring the area under the peaks of the chromatogram was
found to be within ± two percent by McCumber. Points on "distillation curves" were produced by duplicate runs, and chromatographic analysis of samples gave reproducible results. The distillation curves obtained on the one-inch columns were the basis of the optimization calculations. Average purity measurements of product fraction were made in duplicate samples to insure the reliability of planimeter measurements. The use of the planimeter was felt to introduce the largest experimental error in this procedure. Other lesser contributors to experimental error are the difference in boil-up rates and packing efficiency between columns used in the evaluation, reflux ratio differences in both condensing units and the weighing of samples to the desired accuracy.

The results of the verification run on Potlatch crude (See Table XVI) shows that the optimum running conditions predicted by the computer program (See Table XIV) were followed experimentally with deviations less than one percent. The purities agreed with prediction to within two percent for alpha pinene, beta pinene and delta-3-carene. The dipentene fraction was within five percent of the predicted value. This difference could be expected since the distillation could not be carried out as far as predicted by the computer program. This was due to the lack of material in the reboiler of the pilot plant column. All experimental purities, including that of the dipentene fraction are above the predicted purities.
This causes the errors considered previously to be of less importance. It is felt that all the results were within the accuracy of the equipment.

Table XX shows the experimental verification of the optimum conditions predicted for Southwest Forest Industry's crude (Table XVII). The verification followed the predicted operating conditions with less than one percent deviation in the average reflux ratio. The purities of the alpha pinene and delta-3-carene fractions were within one percent of the predicted value. No beta pinene fraction was obtained as indicated by the computer program. The dipentene fraction average purity was ten percent higher than predicted. This was caused by not being able to follow the optimum policy exactly as predicted by the computer because of equipment limitations. The equipment can weigh accurately to one-half a pound. Again all purities were above the predicted values, and this permits less concern over errors considered previously. The average purity of each fraction is above the minimum purity set for sale.

Table XXIV shows the operating schedule followed during the experimental verification for a charge of Hoerner Waldorf crude. To enable use of comparison of Table XXII (the computer predicted values) and Table XXIV, the average reflux ratio was calculated for both. The results of the optimization on Hoerner
Waldorf shows that the optimum running conditions were followed experimentally with deviations less than one percent.

The chromatographic analysis of the average purity of each fraction was used again as a criterion of the optimization programs validity. Tables XX and XXII shows the average purity agreed with predicted value within three percent for alpha pinene, beta pinene and delta-3-carene. The dipentene fraction was within five percent of the predicted value.

As in all the previous runs, all experimental purities were above the predicted purities. The dipentene fraction was consistently above the computer program predicted value. This can be partially contributed to the experimental errors in obtaining distillation data. The dipentene fraction being the final fractionation would require a "chaser" in the charge to establish more reliable data at the end of the distillation. This is due to the hold-up in the column which is used for obtaining experimental data.
CONCLUSIONS

1. Dynamic programming proved to be an effective technique to maximize profit and to determine the optimum running conditions. The running time on the computer is short enough to direct the operating schedule for each batch distillation charge using any average size "third-generation" computer.

2. Data can be supplied to the dynamic programming model either by use of experimental quantities or mathematically simulated values.

3. The mathematical simulation is felt to be too expensive to be used for supplying the data necessary for the optimization program. This is due to the complexity of the distillation -- 52 theoretical plates with 8 compounds. The simulation of this complex distillation yielded poor results with convergence tolerances large enough for reasonable running time on one of the fastest "third-generation" computers (UNIVAC 1108).

4. The complicated distillation of the separation of terpenes can be effectively optimized with experimental data obtained on laboratory equipment. The laboratory time required to obtain data would be more economical and dependable, at least until computer costs decline considerably.

5. The interstage and return relationships for the optimization of terpenes proved to be correct within the accuracy of the experimental equipment. These relationships
were verified on pilot plant equipment for three crude sulfate turpentine of varying compositions.

6. The optimization program is general and can be used for any batch distillation for which the distillation curves can be supplied. Confidence can be gained by verifications under different systems.
RECOMMENDATIONS

The nature of this research opened the door to an area of research which could not be followed up because of time and computer facilities limitations. Some of the interesting possibilities listed below are recommended for future research.

1. As computer facilities increase, work should be done on attempting to develop or employ a mathematical model which will simulate this complicated distillation of terpenes. The one method evaluated for this simulation was developed by Holland. Numerous other methods are available in the literature (7-11) and could be evaluated for this simulation. A satisfactory model would eliminate the need for laboratory preparation of data.

2. As the commercial interest in pure terpene hydrocarbons increases, it would be desirable to experimentally determine the physical properties of these chemicals. The vapor pressure and enthalpy relationships with temperature are a necessity for satisfactory simulation. Most of the values supplied for this study were based on estimation techniques and their validity should be checked. Other physical properties such as specific gravity, refraction index, flash point and color, APHA, would be of value for marketing of the terpene fractions.
3. In order to prove the generality of the relationships used in the dynamic programming model, other systems different from the terpenes should be evaluated by the verification procedure used in this study. The program has been written to apply to any batch distillation. Thus only the interstage and return relationships need to be verified.
APPENDIX
TABLE I

STRUCTURES OF TERPENES ASSOCIATED WITH CRUDE SULFATE TURPENTINE FROM NORTHWEST PULP MILLS

<table>
<thead>
<tr>
<th>Terpene</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Pinene</td>
<td><img src="image" alt="Alpha Pinene" /></td>
</tr>
<tr>
<td>Camphene</td>
<td><img src="image" alt="Camphene" /></td>
</tr>
<tr>
<td>Beta Pinene</td>
<td><img src="image" alt="Beta Pinene" /></td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td><img src="image" alt="Delta-3-Carene" /></td>
</tr>
<tr>
<td>Myrcene</td>
<td><img src="image" alt="Myrcene" /></td>
</tr>
<tr>
<td>Dipentene</td>
<td><img src="image" alt="Dipentene" /></td>
</tr>
<tr>
<td>Beta Phellandrene</td>
<td><img src="image" alt="Beta Phellandrene" /></td>
</tr>
<tr>
<td>Terpinolene</td>
<td><img src="image" alt="Terpinolene" /></td>
</tr>
</tbody>
</table>
TABLE II
TYPICAL COMPOSITION OF CRUDE SULFATE TURPENTINE

<table>
<thead>
<tr>
<th></th>
<th>Hoerner Waldorf Missoula, Montana</th>
<th>Southwest Forest Ind. Snowflake, Arizona</th>
<th>Potlatch Forests Lewiston, Idaho</th>
<th>Boiling Point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Pinene</td>
<td>37.7%</td>
<td>47.5%</td>
<td>56.5%</td>
<td>155.0</td>
</tr>
<tr>
<td>Camphene</td>
<td>1.1</td>
<td>0.4</td>
<td>2.80</td>
<td>160.5</td>
</tr>
<tr>
<td>Beta Pinene</td>
<td>8.0</td>
<td>0.9</td>
<td>7.40</td>
<td>158.3</td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td>39.2</td>
<td>40.5</td>
<td>16.1</td>
<td>170.2</td>
</tr>
<tr>
<td>Myrcene</td>
<td>1.3</td>
<td>--</td>
<td>0.4</td>
<td>171.5</td>
</tr>
<tr>
<td>Dipentene</td>
<td>5.2</td>
<td>6.3</td>
<td>8.5</td>
<td>174.6</td>
</tr>
<tr>
<td>Beta Phellandrene</td>
<td>4.5</td>
<td>--</td>
<td>1.9</td>
<td>174.8</td>
</tr>
<tr>
<td>Terinolene</td>
<td>3.6</td>
<td>4.8</td>
<td>5.9</td>
<td>185.0</td>
</tr>
</tbody>
</table>
TABLE III
VAPOR PRESSURE EQUATION FOR TERPENES*

Log \( P = A - \frac{B}{(T + 240)} \)

\( P = \text{mmHg} \)

\( T = ^\circ\text{C} \)

\( A = 14.47981 + 0.0157748 \times TB \)

\( B = 1466.280 + 16.76439 \times TB \)

TB = Atmospheric boiling point, \(^\circ\text{C}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Pinene</td>
<td>7.3495</td>
<td>1768.4714</td>
</tr>
<tr>
<td>Camphene</td>
<td>7.3755</td>
<td>1796.1192</td>
</tr>
<tr>
<td>Beta Pinene</td>
<td>7.3888</td>
<td>1810.3070</td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td>7.4494</td>
<td>1874.6973</td>
</tr>
<tr>
<td>Myrcene</td>
<td>7.4429</td>
<td>1867.7854</td>
</tr>
<tr>
<td>Dipentene</td>
<td>7.4645</td>
<td>1890.7039</td>
</tr>
<tr>
<td>Beta Phellandiene</td>
<td>7.4617</td>
<td>1887.7936</td>
</tr>
<tr>
<td>Terpinolene</td>
<td>7.5507</td>
<td>1982.3782</td>
</tr>
</tbody>
</table>

*Courtesy of: The Glidden Company
Organic Chemical Division
Jacksonville, Florida
TABLE IV
ENTHALPY EQUATIONS FOR TERPENES

Vapor
\[ h_V = W + U(t^0F + 460) \text{ BTU/Lb. mole} \]

Liquid
\[ h_L = L + K(t^0F + 460) \text{ BTU/Lb. mole} \]

Molal heat of vaporization
\[ H_V = (N)(1-\text{Tr})^{0.38} \text{ BTU/Mole} \]

Tr is any reduced temperature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>W</th>
<th>U</th>
<th>L</th>
<th>K</th>
<th>N</th>
<th>Tc°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Pinene</td>
<td>-10,881.5</td>
<td>61.768</td>
<td>-34,776</td>
<td>75.6</td>
<td>23,467.0</td>
<td>669.1</td>
</tr>
<tr>
<td>Camphene</td>
<td>-8,720.2</td>
<td>61.915</td>
<td>-31,226</td>
<td>68.2</td>
<td>25,892.8</td>
<td>670.1</td>
</tr>
<tr>
<td>Beta Pinene</td>
<td>-11,436.0</td>
<td>68.038</td>
<td>-37,536</td>
<td>81.6</td>
<td>24,383.9</td>
<td>650.0</td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td>-8,688.5</td>
<td>59.488</td>
<td>-30,932</td>
<td>65.46</td>
<td>24,388.9</td>
<td>648.6</td>
</tr>
<tr>
<td>Myrcene</td>
<td>-11,570.8</td>
<td>60.833</td>
<td>-37,720</td>
<td>82.0</td>
<td>25,806.6</td>
<td>638.7</td>
</tr>
<tr>
<td>Dipentene</td>
<td>-9,327.1</td>
<td>66.899</td>
<td>-36,938</td>
<td>80.3</td>
<td>25,892.8</td>
<td>636.1</td>
</tr>
<tr>
<td>Beta Phellandrene</td>
<td>-6,561.2</td>
<td>61.460</td>
<td>-35,190</td>
<td>76.5</td>
<td>26,280.6</td>
<td>646.9</td>
</tr>
<tr>
<td>Terpinolene</td>
<td>-9,673.8</td>
<td>60.312</td>
<td>-31,240</td>
<td>66.1</td>
<td>23,467.0</td>
<td>634.7</td>
</tr>
</tbody>
</table>

*Courtesy of: Hercules Incorporated
Hattiesburg, Mississippi
## TABLE V
### SELLING PRICE OF TERPENES

<table>
<thead>
<tr>
<th>Compound</th>
<th>Purity</th>
<th>Selling Price (bulk) $/lb.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Pinene</td>
<td>95%</td>
<td>.0792</td>
</tr>
<tr>
<td>Beta Pinene</td>
<td>80%</td>
<td>.1500</td>
</tr>
<tr>
<td>Dipentene</td>
<td>55%</td>
<td>.0761</td>
</tr>
<tr>
<td></td>
<td>33%</td>
<td>.0485</td>
</tr>
<tr>
<td>Delta-3-Carene***</td>
<td>95%</td>
<td>.1390</td>
</tr>
</tbody>
</table>

* Union Bag - Camp Paper Corporation
  Nelio Chemicals Division
  Jacksonville, Florida

**Tenneco Chemical Incorporated
  Newport Division
  Pensacola, Florida

***Chemical Engineering Department
  Montana State University
  Bozeman, Montana
TABLE VI

PROGRAM LIST FOR SIMULATION OF A BATCH COLUMN
C SIMULATOR-BASED ON HOLLANDS METHOD - REFERENCE - UNSTEADY STATE
C PROCESSES WITH APPLICATIONS IN MULTICOMPONENT DISTILLATION-
C
C PROGRAM IS WRITTEN IN FORTRAN II
C LIBRARY SUBROUTINES HAVE BEEN MODIFIED TO ENABLE USE OF
C UNIVAC 1108, SEPTEMBER, 1967, ALSO I/O STATEMENTS

C
DIMENSION XK(54,8), O(54), P(54), UCO(54,8), X(8), UCA(54,8), USUM(54),
1 G(54), PSUM(54), AP(54), GP(54,54), DELO(54), ON(54), UA(54), UO(54),
2CX(54,8), F(54,8), T(I), AT(I), V(I), Z(I), SL(54,8), Y(I),
3SV(54,8), TO(I), ZO(I), VO(I), XCO(I), ZO(I), VO(I), YO(I), ABF(I),
4TOU(I), AV(I), BV(I), CV(I), DV(I), FV(I), GV(I), SD(I), L(I),
DIMFNSION R(I), YEN(I), SD(I), UL(I), WL(I), VL(I), VK(I),
1,CX(54,8), T20(I), V20(I), TC(I), XN(I), PTOT(54), SZ(54,8),
2,PCO(54,8), D(I), PD(I), IMT(I), XO(I),
COMMON YEN, WL, UL, VL, VK, NCMPS
C READ IN NECESSARY DATE FOR SIMULATION OF BATCH DISTILLATION COL.
C READ - NUMBER OF PLATES - NUMBER OF COMPONENTS
200  READ 901, NPLTS, NCMPS
   IF (NPLTS) 201, 201, 202
202  NCI = NCMPS
   NN=NPLTS+1
   N2=NPLTS+2
   AMOUNT = 0.0
C READ - MOLES TOTAL CHARGE - TOTAL MOLES OF EACH COMPONENT
C READ 900, UF, (X(I), I=1, NCMPS)
C READ - HOLD-UP ON EACH PLATE-ASSUMED TEMPERATURE PROFILE AND EFF.
   DO 1 I=1, N2
1  READ 901, UA(I), AT(I)
   DO 400 J = 1, N2
   DO 400 I = 1, NCMPS
400  E(J, I) = 1.0
C READ - V RPOR PRESSURE EQUATION IN THE FORM LOGP=A/T+B
C READ 900, B(I), A(I)
READ - INITIAL BOIL-UP-RATE, DIFFERENTIAL EQUATION WEIGHT FACTOR
READ - REFLUX RATIO, PERCENT TO RF DISTILLED
READ 900, BUR, XMU, RR, PCDT
READ - CONSTANTS FOR ENTHALPY EQUATIONS - H=A+ B*T
VAPOR - LIQUID - CONSTANTS FOR LATENT HEAT - CRITICAL TEMP
DO 3 I=1, NCMPS
3 READ 900, UL(I), WL(I), VK(I), VL(I), XN(I), TC(I)
READ - PRESSURE ON EACH PLATE
READ900,(PTOT(J), J=1, N2)
BEGIN CALCULATION FOR STARTUP, STEADY STATE
DO 3 1=1, NCMPS
3 IMT(I) = I
DO 4 J = 1, N2
4 T(J) = AT(J)
DO 10 J = 1, NP
10 O(J) = 1.0
37 DO 8 I=1, NC1
8 XM=1.
DO 9 J=2, N2
9 XK(J,I) = (10.0)**[(A(I)/T(J)-33.)+B(I)]/PTOT(J)
XM=XM/(E(J,I)*XK(J,I))
9 UCA(J,I)=XM*UA(J)/UA(I)
8 XK(1,I) = (10.0)**[(A(I)/T(1)-33.1)+B(I)]/PTOT(I)
10 DO 11 J=1, N2
11 P(J) = 0.5*O(J)*10.0E-4
**Calculation of the Corrected Molar Hold Up at Plate Zero**

Uco = Corrected Molar Holdup on Plate J of Component I

Uco(1,I) Calculated by Equation 8-41

DO 13 I = 1, NCMPS
SUM = 0.0
DO 12 J = 2, N2
SUM = SUM + O(J)*UCA(J,I)
13 UCO(I,I) = (UF*X(I))/(1.*SUM)

DO 14 I = 1, NCMPS
DO 14 J = 2, NNN
14 UCO(J,I) = 0(J)*UCA(J,I)*Uco(1,I)

DO 253 I = 1, NCMPS
SUM = 0.0
DO 252 J = 1, NNN
252 SUM = SUM + UCO(J,I)
253 UCO(NZ,I) = UF*X(I) - SUM

**Calculation of G-S for the Delta Convergence Method**

Fill matrix G(J) for Newton Raphson Convergence

Such that all G-S are zero simultaneously

DO 15 J = 1, NNN
USUM(J) = 0.0
DO 16 I = 1, NCMPS
16 USUM(J) = USUM(J) + UCO(J,I)
15 G(J) = UA(J) - USUM(J)

USUM(N2) = 0.0
DO 255 I = 1, NCMPS
255 USUM(N2) = USUM(N2) + UCO(N2,I)

DO 17 JD = 1, NNN
DO 17 JK = 1, NNN

Calculate the partial derivative of G(JK) with respect to O(JD)

RO = 0(JK+1)
O(JK+1) = O(JK+1) + P(JK+1)
DO 98 I = 1, NCMPS
SUM=0.0

DO 7 J=2,N2
7 SUM=SUM+O(J)*UCA(J,I)

98 PCO(1,I)=(UF*X(I))/(1.*SUM)

DO 18 I=1,NCMPS
DO 18 J=2, N2

18 PCO(J,I)=O(J)*UCA(J,I)*PCO(1,I)

DO 19 J=1,NN

PSUM(J)=O(J)

DO 20 I=1,NCMPS

20 PSUM(J)=PSUM(J)+PCO(J,I)

19 AP(J)=PSUM(J)-UA(J)

GP(JD,JK)=(AP(JD)+G(JD))/P(JK+1)

17 O(JK+1)=RO

CALL MTRIX(NN,GP,G,DELO)

ON(1)=O(1)

DO 21 J=1,NN

21 ON(J+1)=O(J+1)+DELO(J)

DO 22 J=1,N2

C TEST FOR CONVERGENCE

C IF (ABS(O(J)-ON(J))-0.001)), 22,22,23

22 CONTINUE

GO TO 24

23 DO 242 J=1,NN

IF (ON(J+1))240, 241, 241

240 O(J+1)=O(J+1)/2.

C NEGATIVE O(J) IS SET TO 1/2 LAST POSITIVE VALUE

C GO TO 242

241 O(J+1)=ON(J+1)

242 CONTINUE

GO TO 37

24 DO 26 J=1,N2

DO 26 I=1,NCMPS

C CALCULATE MOL FRACTION ON PLATE J OF COMPONENT I

C
26 CX(J,I) = UCO(J,I)/USUM(J)
XCMPS = NCMPS
C CALCULATE TEMPERATURES BY KB METHOD, KB=1, NUMBER COMPS
C
DO 31 J=1,N2
DUM = 0.0
DO 29 IB = 1,NCMPS
SUM=0.0
DO 32 IB = 1,NCMPS

32 SUM=SUM+F(J,I)*CX(J,I)*XK(J,I)/XK(J,IB)
R=1./SUM
PV=R*(PTOT(J))
T(J) = A(IB)/(ALOG10(PV)-B(IB)) + 33.0
DUM = DUM + T(J)
DO 33 J = 1,N2

C CHECK TEMPERATURES FOR CONVERGENCE
C
IF (ABS (T(J)-AT(J))- .5)33,33,34
CONTINUE
GO TO 35
DO 36 J = 1,N2
AT(J) = T(J)
GO TO 37
DO 39 I =1,NCMPS
DO 39 J= I,NN
V(J)=BUR
Z(J)=BUR
SL(J,I)=Z(J)*CX(J,I)
Y(J,I)=E(J+I,I)*XK(J+I, I)*CX(J+I, I)
SZ(J,I)=V(J)*Y(J,I)
DO 210 J=1,NN

C SET VALUE FOR CALCULATIONS OF PRODUCT PERIOD
DO 209 I=1, NCMPS
DO 209 J= 1,N2
XCO(J,I)=CX(J,I)
Y0(J,I)=Y(J,I)
DO 210 J=1,NN

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1840
UO(J)=UA(J)  
Z(J)=Z(J)  
VO(J)=V(J)  

TO(J)=AT(J)  
TO(N2)=AT(N2)  
UO(N2)=UA(N2)  
DRO=0.0  
QCO=0.0  

C CALCULATE LATENT HEATS OF OVERHEAD PRODUCT  

C  
DO 213 I = 1, NCMPS  
213 XLHV(I) = XN(I)*(1. - T(I)/TC(I))**.38  
C CALCULATE CONDENSER HEAT DUTY - STEADY STATE  

C  
DO 211 I=1, NCMPS  
211 QCO=QCO+XLHV(I)*CX(1,I)*BUR  
SIG=(1.-XMU)/XMU  
TIME = 0.0  
C PRINT - OVERHEAD COMPOSITION - STEADY STATE  

C  
PRINT 801  
PRINT 800, TIME,(CX(1,I),I=1,NCMPS)  
DR=BUR/(RR+1.0)  
DT=UF/(DR*50.)  
DO 214 I = 1, NCMPS  
XO(I) = X(I)  

214 SDSO(I)=0.0  
UFP = UF  
PRINT 701  
DO 61 J = 1, N2  
61 O(J) = 1.  
C CALCULATE ABSORPTION FACTOR ON PLATE J OF COMPONENT I  

C  
DO 40 I=1,NCMPS  
DO 41 J=2,NN  
41 ABF(J,I)=Z(J)/(V(J-1)*E(J,I)*XK(J,I))
40 ABF(1,I)=Z(1)/DR
DO 42 J=1,NN
42 TOU(J)=UA(J)*DT/Z(J)
DO 52 I=1,NCMPS
C CALCULATE A, B, C D OF TRIDIAGONAL MATRIX SOLUTION
C
BV(I)=-1.-ABF(1,I)*(1.+TOU(1)/XMU)
AV(I)=0.0
CV(I)=1.0
DV(I)=-SIG*(SZ(I)+SL(I)+SDO(I))UCO(I,I)/(XMU*DT)
DO 53 J=2,NN
AV(J)=ABF(J-1,I)
BV(J)=-1.0-ABF(J,I)*(1.+TOU(J)/XMU)
CV(J)=1.0
DO 53 J=2,NN
DV(J)=-SIG*(SZ(J,I)+SL(J-1,I)-SL(J-1,I)-SL(J,I))-UCO
1(J,I)/(XMU*DT)
AV(N2)=ABF(NN,I)
BV(N2)=-1.-{UA(N2)/V(NN)}/(XMU*DT*XK(N2,I))
CV(N2)=0.0
DV(N2)=-SIG*(SL(NN,I)+SL(NN,I))UCO(N2,I)/(XMU*DT)
C SOLVE TRIDIAGONAL MATRIX FOR COMPONENT VAPORRATE
C LEAVING PLATE J
FV(I)=CV(I)/BV(I)
GV(I)=DV(I)/BV(I)
DO 54 J=2,NN
FV(J)=CV(J)/(BV(J)-AV(J)*FV(J-1))
54 GV(J)=(DV(J)-AV(J)*GV(J-1))/(BV(J)-AV(J)*FV(J-1))
GV(N2)=(DV(N2)-AV(N2)*GV(NN))/(BV(N2)-AV(N2)*FV(N2-1))
SV(N2,I)=GV(N2)
K=NN
56 SV(K,I)=GV(K)-FV(K)*SV(K+1,I)
K=K-1
IF(K) 57,57,56
57 SD(I)=SV(1,I)
C CHECK TO SEE IF COMPONENT HAS BEEN DISTILLED OFF.  2570
IF (IMT(I)) 563,563,562
       563 DO 564 J = 1,N2
       564 UCA(J,I) = 0.0
       GO TO 52
       562 SUM = 0.0

      CALCULATE RATIO OF COMPONENT MOLAR HOLD-UP TO THE
      DISTILLATION RATE - EQUATION ON PAGE 77
      C

      DO 58 J = 1,NN
      IF (SV(J,I)) 998,998,999
      998 UCA(J,I) = 0.0
      GO TO 58
      999 IF (SD(I)) 560,560,561
      560 SD(I) = SV(J,I)
      561 UCA(J,I) = (UA(J)*ABF(J,I)*SV(J,I))/(Z(J)*SD(I))
      58 SUM = SUM + UCA(J,I)
      UCA(N2,I) = UFP*X(I)/SD(I) - SUM
      52 CONTINUE

       620 DO 62 J=1,N2
       62 P(J)=-5.0*(J)*10.E-4
       DO 64 I=1,NCMPS
       SUM=UFP*X(I)
       CUM=0.0
       DO 63 J=1,NN
       63 CUM=CUM+O(J+1)*UCA(J,I)
       CUM=CUM+O(I)*UCA(N2,I)
       IF (IMT(I)) 641,641,642
       641 D(I) = 0.0
       GO TO 64

      C CALCULATE CORRECTED COMPONENT DISTILLATION RATE
      C - EQUATION 8-47
      C

       642 D(I)=(-SIG*SDO(I)+1./((XMU*DT)*SUM)/(1.+1./((XMU*DT)*CUM))
       64 CONTINUE
       DO 650 I=1,NCMPS
       DO 65 J=1,NN
DO 67 J=2, N2
USUM(J)=0.0

DO 68 I=1, NCMPS
USUM(J)=USUM(J)+UC01(J-I,I)

C CALCULATE NEWTON-RAPHSON MATRIX - G(J)

67 G(J)=UA(J-1)-USUM(J)
USUM(1)=0.0
DO 69 I=1, NCMPS
USUM(I)=USUM(I)+D(I)
G(I)=DR-USUM(I)
DO 70 JD=I,N2
DO 70 JK=1,N2
RO=O(JK)
O(JK)=O(JK)+P(JK)
DO 640 I=1, NCMPS
SUM=UFP*X(I)
CUM=0.0
DO 630 J=1, NN
CUM=CUM+O(J+1)*UCA(J,I)
CUM=CUM+O(I)*UCA(N2,I)
IF (IMT(I)) 643, 643, 644
PD(I)=0.0
GO TO 640
644 PD(J, I)=(-SIG*SDO(I)+1./(XMU*DT) *SUM)/(1.+1./(XMU*DT) *CUM)
CONTINUE

DO 71 I=1, NCMPS
DO 72 J=1, NN
PCO(J, I)=O(J+1)*UCA(J, I)*PD(J, I)
PCO(N2, I)=O(I)*UCA(N2, I)*PD(J, I)
DO 74 J=2, N2
PSUM(J)=0.0
DO 73 I=1, NCMPS
73 PSUM(J) = PSUM(J) + PCO(J-1, I)
74 AP(J) = PSUM(J) - UA(J-1)

PSUM(I) = 0.0
DO 75 I = 1, NCMPS.
75 PSUM(1) = PSUM(1) + PD(I)

A P(I) = PSUM(1) - DR

C CALCULATE THE PARTIAL DERIVATIVE OF G(JK) WITH
C RESPECT TO O(JD)
C
G P(JD, JK) = (AP(JD) + G(JD))/P(JK)

-70 O(JK) = RO

C SOLVE MATRIX GP*X = G FOR X, WHICH EQUALS DELTA O
C
CALL MTRIX(N2, GP, G, DEL0)
DO 76 J = 1, N2.
76 ON(J) = O(J) + DEL0(J)

DO 77 J = 1, N2

C CHECK FOR CONVERGENCE
C
IF (ABS(ON(J) - O(J)) .GT. 0.01) 77, 77, 78
77 CONTINUE
GO TO 79

78 DO 80 J = 1, N2

C NEGATIVE O IS SET TO 1/2 LAST POSITIVE VALUE
C
IF (ON(J) .LT. 0.0) 280, 280, 281

280 O(J) = O(J)/2.
GO TO 80

281 O(J) = ON(J)

80 CONTINUE
GO TO 620

79 DO 81 J = 1, N2

UA(J) = 0.0

DO 81 I = 1, NCMPS

81 UA(I) = UA(J) + UCO(J, I)

C CALCULATE MOL FRACTION ON PLATE J OF COMPONENT I
C
DO 82 J = 1,N2
DO 82 I = 1,NCMPS
IF (IMT(I)) 821,821,822
821 CX(J,I) = 0.0
GO TO 82
822 CX(J,I) = UCO(J,I)/UA(J)
82 CONTINUE

CALCULATE TEMPERATURES ON EACH PLATE

DO 86 J=1,N2
XCMPS = NCMPS
DUM = 0.0
DO 84 IB = 1,NCMPS
CHECK TO SEE IF COMPONENT HAS BEEN DISTILLED OFF

IF(IMT(IB)) 840,840,841
840 T(J) = 0.0
XCMPS = XCMPS -1.0
GO TO 84
841 SUM = 0
DO 85 I=1,NCMPS
85 SUM=SUM+E(J,I)*CX(J,I)*XK(J,I)/XK(J,IB)
R=1.0/SUM
PV=R*(PTOT(J))
T(J) = A(IB)/(ALOG10(PV)-B(IB)) + 33.0
84 DIJM = DUM + T(J)
86 T(J) = DIJM/XCMPS
DO 830 J=1,N2
DO 630 I=1,NCMPS
630 XK(J,I)=(10.0**((A(I)/(T(J)-33.0)+B(I)))/PTOT(J)
89 Z(I)=DR*RR
DO 500 I=1,NCMPS
500 YEN(I) = CX (1,I)
HXOl = ENTHPY (T(2), 2)
DO 501 I=1,NCMPS
501 YEN(I)=CX(I,I)
SH = ENTHPY(T(I),1)
DO 502 I=1,NCMPS
502 YEN(I) = XCO(1,I)
HXO10= ENTHPY(T(2),2)
DO 503 I=1,NCMPS
503 YEN(I)=XCO(1,I)
SHO=ENTHPY(T0(1),1)
DO 504 I=1,NCMPS
504 YFN(I) = YO(1,I)
HYO1 = ENTHPY(T(2), 2)
HYOO = ENTHPY(T0(2), 2)
QC = Z(I) * (HXO1-SH) + DR *(HXO1-SH) + SIG*(Z0(1)* (H
1XO10 - SHO)+DRO*(HXO1-SHO) -VO(I)*(HYO1-HYOO)- QCO)
2+ UA(I)/(XMU*DT) * (HXO1-SH) -UO(I)/(XMU*DT) *(HXO10-SHO)
DO 401 J=2,NN
DO 505 I=I, NCMPS
505 YEN(I) = CX(I,I)
HXDJ=ENTHPY(T(J+1),2)
DO 506 I=1,NCMPS
506 YEN(I) = YO(J, I)
HYJ = ENTHPY(T(J+1),2)
HYJO = ENTHPY(TO(J+1),2)
DO 507 I=1,NCMPS
507 YEN(I) = XCO(J, I)
HXJO = ENTHPY(T(J+1),2)
SHJO = ENTHPY(T(J+1), 1)
DO 508 I=1,NCMPS
508 YEN(I) = XCO(1, I)
HXDJO = ENTHPY(T(J+1),2)
DO 509 I=1,NCMPS
509 YEN(I) = CX(J, I)
HXOJ = ENTHPY(T(J+1),2)
SHJ = ENTHPY(T(J),1)
DIV = HXO J-SHJ
SIM=0.0
NJ=J
DO 402 K=1,NJ
DO 520 I=1,NCMPS

520 YEN(I)=CX(K,I)
HE1=ENTHPY(T(J+1),2)
HE2=ENTHPY(T(K),1)
DO 521 I=1,NCMPS
521 YEN(I)=XCO(K,I)
HE3=ENTHPY(T(J+1),2)
HE4=ENTHPY(TO(K),1)

402 SUM=SUM+UA(K)*(HE1-HE2)-UO(K)*(HE3-HF4)
C CALCULATE LIQUID FLOW RATES BY ENTHALPY BALANCE

401 Z(J)=(-DR*(HXDJ-SH) +QC +SIG*(V0(J)*(HYJ-HYJO)))/
IDIV + (-ZO(J)*(HXJO-SHJO) -DRO *(HXDJO - SHO) +QCO)/DI
2V-SUM/(XMU*DT*DIV)
C TOTAL MATERIAL BALANCE
SUM=0.0
DO 99 J=1,NN
SUM=SUM+UA(J)-UO(J)
C CALCULATE TOTAL VAPOR FLOW RATES BY TOTAL MATERIAL BALANCE

460 V(J)=Z(J)+DR -SIG*(V0(J)-Z0(J)-DRO)+SUM/(XMU*DT)
DO 100 I=1,NC1
DO 100 J=1,NN
Y(J,I,)=SV(J+1,I)/V(J)
S2(J,I)=SV(J+1,I)
100 SL(J,I)=Z(J)*CX(J,I)
DO 87 J=1,N2
C CHECK FOR CONVERGENCE ON TEMPERATURES

163 IF (ABS (T(J)-AT(J))- .4)87,87,88
87 CONTINUE
GO TO 189
88 DO 90 J=1,N2
90 AT(J)=T(J)
GO TO 162
DO 212 I=1,NCMPS
   SD(I)=CX(1,I)*DR
   UA(N2) = UO(N2) - DR*DT
   IF (IMT(I)) 221,221,222
   DO 223 J = 1,N2
   UFP= UFP+ UA(J)
223 CALCULATE OVERALL COLUMN COMPOSITION
   X(I) =(UFXO(I) -DR*CX(I,I)*DT)/UFP
   GO TO 212
221 X(I) = 0.0
212 CONTINUE
   TIME = TIME + DT
   PRINT 800, TIME, OVERHEAD COMPOSITION AND AMOUNT
   PRINT 802, AMOUNT
   DO 409 J = 1,N2
   UO(J) = UA(J)
409 DO 310 J=1,NN
   T20(J)=TO(J)
   V20(J)=VO(J)
   TO(J)=AT(J)
   AT(J)=T(J)
   Z0(J)=Z(J)
310 VO(J)=V(J)
   T20(N2)=TO(N2)
   TO(N2)=AT(N2)
   AT(N2)=T(N2)
314 DO 309 I=1,NCMPS
   DO 309 J = 1,N2
   YO(J,I)=Y(J,I)
   XCO(J,I)=CX(J,I)
309 QC0=QC
   DRO=DR
   AMOUNT = DR*DT*136.42
   PRINT 802, AMOUNT
UF = UFP
C CHECK FOR END OF RUN
C IF ((UFO-UF)/UFO-PC DT) 311,311,312
311 DO 330 I=1,NCMPS
X(I) = X(I)
C CHECK TO SEE IF COMPONENT HAS BEEN DISTILLED OFF
IF (X(I)-.001) 320,321,321
320 IF(IMT(I)) 322,322,323
321 SDO(I) = S D(I)
322 SDO(I) = S D(I)
323 IMT(I) = 0
X(I) = 0.0
SDO(I) = SD(I)
GO TO 330
321 SDO(I) = S D(I)
330 CONTINUE
DT = UFO/(DR* 50.)
GO TO 162
C PRINT - BOTTOMS COMPOSITION
C 312 WRITE (6,803)
WRITE (6,800) TIME,(X(I),I=1,NCMPS)
GO TO 200
201 CALL EXIT
700 FORMAT (1H ,7E14.8)
701 FORMAT (21H START PRODUCT PERIOD)
800 FORMAT (9F14.3)
801 FORMAT(32H ANSWER-TIME AND TOP COMPOSITION)
802 FORMAT (9H AMOUNT =,F10.3)
803 FORMAT (16H END COMPOSITION)
900 FORMAT (8F10.0)
901 FORMAT (212)
END
FUNCTION ENTHPY( T, IVAP)  
C THIS ROUTINE CALCULATES THE ENTHALPY OF A VAPOR OR LIQUID  
C AT TEMPERATURE T IN DEGREES K, BY THE SUM OF ENTHALPIES OF  
C THE PURE COMPONENT TIMES THE MOLE FRACTION  
C  
DIMENSION UL(8), WL(8), VL(8), VK(8), YEN(8)  
COMMON YEN, WL, UL, VL, VK, NCMPS  
Q = T * 1.8  
ENTHPY = 0.0  
IF (IVAP - 1) .EQ. 2, 2, 1  
1 DO 3 I = 1, NCMPS  
3 ENTHPY = ENTHPY + (WL(I) + UL(I) * Q) * YEN(I)  
RETURN  
2 DO 4 I = 1, NCMPS  
4 ENTHPY = ENTHPY + (VL(I) + VK(I) * Q) * YEN(I)  
RETURN  
END
SUBROUTINE MTRIX (N,A,B,X)
C
THIS ROUTINE SOLVES THE MATRIX AX=B FORX
C
WHERE A IS N BY N AND -B IS N BY 1
C
GAUSSIAN ELIMINATION IS USED WITH PIVOTAL COMPENSATION
C

DIMENSION A(54,54),B(54),X(54)
K = 1
4 I = K +1
L = K
99 IFABS (A(I,K)) -ABS (A(L,K))) 100,100,101
100 L=I
100 IF(I-N) 102,103,103
102 I= I+1
GO TO 99
103 IF(L- K) 104,104,105
104 J=K
108 CON = A(K,J)
A(K,J) = A(L,J)
A(L,J) = CON
IF(J- N) 106,107,107
106 J=J+1
GO TO 108
107 CON = B(K)
B(K) = B(L)
B(L) = CON
105 I=K+1
5 Y = A(I,K)/A(K,K)
A(I,K) = 0.0
J = K +1
80 A(I,J) = A(I,J) -Y*A(K,J)
IF (J-N) 8,9,9
8 J = J +1
GO TO 80
9 B(I) = B(I) -Y*B(K)
IF(I-N) 10,11,11
10 I = I + 1
   GO TO 5
11 IF ( K-(N-1) ) 12,13,13
12 K = K+1
   GO TO 4
13 X(N) = B(N)/A(N,N)
   I = N-1
19 J = I + 1
   S = 0.0
16 S = S+A(I,J)*X(J)
   IF(J-N) 14,15,15
14 J = J+1
   GO TO 16
15 X(I) = (B(I)-S)/A(I,I)
   IF (I-I) 17,17,18
18 I = I-1
   GO TO 19
17 RETURN
END
TABLE VII
DEFINITION OF VARIABLES USED IN SIMULATION PROGRAM

A(I) = Constant for calculation of the vapor pressure of component I: \( \log P = A + B/T. \)

ABF(J) = Absorption factor for plate J.

AT(J) = Assumed value of the temperature of the liquid leaving plate J.

AV(J) = Jth diagonal element of the matrix resulting from the component material balance.

B(I) = Constant for calculation of the vapor pressure of component I: \( \log P = A - B/T. \)

BV(J) = Jth subdiagonal element of the matrix resulting from the component material balance.

CV(J) = Jth superdiagonal element of the matrix resulting from the component material balance.

CX(J,I) = Mole fraction of component I in the liquid leaving plate J.

D(I) = Molal flow rate of component I in the distillate.

DELT0(J) = Jth incremental change in \( \Delta \theta. \)

DV(J) = Jth element of the vector resulting from the component material balance.

E(J,I) = Instanteous value of vapor efficiency on plate J for component I.

FV(J) = Jth constant that appears in reversion formulas used to solve the component material balance.

G(J) = the Jth function of the \( \theta \)s.

GP(JK,JD) = The partial derivative of \( G(JK) \) with respect to \( \theta(JD) \).

GV(J) = The Jth constant that appears in recursion formula used to solve component material balance.
(Variables used in Simulation Program)

I = Compound index.
IMT(I) = Switch setting to indicate the absence or presence of compound I in the column.
J = Plate index.
O(J) = Multiplier associated with plate J.
P(J) = Constant for calculation of the partial derivative with respect to O(J).
RR = Reflux ratio for operating the column.
SL(J,I) = Molal flow rate at which component I in liquid phase leaves plate J.
SV(J,I) = Molal flow rate at which component I in vapor phase leaves plate J.
T(J) = Temperature of the liquid leaving plate J.
TC(J) = Critical temperature of compound I.
TO(J) = Value at the beginning of the time increment of the temperature of the liquid leaving plate J.
TOU(J) = Dimensionless time factor for plate J.
UA(J) = Assumed value of the molal holdup on plate J.
UO(J) = Value at the beginning of the time increment of the molal holdup on plate J.
UCA(J) = Calculated value of the ratio of molal holdups of component I on plate J to that of the calculated value of the ratio of molal holdup of component I on plate J to the component distillation ratio for unsteady state calculations.
UCO(J,I) = Corrected value of liquid molar holdup of component I on plate J.
UL(I) = Constant for calculation of the enthalpy of component I in liquid phase.
(Variables used in Simulation Program)

\[ V(J) = \text{Total molal flow rate of vapor leaving plate } J. \]

\[ VK(J) = \text{Constant for calculation of the enthalpy of component I in vapor phase.} \]

\[ VL(I) = \text{Constant for calculation of the enthalpy of component I in vapor phase.} \]

\[ VO(J) = \text{Value at the beginning of the time increment of the total molal flow rate of vapor leaving plate } J. \]

\[ WL(I) = \text{Constant for calculation of the enthalpy of component I in liquid phase.} \]

\[ X(I) = \text{Total mole fraction of component I, in the column.} \]

\[ XCO(J, I) = \text{Value at the beginning of time increment of mole fraction of component I on plate } J. \]

\[ XK(J, I) = \text{Equilibrium constant for component I on plate } J. \]

\[ XLHV(I) = \text{Latent heat of vaporization of component I.} \]

\[ Y(J, I) = \text{Mole fraction of component I in vapor leaving plate } J. \]

\[ YO(J, I) = \text{Value at the beginning of the time increment of the mole fraction of component I in vapor leaving plate } J. \]

\[ Z(J) = \text{Total molal flow rate of liquid leaving plate } J. \]

\[ ZO(J) = \text{Value at the beginning of the time increment of the total molal flow rate of liquid leaving plate } J. \]
TABLE VIII

TYPICAL INPUT DATA FOR SIMULATION OF A BATCH COLUMN
<table>
<thead>
<tr>
<th>TABLE HOERNER WALDORF CRUDE INPUT DATA</th>
</tr>
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<table>
<thead>
<tr>
<th>NUMBER OF COMPOUNDS, PURITIES PER COMPOUND, NUMBER OF REFLUX RATIOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 4 1 1 1 1 4</td>
</tr>
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<table>
<thead>
<tr>
<th>TOTAL CHARGE</th>
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<tr>
<td>408.</td>
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</table>

<table>
<thead>
<tr>
<th>PERCENT DISTILLED PRECEDING THE CUT AT PURITY 1</th>
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<tbody>
<tr>
<td>3n TO 1</td>
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<tr>
<td>.738</td>
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<tr>
<td>.546</td>
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<tr>
<td>.422</td>
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<td></td>
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</table>

<table>
<thead>
<tr>
<th>PERCENT DISTILLED SUCCEEDING THE CUT AT PURITY 1</th>
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<tr>
<td>3n TO 1</td>
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<tr>
<td>.701</td>
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<table>
<thead>
<tr>
<th>REFLUX RATIOS</th>
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<tr>
<td>3n</td>
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<table>
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<th>PRICE DATA IN DOLLARS PER POUND</th>
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<td>976</td>
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<tr>
<td>1359</td>
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<td>150</td>
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<table>
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<th>PURITIES OF EACH COMPOUND</th>
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<td>85.0</td>
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<tr>
<td>95.0</td>
</tr>
<tr>
<td>Bottoms Product</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>Bottoms Product</td>
</tr>
<tr>
<td>Boil Up Rate, Cost of Bottoms</td>
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<tr>
<td>Time (10 runs per year)</td>
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</table>

TABLE (CONTINUED) 
COST DATA INCLUDES OPERATING COST, BOIL UP RATE, COST OF BOTTOMS AND NUMBER OF RUNS PER YEAR.
TABLE IX

TYPICAL OUTPUT OF SIMULATION PROGRAM
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<th>CMP. NO.</th>
<th>1</th>
<th>2</th>
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<td>0.012</td>
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</tr>
</tbody>
</table>

END OF RUN
TABLE X

PROGRAM LIST OF OPTIMIZATION PROGRAMS
MAINLINE

THIS ROUTINE SERVES AS AN EXECUTIVE ROUTINE, READS DATA AND SETS INDEXES.

DIMENSION IPT(IO), IORIN(4,4), PDT(16,4,2), XMID(16,4,4), RR(4), PP(14,4), PUR(4,4), FX(16,16), DMAX(16), IORD(16,16), AMOT(8), RSR(8), OPER1(2,8), OPER2(8,8), ANS(5,5), IE(40,8), ICM(4)

DIMENSION TMOT(8), TSR(8)

DIMENSION H(I20)

COMMON ISENT, ICMP, IPT, IRR, TOTAL, IORIN, PDT, XMID, RR, PP, PUR, OC, IBUR, CB, CDBR, AMOUNT, AVERR, RTN, FX, DMAX, IORD, FMAX, INP, AMOT, RSR, OPER1, OPER2, ANS, IE, ICM, IMD, RYEAR, IPM

READ 851, ISENT

DEFINE DISK(20,2000)

SPACEING OF THE PAGE FOR PRINTING OUT INPUT DATA

READ - ISENT - BLANK = END OF JOB, POSTIVE NUMBER= NEW JOB

PRINT 800

DO 1000 I = 1,10

1000 PRINT 804

IF(ISENT)100,100,101

CALL DECP PRINTER HEADINGS FOR INPUT DATA

101 CALL DECP

READ - NUMBER OF STAGES - ICMP

- NUMBER OF PURITIES PER STAGE - IPT(I)

- NUMBER OF REFUX RATIO'S - IRR

READ 851, ICMP, (IPT(I),I=1, ICMP), IRR

PRINT851, ICMP, (IPT(I),I=1, ICMP), IRR

CALL DECP

READ - TOTAL POUND OF CHARGE

READ 802, TOTAL

PRINT 802, TOTAL

SORT FOR MAXIMUM PURITIES ON ALL STAGES
C
IPMX=1
DO 2 I=1,ICMP
IF (IPT(I)-IPMX) 2,2,3
3, IPMX=IPT(I)
2 CONTINUE
C
GENERATE INDEX FOR PURITY AND REFLUX RATIO
C
IANT=0
DO 6 IP=1,IPMX
DO 7 I=1,IRR
7 IORIN(IP,I) =I+IANT
IANT=IANT+IRR
6 CONTINUE
C
READ - DISTILLATION DATA - PDT (J,IK, 1) = PERCENTAGE PRIOR
C - PDT (J,IK, 2) = PERCENTAGE FOLLOWIN
C
DO 1 K=1,2
CALL DECP
C
IK = STAGE NUMBER, J = REFLUX RATIO-PURITY INDEX
C
DO 1 IK=1,ICMP
IPM=IPT(IK)
DO 1 IP=1,IPM
NBF=IORIN(IP,1)
NBG=IORIN(IP,IRR)
READ 802,(PDT(J,IK,K),J=NBF,NBG),(H(M),M = 1,20)
1 PRINT802,(PDT(J,IK,K),J=NBF,NBG),(H(M),M = 1,20)
C
DETERMINE AMOUNT OF MIDFRACTION FOR EACH INPUT AND DECISION
C
DO 4 IS = 1,ICMP
DO 4 IK=1,IRR
IPM=IPT(IS)
DO 4 IP=1,IPM
I=IORIN(IP,IK)
DO 4 IPP=1,IPM
ID=IORIN(IPP,IK)
IF(PDT(ID,IS,2)) 12,13,13
4 730
13 IF(IS-1) 14,14,15
14 XMID (I,IPP,IS)=(1.00-PDT(ID,IS,2))*TOTAL
GO TO 4
15 IF(PDT(I;IS-1,1)) 16,17,17
16 ISM= IS
17 XMID(I,IPP,IS)=(PDT(I,IS-1,1)-PDT(ID,IS,2))*TOTAL
GO TO 4
18 IF(PDT(I,ISM-1,1))160,21,21
21 XMID(I,IPP,IS)=(PDT(I,ISM-1,1)-PDT(ID,IS,2))*TOTAL
GO TO 4
12 XMID(I,IPP,IS)=0.0
4 CONTINUE
CALL DECP
READ-VALUES FOR THE REFLUX RATIOS TO BE EVALUATED
CALL DECP
READ 802,(RR(I),I=1,IRR)
PRINT 802,(RR(I),I=1,IRR)
CALL DECP
READ-PRICES AT VARIOUS PURITIES FOR EACH STAGE
DO 10 IK=I,ICMP
IPM=IPT(IK)
READ 801,(PP(I,IK),I=1,IPM),(H(M),M=1,20)
10 PRINT801,(PP(I,IK),I=1,IPM),(H(M),M=1,20)
CALL DECP
READ-PURITIES OF COMPOUNDS TO BE EVALUATED
DO 11 IK=I,ICMP
IPM=IPT(IK)
READ 801,(PUR(I,IK), I=1,IPM),(H(M),M=1,20)
11 PRINT801,(PUR(I,IK), I=1,IPM),(H(M),M=1,20)
CALL DECP

READ-COST DATA-HOURLY OPERATING COST-OC
  - BOIL UP RATE - BUR
  - COST OF BOTTOMS - CB
  - NUMBER OF RUN/YEAR - R YEAR

READ 802,OC,BUR,CB,RYEAR
PRINT 802,OC,BUR,CB,RYEAR
PRINT 901
NQ = ICMP*2
READ-HEADING CARDS - 2 PER STAGE - 40 COLUMNS/CARD
  - IE(J,1) = BOTTOMS -
  - IE(J,2) = STAGE 1 -
  - IE(J,3) = MIDFRACTION BETWEEN STAGE 1 AND 2 -
  - ... ...
  - IE(J,2N-1) = MIDFRACTION BETWEEN STAGE N-1 AN N -
  - IE(J,2N) = STAGE N-

DO 5 I = 1,NQ
  5 READ 900,(IE(J,1),J=1,20)
  PRINT 800
  CALL ROUTINES FOR OPTIMIZATION
  CALL DPMOD
  CALL SORT
  CALL EDIT
  GO TO 102
800 FORMAT(1H1)
802 FORMAT(4F10.4,20A2)
801 FORMAT(4F10.3,20A2)
804 FORMAT(1H )
851 FORMAT( 6I 3)
901 FORMAT(15H END OF DATA)
902 FORMAT(15H END OF RUN )
100 PRINT902
900 FORMAT(20A2)
CALL EXIT
END
SUBROUTINE DPMOD

SUBROUTINE DPMOD—DYNAMIC PROGRAMMING MODEL

THIS ROUTINE DETERMINES THE VALUES OF THE OBJECTIVE

FUNCTION, SORTS AND DETERMINES OPTIMUM DECISIONS

DIMENSION IPT(10), IORIN(4,4), PDT(16,4,2), XMID(16,4,4), RR(4,14,4), PUR(4,4), FX(16,16), DMAX(16), IORD(16,16), AMOT(8), RSR(8), OPER1(2,8), OPER2(8,8), ANS(5,5), IE(40,8), ICM(4)

DIMENSION TMOT(8), TSR(8)

COMMON /SENT/ ICMP, IPT, IRR, TOTAL, IORIN, PDT, XMID, RR, PP, PUR, OC, IBUR, CB, CDBR, AMOUNT, AVERR, RTN, FX, DMAX, IORD, FMAX, INP, AMOT, RSR, OPER1, OPER2, ANS, IE, ICM, IMD, RYEAR, IPM

CDENR = OCZBUR + I 150
IZ = 1

CYCLE THROUGH ALL THE StAGES, NUMBER OF COMPONENTS

DO 2IS=I, ICMP

SET NUMBER OF PURITIES FOR THE COMPOUND

IPM=IPT(IS)

CYCLE THROUGH ALL INPUTS—REFLUX RATIOS—PURITIES

DO IRR=I, IRR
DO 1IP=1, IPM

SET INDEX FOR INPUT COMBINATION—I

I=IORIN(IP, IRR)

CHECK TO SEE IF PRODUCT AT INPUT CONDITIONS

IF (PDT(I, IS, I)) 21, 19, 22

19 I = IORIN(IP, IRR)
GO TO 22

21 ISM=IS

CYCLE THROUGH ALL DECISIONS—WITH NO SUITABLE INPUT
C
DO 111 IDD=1,IRR
DO 111 IPS=1, IPM
TO = IORD(IP, IR)
ID = IORD(IPS, IR)
C
SORT TO SEE IF THIS IS TO BE CONSIDERED A STAGE
C
IF(PDT(I, IS+1, 2)) 23, 26, 26
23 RTN = 0.0
IF(IS-1) 200, 200, 201
200 FX(I, IO) = RTN
GO TO 110
26 IF(ISM-1) 28, 28, 29
29 IF(PDT(I, ISM-1, 1)) 24, 25, 25
24 ISM = ISM - 1
GO TO 26
C
DETERMINE RETURN FOR STAGE 1
C
28 RTN = XMIN(ID, IPS, IS) * CB
FX(I, IO) = RTN
GO TO 110
C
DETERMINE FOR STAGE 2....N
C
25 RTN = XMIN(ID, IPS, IS) * CDGR * (RR(IR) + 1.0
C
FIND INDEX FOR OPTIMUM DECISION FOR STAGE IS-1, INPUT IO
C
201 K = IORD(IO, IS-1)
C
FIND LOCATION OF DECISION ON DISK FILE
C
IFF = (IS-2) * (IPM*IRR*IPM*IRR) + (IO-1) * IPM*IRR + K
FIND(IFF)
C
FETCH OPTIMUM DECISION STAGE IS-1, INPUT IO
C
FETCH(IFF) FOFX, TMOUNT, TVERR, IW, IX, IMB, (TMOT(J), TSR(J), J=1, IMB)
FX(I, IO) = FOFX + RTN
110 IMD = 1
AMOUNT = 0.
AVERR = RP(IR)
AMOT(1) = 0.
RSR(1) = RR(IR)
C RECORD OPTIMUM DECISION STAGE IS, INPUT I
C RECORD (IZ) FX(I,IO),AMOUNT,AVERR,IR,IP,IMD,(AMOT(J),RSR(J),J=1,IM
ID)
111 PRINT 900,I,IS,ID,IO,FX(I,IO),RTN
GO TO 1
C CYCLE THROUGH ALL DECISIONS WITH SUITABLE INPUT
C 22 DO 10IDD=1,IRR
DO 10IPS=1,IPM
C SET INDEX ON DECISION-FINIAL REFLUX RATIO-AND
C INPUT PURITY STAGE IS-1
C IO= IORIN(IPS,IDD)
ID=IORIN(IP,IDD)
C CHECK TO SEE IF DECISION IS VALID FOR INPUT
C IF(PDT(ID,IS,2))30,30,31
30 AVERR = RR(IDD)
ISM = IS
AMOUNT = 0.0
IMD = 1
AMOT(1) = 0.0
RSR(1) = RR(IR)
300 ISM = ISM+ 1
C SORT TO SEE IF COMPOUND SHOULD BE CONSIDERED A STAGE
C IF(PDT(ID,ISM,2)) 300,300,301
301 ISN = IS
304 IF(PDT(ID,ISN,1))302,302,303
302 ISN = ISN -1
IF (ISN) 305,305,304
305 XMID(IO,IP,ISN+1) = XMID(IO,IP,ISM) - TOTAL*(PDT(I-ISJ)-PDT(ID,ISM,12))
C DETERMINE RETURN FOR IMPROPER DECISION
C
RTN = -CB*XMID(IO,IP,ISN+1)
FX(I,IO) = RTN
GO TO 121
303 XMID(IO,IP,IS) = XMID(IO,IP,ISM) - TOTAL*(PDT(I-IS,1)-PDT(ID,ISM,2))
GO TO 32
31 CALL RRORPT(I,ID,IS,IR,IP)
ISZ = IS
311 ISZ = ISZ-1
IF(ISZ) 11,11,312
312 IF(PDT(ID,ISZ,1)) 311,311,12
RETURN FOR STAGE 1
C
11 RTN = PP(IP,IS)*AMOUNT-CDBR*AMOUNT*(AVERR+1.1)-XMID(IO,IP,IS)*C B
FX(I,IO) = RTN
GO TO 121
RETURN FOR STAGE 2...N
C
12 RTN = PP(IP,IS)*AMOUNT-CDBR*AMOUNT*(AVERR+1.1)-XMID(IO,IP,IS)*C B
IRR(TDD)+1.)*CDBR
DETERMINE INDEX FOR OPTIMUM DECISION STAGE IS-1 INPUT IO
C
203 K=IORD(IO,IS-1)
C FIND LOCATION OF DECISION ON DISK FILE
C
.IFF = (IS-2) * (IPM*IRR*IPM*IRR) +(10-1)*IPM*IRR +K
C FETCH OPTIMUM DECISION STAGE IS-1 INPUT ID
C
FETCH(IFF) FOFX,TMOUNT,TVERR,1W,IX,IMB,(TMOT(J),TSR(J),J=1,IMB)
FX(I,IO) = FOFX + RTN
121 PRINT 900,I,IS ,ID,IO,FX(I,IO) ,RTN
C RECORD OPTIMUM DECISION DECISION STAGE IS INPUT I
C
10 RECORD (IZ) FX(I,IO),AMOUNT,AVERR,IDD,IP,IMD,(AMOT(J),RSR(J),J=1,IMD)
1 CONTINUE
C SORT FOR MAXIMUM VALUE OF OBJECTIVE FUNCTION FOR EACH I
C
DO 3 IR=I,IRR
DO 3 IPS=I,IPM
IF(IS=ICMP)51,50,50
50 I = IORIN(IPS,IRR)
GO TO 52
51 I = IORIN(IPS,IR)
52 IF (PDT(I,IS,1))40,41,41
40 IORD(I,IS) = I
DMAX(I) = FX(I,I)
GO TO 3
C STORE MAXIMUM VALUE OF FX(I,IO) FOR ALL I IN DMAX(I)
C
41 DMAX(I) = FX(I,1)
IORD(I,IS)=1
IKK=IRR*IPM     -1
DO 3 ID=1, IKK
IF(FX(I,ID+1)-DMAX(I)) 3,3,4
4 IORD(I,IS)=ID+1
DMAX(I)= FX(I,ID+1)
3 CONTINUE
2 CONTINUE
C SORT FOR OPTIMUM INPUT TO STAGE N AND STORE IN FMAX
C
INP= IRR
FMAX = DMAX(INP)
IPM=IPT(ICMP)
IF(IPM-1) 7,7,8
8 DO 5 IP=2,IPM
IW=IORIN(IP,IRR)
IF(FMAX=DMAX(IW))5,5,6
6 INP=IW
FMAX=DMAX(IW)
5 CONTINUE
7 RETURN
900 FORMAT(IH,4I2,2F10.2)
END

SUBROUTINE SORT
C THIS ROUTINE RETURNS OPTIMUM DECISIONS FROM DISK FILE
C STARTING WITH OPTIMUM INPUT TO STAGE N, PROCEEDING TO 1
C DECISION ARE STORED IN ANS, OPER1 AND OPER2 ARRAYS
DIMENSION IPT(10), IORIN(4,4), PDT(16,4,2), XMD(16,4,4), RR(4,14,4), PUR(4,4), FX(16,16), DMAX(16), IORD(16,16), AMOT(8), RSR(8), OPER1(2,8), OPER2(8,8), ANS(5,5), IE(40,8), ICM(4)

DIMENSION TMOT(8), TSR(8)
DIMENSION H(20)
COMMON SSENT, ICMP, IPT, IRR, TOTAL, IORIN, PDT, XMD, RR, PP, PUR, OC, IRR, CB, CDAR, AMOUNT, AVERR, RTN, FX, DMAX, IORD, FMAX, INP, AMOT, RSR, OPER1, OPER2, ANS, IE, ICM, IMD, RYEAR, IPM

IS=ICMP
INDF.N ON OPTIMUM DECISION WITH OPTIMAL INPUT-INPUT

3 K=IORD(INP, IS)

3 IF(IS-1) = (IPM*IRR*IPM*IRR)+(INP-1)*IPM*IRR +K

3 FETCH(IF(IS)) FOFX, AMOUNT, AVERR, IR, IX, IMD, (AMOT(I), RSR(I), I=1, IMD)

3 ANS(1, IS)=AMOUNT
3 ANS(2, IS)=AVERR
3 ANS(3, IS)=XMD(K, IX, IS)
3 ANS(5, IS)=RR(IR)
3 ANS(4, IS)=PUR(IX, IS)
3 ICM(IS)=IMD
3 DO 100 M=1, IMD
3 OPER1(IS, M) = AMOT(M)
3 OPER2(IS, M) = RSR(M)
3 CHECK TO SEE IF STAGE 1 HAS BEEN COMPLETED
3 YFS=RETURN TO MAIN LINE
3 NO-DECREASE STAGE COUNT BY 1, CONTINUE
3 IF(IS-1) = 1, 1, 2
3 IS=IS-1
3 INP = K
3 GO TO 3
3 RETURN
3 END
SUBROUTINE DECP

TOURMINE DECP-DESCRIPTION-

THIS ROUTINE PRINTS HEADING CARDS FOR INPUT DATA

RETURN CONTROL TO MAINLINE

DIMENSION A(20)

READ 900, IA, (A(I), I=1, 20)

PRINT 901, (A(I), I=1, 20)

IF (IA) 1, 1, 2

RETURN

900 FORMAT (I1, A3, 19A4)

901 FORMAT (A3, 19A4)

END
SUBROUTINE EDIT

C    SUBROUTINE EDIT .  2 C
C    THIS ROUTINE EDITS BOTH THE SUMMARY AND OVERALL SUMMARY 3C
C    OF OPTIMUM OPERATING CONDITIONS  .  S C
C
DIMENSION IPT(10), IORIN(4,4), PDT(16,4,2), XMID(16,4,4), RR(4 8C
14,4), PUR(4,4), FX(16,16), DMAX(16), IORD(16,16), AMOT(8), RSR(8), OPER1 9C
2(8, 8), OPER2(8,8), ANS(5,5), IE(40,8), ICM(4)
C
DIMENSION TMOT(8), TSR(8)
C
DIMENSION H(20)
C
COMMON ISENT, ICMP, IPT, IRR, TOTAL, IORIN, PDT, XMID, RR, PP, PUR, OC, 13C
1BUR, CB, CBDR, AMOUNT, AVERR, RTN, FX, DMAX, IORD, FMAX, INP, AMOT, RSR, OPER1, 14C
2 OPER2, ANS, IE, ICM, IMD, RYEAR, IPM
C
TIME = 0.0 ISC
C
PRINT OUT SUMMARY

C
PRINT 900
DO 10 I = 1, 10
10 PRINT 902
PRINT 901
PRINT 902
PRINT 9002
I = ICMP
3 II = 2*I
30 PRINT 903, (IE(J, II), J=1,20), ANS(1, I), ANS(4, I), ANS(2, I)
40 IF(I-I) 2,2,1
1 II = II - 1
PRINT 905, (IE(J, II), J=1,20), ANS(3, I), ANS(5, I)
1 I = I - 1
GO TO 3
2 PRINT 906, (IE(J, I), J=1, 20), ANS(3, I)
C
PRINT OUT DETAILED SUMMARY
C
PRINT 900
DO 11 I = 1,10.
11 PRINT 902
PRINT 907
TIME=0.0
PRINT 908
PRINT 902
IS=ICMP
50 NN = ICM(IS)
DO 5 N=I,NN.
51 TIM=OPER1(IS,N)/(BUR/(OPER2(IS,N)+1.))
PRINT 909,TIME,OPER2(IS,N),OPER1(IS,N)
TIM=TIME+TIM
5 TIME=TIME+TIM
60 NQ = 2 * IS
PRINT 910, (IE(I,NQ),I=1,20)
IF (IS=1) 6,6,7
7 TIM=ANS(3,IS)/(BUR/(ANS(5,IS)+1.))
PRINT 909,TIME,ANS(5,IS),ANS(3,IS)
TIM=TIME+TIM
.NQ=NQ-1
PRINT 910, (IE(I,NQ),I=1,20)
IS=IS-1
GO TO 50
6 PRINT 911, ANS(3,IS),TIME
GYEAR=FMAX*RYEAR
PRINT 912,FMAX,GYEAR
900 FORMAT (1H1)
901 FORMAT (38H SUMMARY OF OPTIMUM RUNNING CONDITIONS)
902 FORMAT (1H )
9002 FORMAT (16X,7HPRODUCT,19X,16HAMOUNT IN POUNDS,5X,35H AVERAGE PURITY 1 AVERAGE REFLUX RATIO)
903 FORMAT (20A2, F13.2,15X,F6.1,13X,F6.1,5H TO 1)
905 FORMAT(20A2,F13.2,15X,4H****,13X,F6.1,5H TO 1)
906 FORMAT(20A2,F13.2,15X,4H****,13X,10H**********)
907 FORMAT(47H DETAILED SUMMARY OF OPTIMUM RUNNING CONDITIONS)
908 FORMAT( 3X,13HTIME IN HOURS,6X,12HREFLUX RATIO,12X,6HAMOUNT)
909 FORMAT( F12.2,16X,F6.1,5H TO 1,8X,F7.2)
910 FORMAT( 8X END OF,20A2)
911 FORMAT( 14H END OF RUN , F13.2,32H POUNDS OF BOTTOMS TIME OF R 1UN,F13.2)
912 FORMAT( 21H GROSS PROFIT PER RUN,F13.2,9HPER YEAR ,F14.2)
RETURN
END

SUBROUTINE RROPT( L,M,N,IPI)
DIMENSION IPT(10),IORIN(4,4),PDT(16,4,2),XMID(16,4,4),RR(4 ),PP( 14,4), PUR(4,4),FX(16,16),DMAX(16),IORD(16,16),AMOT(8),RSR(8),OPER1( 2(8, 8),OPER2(8,8),ANS(5,5),IE(40,8),ICM(4)
DIMENSION ISENT,ICMP, IPT, IRR,TOTAL, IORIN, PDT, XMID, RR, PP, PUR, OC, 1BUR, CB, CDBR, AMOUNT, AVERRR, RTN, FX, DMAX, IORD, FMAX, INP, AMOT, RSR, OPER1, 2 OPER2, ANS, IF, ICM, IMD, RYEAR, IPM
COMMON ISENT,ICMP, IPT, IRR, TOTAL, IORIN, PDT, XMID, RR, PP, PUR, OC, 1BUR, CB, CDBR, AMOUNT, AVERRR, RTN, FX, DMAX, IORD, FMAX, INP, AMOT, RSR, OPER1, 2 OPER2, ANS, IF, ICM, IMD, RYEAR, IPM
SUBROUTINE PROPT-REFLUX RATIO OPERATOR-

THIS ROUTINE DETERMINES AMOUNT AND FOR A GIVEN INPUT (L) AND DECISION(M)
REFLUX.RATIO CHANGES BETWEEN INPUT AND DECISION ARE DETERMINE AND STORED IN THE RSR ARRAY
THE AMOUNT OF PRODUCT FOR INTERMEDIATE REFLUX RATIO CHANGE IS CALCULATED AND STORED IN THE AMOT ARRAY
IMD IS THE NUMBER OF CHANGES OCCURRING IN EACH FRACTION
I = L
ID = M
IS = N
TIME = 0.0
IP = IPI
IMD = 0
IZ = IRI
IF (PDT(I, IS, I)) 11, 11, 12
11 IZ = IRR
12 IF (I-IRR*IP) 1, 13, 13
13 K = I
KZ = IZ
GO TO 14.
1 IF (PDT(I+1, IS, I)) 4, 8, 8
8 AMT = (PDT(I+1, IS, I) - PDT(I, IS, I)) * TOTAL
TIME = AMT / (BUR / (RR(IZ)+1.))
IMD = IMD + 1
AMOT(IMD) = AMT
RSR(IMD) = RR(I)
TIME = TIME + TIME1
IF (I-IRR*IP+1) 2, 3, 3
2 I = I+1
IZ = IZ + 1
GO TO 1
3 K = I+1
KZ = IZ + 1
14 IF (K-ID) 6, 24, 24
4 K = I
KZ = IZ
24 AMT = (PDT(K, IS, 2) - PDT(K, IS, 1)) * TOTAL
TIME1 = AMT / (BUR / (RR(KZ)+1.))
IMD = IMD + 1
AMOT(IMD) = AMT
RSR(IMD) = RR(KZ)
TIME = TIME + TIME1
5 IF (K-ID) 6, 6, 7
7  K  =  K-1
   KZ  =  KZ - 1
   AMT  =  (PDT(K,IS,2)-PDT(K+1,IS,2))*TOTAL
   TIME1  =  AMT/(BUR / (RR(KZ)+1.))
   TIME  =  TIME + TIME1
   IMD  =  IMD +1
   AMOT(IMD)  =  AMT
   RSRR(IMD)  =  RR(KZ)
   GO TO 5
   C  CALCULATE AMOUNT
   C
   6  AMOUNT  =  0.0
   DO 10  JJ = 1,IMD
   10  AMOUNT  =  AMOUNT + AMOT(JJ)
   C  CALCULATE THE TIME AVERAGED REFLUX RATIO
   C
   ARR  =  AMOUNT/(BUR*TIME)
   ARR  =  1./ARR
   AVERR  =  ARR -1.0
   C  RETURN TO DPMOD
   C
   RETURN
   END
TABLE XI
DEFINITION OF SYMBOLS IN OPTIMIZATION PROGRAM

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMOT(I)</td>
<td>The amount of product obtained at I intermediate reflux ratio.</td>
</tr>
<tr>
<td>AMOUNT</td>
<td>Total pounds of product for the stage.</td>
</tr>
<tr>
<td>ANS(K,I)</td>
<td>Optimum decision I for stage K.</td>
</tr>
<tr>
<td>AVERR</td>
<td>Average reflux ratio for the stage.</td>
</tr>
<tr>
<td>BUR</td>
<td>Boil up rate -- pounds/hour.</td>
</tr>
<tr>
<td>CB</td>
<td>Cost of bottoms product -- $/pound.</td>
</tr>
<tr>
<td>CDBR</td>
<td>Operating cost divided by boil up rate.</td>
</tr>
<tr>
<td>DMAX(I)</td>
<td>Maximum value of objective function over all decisions with an input I.</td>
</tr>
<tr>
<td>FX(I,J)</td>
<td>Value of the objective function for input I and decision J.</td>
</tr>
<tr>
<td>ICM(K)</td>
<td>Number of intermediate reflux ratio changes for stage K.</td>
</tr>
<tr>
<td>ICMP</td>
<td>Number of stages to be considered.</td>
</tr>
<tr>
<td>IE(J,I)</td>
<td>Heading for editing of fraction I, J equals the word number.</td>
</tr>
<tr>
<td>INP</td>
<td>Optimum input for the stage.</td>
</tr>
<tr>
<td>IORIN(I,J)</td>
<td>Index associated with purity I and reflux ratio J.</td>
</tr>
<tr>
<td>IORD(I,K)</td>
<td>Index on optimum decision for input I and stage K.</td>
</tr>
<tr>
<td>IRR</td>
<td>Number of reflux ratios to be evaluated</td>
</tr>
<tr>
<td>ISENT</td>
<td>Sentinal indicating beginning or ending of a job.</td>
</tr>
<tr>
<td>OC</td>
<td>Hourly operating cost -- $/hour.</td>
</tr>
</tbody>
</table>
OPER1(K,I)  Optimum reflux ratio I for stage K.
OPER2(K,I)  Optimum amount I for stage K.
PDT(I,K,1)  Weight fraction distilled preceding stage K for index, purity and reflux ratio, I.
PDT(I,K,2)  Weight fraction distilled following stage K for index, purity and reflux ratio, I.
PP(I,K)    Selling price of stage K for purity I.
PUR(I,K)   Purity I for stage K.
RR(I)      Reflux ratio I.
RSR(I)     The I intermediate reflux ratio.
RTN        Return or profit for the stage.
RYEAR      Number of runs per year.
XMID(I,J,K) Amount of MID fraction between stages K and K-1 for input I and decision J.
TABLE XII

TYPICAL INPUT DATA FOR OPTIMIZATION PROGRAM
<table>
<thead>
<tr>
<th>PLATES-COMPOUNDS</th>
<th>NUMBER OF PLATES</th>
<th>15 6</th>
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</thead>
<tbody>
<tr>
<td>TOTAL MOLES CHARGED-WEIGHT FRACTION OF EACH COMPOUND</td>
<td>5.86</td>
<td>0.474</td>
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<tr>
<td>HOLDUP ON EACH PLATE - ASSUMED TEMPERATURE</td>
<td>0.00075</td>
<td>430.0</td>
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<tr>
<td></td>
<td>0.00075</td>
<td>431.0</td>
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<tr>
<td>Initial Data Card</td>
<td>Enthalpy Data</td>
<td>Pressure on Each Plate</td>
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<tr>
<td>-------------------</td>
<td>--------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>1.5000</td>
<td>0.85</td>
<td>45.0</td>
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</table>

*Enthalpy Data*

<p>| | | | | | | | | |</p>
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<td>59.489</td>
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<td>65.45891</td>
<td>-30932.28</td>
<td>24383.9</td>
<td>648.63</td>
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<td></td>
<td></td>
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<tr>
<td>61.80</td>
<td>-13550.0</td>
<td>84.2</td>
<td>-38790.0</td>
<td>22810.0</td>
<td>636.13</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>60.312</td>
<td>-9673.250</td>
<td>66.103149</td>
<td>-31240.79</td>
<td>23467.0</td>
<td>634.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Pressure on Each Plate*

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>759.88</td>
<td>761.95</td>
<td>764.02</td>
<td>766.02</td>
<td>768.02</td>
<td>770.09</td>
<td>772.16</td>
<td>774.25</td>
</tr>
<tr>
<td>776.36</td>
<td>778.43</td>
<td>780.50</td>
<td>782.57</td>
<td>784.64</td>
<td>786.71</td>
<td>788.78</td>
<td>790.85</td>
</tr>
<tr>
<td>792.92</td>
<td>794.99</td>
<td>797.06</td>
<td>799.13</td>
<td>801.20</td>
<td>803.27</td>
<td>805.34</td>
<td>807.41</td>
</tr>
</tbody>
</table>
### TABLE XIII

**INPUT FOR OPTIMIZATION USING POTLATCH INDUSTRY'S CRUDE**

<table>
<thead>
<tr>
<th>Number of Compounds</th>
<th>Purities per Compound</th>
<th>Number of Reflux Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

**Total Charge**

388.0

**Percent Distilled Preceeding the Cut at Purity 1**

<table>
<thead>
<tr>
<th>30 to 1</th>
<th>15 to 1</th>
<th>10 to 1</th>
<th>5 to 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>.732</td>
<td>.746</td>
<td>.750</td>
<td>.755</td>
</tr>
<tr>
<td>.678</td>
<td>-1.0</td>
<td>-1.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>.560</td>
<td>.571</td>
<td>.578</td>
<td>-1.0</td>
</tr>
<tr>
<td>.0</td>
<td></td>
<td>.0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Percent Distilled Succeeding the Cut at Purity 1**

<table>
<thead>
<tr>
<th>30 to 1</th>
<th>15 to 1</th>
<th>10 to 1</th>
<th>5 to 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>.831</td>
<td>.811</td>
<td>.800</td>
<td>.794</td>
</tr>
<tr>
<td>.720</td>
<td>-1.0</td>
<td>-1.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>.601</td>
<td>.591</td>
<td>.583</td>
<td>-1.0</td>
</tr>
<tr>
<td>.519</td>
<td>.496</td>
<td>.493</td>
<td>.490</td>
</tr>
</tbody>
</table>

**Refux Ratios**

| 30.0   | 15.0   | 10.0   | 5.0    |

**Price Data in Dollars per Pound**

| .076   | Dipentene |
| .1350  | Delta-3-Carene |
| .150   | Beta Pinene  |
| .079   | Alpha Pinene |

**Purities of Each Compound, Cost Data Includes Operating Cost, Boil-up Rate, Cost of Bottoms and Number of Runs per Year:**

| .10    | 100.0    | -.0185  | 50.0    |
### TABLE XIV

**DETAILED SUMMARY OF OPTIMUM RUNNING CONDITIONS FOR POTLATCH INDUSTRY CRUDE**

<table>
<thead>
<tr>
<th>Time in Hours</th>
<th>Reflux Ratio</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5.0 to 1</td>
<td>190.12</td>
</tr>
<tr>
<td>11.40</td>
<td>10.0 to 1</td>
<td>1.16</td>
</tr>
<tr>
<td>11.53</td>
<td>15.0 to 1</td>
<td>1.16</td>
</tr>
<tr>
<td>11.72</td>
<td>30.0 to 1</td>
<td>8.92</td>
</tr>
<tr>
<td>End of Alpha Pinene Fraction</td>
<td></td>
<td>15.90</td>
</tr>
<tr>
<td>14.48</td>
<td>30.0 to 1</td>
<td>15.90</td>
</tr>
<tr>
<td>End of Alpha Pinene Beta Pinene Midfraction</td>
<td></td>
<td>4.26</td>
</tr>
<tr>
<td>19.41</td>
<td>30.0 to 1</td>
<td>4.26</td>
</tr>
<tr>
<td>20.74</td>
<td>15.0 to 1</td>
<td>2.71</td>
</tr>
<tr>
<td>21.17</td>
<td>10.0 to 1</td>
<td>1.94</td>
</tr>
<tr>
<td>21.39</td>
<td>15.0 to 1</td>
<td>3.10</td>
</tr>
<tr>
<td>21.88</td>
<td>30.0 to 1</td>
<td>3.88</td>
</tr>
<tr>
<td>End of Beta Pinene Fraction</td>
<td></td>
<td>29.87</td>
</tr>
<tr>
<td>23.08</td>
<td>30.0 to 1</td>
<td>29.87</td>
</tr>
<tr>
<td>End of Beta Pinene Delta-3-Carene Midfraction</td>
<td></td>
<td>16.29</td>
</tr>
<tr>
<td>32.35</td>
<td>30.0 to 1</td>
<td>16.29</td>
</tr>
<tr>
<td>End of Delta-3-Carene Fraction</td>
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<td>4.65</td>
</tr>
<tr>
<td>37.40</td>
<td>30.0 to 1</td>
<td>4.65</td>
</tr>
<tr>
<td>End of Delta-3-Carene Dipentene Midfraction</td>
<td></td>
<td>5.43</td>
</tr>
<tr>
<td>38.84</td>
<td>30.0 to 1</td>
<td>5.43</td>
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<td>40.53</td>
<td>15.0 to 1</td>
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<td>40.77</td>
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<td>1.94</td>
</tr>
<tr>
<td>40.99</td>
<td>5.0 to 1</td>
<td>15.13</td>
</tr>
<tr>
<td>41.90</td>
<td>10.0 to 1</td>
<td>2.32</td>
</tr>
<tr>
<td>42.15</td>
<td>15.0 to 1</td>
<td>4.26</td>
</tr>
<tr>
<td>42.83</td>
<td>30.0 to 1</td>
<td>7.76</td>
</tr>
<tr>
<td>End of Dipentene Fraction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>End of Run</td>
<td>Pounds of Bottoms</td>
<td>65.57</td>
</tr>
<tr>
<td>Time of Run</td>
<td>45.98</td>
<td></td>
</tr>
<tr>
<td>Gross Profit per Run</td>
<td>20.11</td>
<td>Per Year</td>
</tr>
<tr>
<td>End of Run</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product</td>
<td>Amount in Pounds</td>
<td>Average Purity</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Alpha Pinene Fraction</td>
<td>201.37</td>
<td>95.0</td>
</tr>
<tr>
<td>Alpha Pinene Beta Pinene Midfraction</td>
<td>15.90</td>
<td>--</td>
</tr>
<tr>
<td>Beta Pinene Fraction</td>
<td>15.90</td>
<td>80.0</td>
</tr>
<tr>
<td>Beta Pinene Delta-3-Carene Midfraction</td>
<td>29.87</td>
<td>--</td>
</tr>
<tr>
<td>Delta-3-Carene Fraction</td>
<td>16.29</td>
<td>95.0</td>
</tr>
<tr>
<td>Delta-3-Carene Dipentene Midfraction</td>
<td>4.65</td>
<td>--</td>
</tr>
<tr>
<td>Dipentene Fraction</td>
<td>38.31</td>
<td>50.0</td>
</tr>
<tr>
<td>Bottoms Product</td>
<td>65.57</td>
<td>--</td>
</tr>
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</table>
### TABLE XVI
EXPERIMENTAL VERIFICATION OF OPTIMUM CONDITIONS FOR POTLATCH CRUDE

<table>
<thead>
<tr>
<th></th>
<th>Amount</th>
<th>Reflux Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Pinene Fraction</td>
<td>190.0</td>
<td>5 to 1</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>10 to 1</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>15 to 1</td>
</tr>
<tr>
<td></td>
<td>9.0</td>
<td>30 to 1</td>
</tr>
<tr>
<td>Average Purity 95.9</td>
<td>201.7</td>
<td>Average 6.2 to 1</td>
</tr>
<tr>
<td>Alpha-Beta Mid-Fraction</td>
<td>16.0</td>
<td>30 to 1</td>
</tr>
<tr>
<td>Beta Pinene Fraction</td>
<td>4.0</td>
<td>30 to 1</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>15 to 1</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>10 to 1</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>15 to 1</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>30 to 1</td>
</tr>
<tr>
<td>Average Purity 81.9</td>
<td>16.0</td>
<td>Average 21.8 to 1</td>
</tr>
<tr>
<td>Beta-Delta-3 Mid-Fraction</td>
<td>29.5</td>
<td>30 to 1</td>
</tr>
<tr>
<td>Delta-3-Carene Fraction</td>
<td>16.0</td>
<td>30 to 1</td>
</tr>
<tr>
<td>Average Purity 95.2</td>
<td>16.0</td>
<td>Average 30 to 1</td>
</tr>
<tr>
<td>Delta-3-Dipentene Mid-Fraction</td>
<td>5.0</td>
<td>30 to 1</td>
</tr>
<tr>
<td>Dipentene Fraction</td>
<td>5.5</td>
<td>30 to 1</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>15 to 1</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>10 to 1</td>
</tr>
<tr>
<td></td>
<td>14.0</td>
<td>5 to 1</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>10 to 1</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>15 to 1</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>30 to 1</td>
</tr>
<tr>
<td>Average Purity 53.5</td>
<td>35.7</td>
<td>Average 16.1 to 1</td>
</tr>
<tr>
<td>Bottoms</td>
<td>64.0</td>
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</tr>
<tr>
<td>TOTAL</td>
<td>382.9</td>
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</tr>
</tbody>
</table>
### TABLE XVII
INPUT FOR OPTIMIZATION USING SOUTHWEST FOREST INDUSTRY’S CRUDE

<table>
<thead>
<tr>
<th>Number of Compounds</th>
<th>Purities per Compound</th>
<th>Number of Reflux Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

**Total Charge**

369.0000

---

**Percent Distilled Preceeding the Cut at Purity 1**

<table>
<thead>
<tr>
<th></th>
<th>30 to 1</th>
<th>15 to 1</th>
<th>10 to 1</th>
<th>5 to 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipentene</td>
<td>.7790</td>
<td>.7793</td>
<td>.7796</td>
<td>.7800</td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td>-.7790</td>
<td>-.7793</td>
<td>-.7796</td>
<td>-.7800</td>
</tr>
<tr>
<td>Beta Pinene</td>
<td>.4270</td>
<td>.4730</td>
<td>-1.0000</td>
<td>-1.0000</td>
</tr>
<tr>
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<td>-.4270</td>
<td>-.4730</td>
<td>-1.0000</td>
<td>-1.0000</td>
</tr>
</tbody>
</table>

---

**Percent Distilled Succeeding the Cut at Purity 1**

<table>
<thead>
<tr>
<th></th>
<th>30 to 1</th>
<th>15 to 1</th>
<th>10 to 1</th>
<th>5 to 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipentene</td>
<td>.8110</td>
<td>.8096</td>
<td>.8093</td>
<td>.8090</td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td>.7640</td>
<td>.7510</td>
<td>.7360</td>
<td>.7230</td>
</tr>
<tr>
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<td>-.8110</td>
<td>-.8096</td>
<td>-.8093</td>
<td>-.8090</td>
</tr>
<tr>
<td>Alpha Pinene</td>
<td>-.7640</td>
<td>-.7510</td>
<td>-.7360</td>
<td>-.7230</td>
</tr>
</tbody>
</table>

---

**Reflux Ratios**

<table>
<thead>
<tr>
<th></th>
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<th>15.0000</th>
<th>10.0000</th>
<th>5.0000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipentene</td>
<td>.076</td>
<td>.135</td>
<td>.150</td>
<td>.079</td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td>.076</td>
<td>.135</td>
<td>.150</td>
<td>.079</td>
</tr>
<tr>
<td>Beta Pinene</td>
<td>.076</td>
<td>.135</td>
<td>.150</td>
<td>.079</td>
</tr>
<tr>
<td>Alpha Pinene</td>
<td>.076</td>
<td>.135</td>
<td>.150</td>
<td>.079</td>
</tr>
</tbody>
</table>

---

**Purities of Each Compound**

<table>
<thead>
<tr>
<th></th>
<th>50.0000</th>
<th>95.0000</th>
<th>80.0000</th>
<th>95.0000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipentene</td>
<td>.076</td>
<td>.135</td>
<td>.150</td>
<td>.079</td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td>.076</td>
<td>.135</td>
<td>.150</td>
<td>.079</td>
</tr>
<tr>
<td>Beta Pinene</td>
<td>.076</td>
<td>.135</td>
<td>.150</td>
<td>.079</td>
</tr>
<tr>
<td>Alpha Pinene</td>
<td>.076</td>
<td>.135</td>
<td>.150</td>
<td>.079</td>
</tr>
</tbody>
</table>

---

**Cost Data Includes Operating Cost, Boil-up Rate, Cost of Bottoms and Number of Runs per Year**

<table>
<thead>
<tr>
<th></th>
<th>.1000</th>
<th>100.0000</th>
<th>-.0185</th>
<th>50.0000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipentene</td>
<td>.076</td>
<td>.135</td>
<td>.150</td>
<td>.079</td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td>.076</td>
<td>.135</td>
<td>.150</td>
<td>.079</td>
</tr>
<tr>
<td>Beta Pinene</td>
<td>.076</td>
<td>.135</td>
<td>.150</td>
<td>.079</td>
</tr>
<tr>
<td>Alpha Pinene</td>
<td>.076</td>
<td>.135</td>
<td>.150</td>
<td>.079</td>
</tr>
</tbody>
</table>

---

End of Data
### TABLE XVIII

**DETAILED SUMMARY OF OPTIMUM RUNNING CONDITIONS FOR SOUTHWEST FOREST INDUSTRY'S CRUDE**

<table>
<thead>
<tr>
<th>Time in Hours</th>
<th>Reflux Ratio</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5.0 to 1</td>
<td>88.56</td>
</tr>
<tr>
<td>5.31</td>
<td>10.0 to 1</td>
<td>11.07</td>
</tr>
<tr>
<td>6.53</td>
<td>15.0 to 1</td>
<td>11.07</td>
</tr>
<tr>
<td>8.30</td>
<td>30.0 to 1</td>
<td>16.60</td>
</tr>
</tbody>
</table>

End of Alpha Pinene Fraction  
13.45  
30.0 to 1  
30.25

End of Alpha Pinene Beta Pinene Midfraction  
22.83  
30.0 to 1  
0.00

End of Beta Pinene Fraction  
22.83  
30.0 to 1  
0.00

End of Beta Pinene Delta-3-Carene Midfraction  
22.83  
30.0 to 1  
16.97
| 28.09 | 15.0 to 1 | 18.45 |
| 31.04 | 10.0 to 1 | 18.08 |
| 33.03 | 5.0 to 1  | 55.71 |
| 36.37 | 10.0 to 1 | 4.79  |
| 36.90 | 15.0 to 1 | 5.53  |
| 37.78 | 30.0 to 1 | 4.79  |

End of Delta-3-Carene Fraction  
39.27  
30.0 to 1  
5.53

End of Delta-3-Carene Dipentene Midfraction  
40.99  
30.0 to 1  
.11
| 41.02 | 15.0 to 1 | .11 |
| 41.04 | 10.0 to 1 | .14 |
| 41.06 | 5.0 to 1  | 10.70 |
| 41.70 | 10.0 to 1 | .11  |
| 41.71 | 15.0 to 1 | .11  |
| 41.73 | 30.0 to 1 | .51  |

End of Dipentene Fraction

End of run  
Pounds of Bottoms 69.74

Time of Run 41.89

Gross Profit per Run 24.85  
Per Year 1247.75
<table>
<thead>
<tr>
<th>Product</th>
<th>Amount in Pounds</th>
<th>Average Purity</th>
<th>Average Reflux Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Pinene Fraction</td>
<td>127.30</td>
<td>95.0</td>
<td>9.5 to 1</td>
</tr>
<tr>
<td>Alpha Pinene Beta Pinene Midfraction</td>
<td>30.25</td>
<td>--</td>
<td>30.0 to 1</td>
</tr>
<tr>
<td>Beta Pinene Fraction</td>
<td>0.00</td>
<td>80.0</td>
<td>30.0 to 1</td>
</tr>
<tr>
<td>Beta Pinene Delta-3-Carene Midfraction</td>
<td>0.00</td>
<td>--</td>
<td>30.0 to 1</td>
</tr>
<tr>
<td>Delta-3-Carene Fraction</td>
<td>124.35</td>
<td>95.0</td>
<td>12.2 to 1</td>
</tr>
<tr>
<td>Delta-3-Carene Dipentene Midfraction</td>
<td>5.33</td>
<td>--</td>
<td>30.0 to 1</td>
</tr>
<tr>
<td>Dipentene Fraction</td>
<td>11.80</td>
<td>50.0</td>
<td>6.6 to 1</td>
</tr>
<tr>
<td>Bottoms Product</td>
<td>69.74</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Amount</td>
<td>Reflux Ratio</td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>--------</td>
<td>--------------</td>
<td></td>
</tr>
<tr>
<td>Alpha Pinene Fraction</td>
<td>88.0</td>
<td>5 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.0</td>
<td>10 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.0</td>
<td>15 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16.0</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td>Average Purity 95.0</td>
<td>126.0</td>
<td>Average 9.5 to 1</td>
<td></td>
</tr>
<tr>
<td>Alpha-Beta-Midfraction</td>
<td>30.0</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td>Beta Fraction</td>
<td>0.0</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Average Purity 0.0</td>
<td>0.0</td>
<td>Average --</td>
<td></td>
</tr>
<tr>
<td>Beta-Delta-3-Carene Midfraction</td>
<td>0.0</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td>16.0</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.5</td>
<td>15 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.0</td>
<td>10 to 1</td>
<td></td>
</tr>
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<td></td>
<td>56.0</td>
<td>5 to 1</td>
<td></td>
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<td></td>
<td>5.0</td>
<td>10 to 1</td>
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<td>5.0</td>
<td>15 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td>Average Purity 95.1</td>
<td>123.5</td>
<td>Average 12.1 to 1</td>
<td></td>
</tr>
<tr>
<td>Delta-3-Dipentene Midfraction</td>
<td>5.5</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td>Dipentene Fraction</td>
<td>0.0</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>15 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>10 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.0</td>
<td>5 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>10 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>15 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td>Average Purity 58.5</td>
<td>12.0</td>
<td>Average 7.1 to 1</td>
<td></td>
</tr>
<tr>
<td>Bottoms</td>
<td>73.0</td>
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<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>370.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE XXI
INPUT FOR OPTIMIZATION USING
HOERNER WALDORF'S CRUDE

<table>
<thead>
<tr>
<th>Number of Compounds</th>
<th>Purities per Compound</th>
<th>Number of Reflux Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 1 1 1 1 4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Total Charge**

408.0000

**Percent Distilled Preceeding the Cut at Purity 1**

<table>
<thead>
<tr>
<th></th>
<th>30 to 1</th>
<th>15 to 1</th>
<th>10 to 1</th>
<th>5 to 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipentene</td>
<td>0.7380</td>
<td>0.7540</td>
<td>0.7750</td>
<td>0.7890</td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td>0.5460</td>
<td>0.6020</td>
<td>0.6570</td>
<td>0.6840</td>
</tr>
<tr>
<td>Beta Pinene</td>
<td>0.4220</td>
<td>0.4350</td>
<td>-1.0000</td>
<td>-1.0000</td>
</tr>
<tr>
<td>Alpha Pinene</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

**Percent Distilled Succeeding the Cut at Purity 1**

<table>
<thead>
<tr>
<th></th>
<th>30 to 1</th>
<th>15 to 1</th>
<th>10 to 1</th>
<th>5 to 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipentene</td>
<td>0.8380</td>
<td>0.8330</td>
<td>0.8310</td>
<td>0.8290</td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td>0.7010</td>
<td>0.6980</td>
<td>0.6960</td>
<td>0.6940</td>
</tr>
<tr>
<td>Beta Pinene</td>
<td>0.4620</td>
<td>0.4500</td>
<td>-1.0000</td>
<td>-1.0000</td>
</tr>
<tr>
<td>Alpha Pinene</td>
<td>0.3600</td>
<td>0.3150</td>
<td>0.3000</td>
<td>0.2950</td>
</tr>
</tbody>
</table>

**Reflux Ratios**

<table>
<thead>
<tr>
<th></th>
<th>30.0000</th>
<th>15.0000</th>
<th>10.0000</th>
<th>5.0000</th>
</tr>
</thead>
</table>

**Price Data in Dollars per Pound**

<table>
<thead>
<tr>
<th></th>
<th>0.076</th>
<th>0.135</th>
<th>0.150</th>
<th>0.079</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipentene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beta Pinene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alpha Pinene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Purities of Each Compound**

<table>
<thead>
<tr>
<th></th>
<th>50.0000</th>
<th>95.0000</th>
<th>80.0000</th>
<th>95.0000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipentene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delta-3-Carene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beta Pinene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alpha Pinene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Cost Data Includes Operating Cost, Boil-up Rate, Cost of Bottoms and Number of Runs per Year**

<table>
<thead>
<tr>
<th></th>
<th>0.1000</th>
<th>100.0000</th>
<th>-0.0185</th>
<th>50.0000</th>
</tr>
</thead>
</table>

End of Data.
## TABLE XXII
DETAILED SUMMARY OF OPTIMUM RUNNING CONDITIONS FOR HOERNER WALDORF'S CRUDE

<table>
<thead>
<tr>
<th>Time in Hours</th>
<th>Reflux Ratio</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5.0 to 1</td>
<td>120.36</td>
</tr>
<tr>
<td>7.22</td>
<td>10.0 to 1</td>
<td>2.04</td>
</tr>
<tr>
<td>7.44</td>
<td>15.0 to 1</td>
<td>6.12</td>
</tr>
<tr>
<td>8.42</td>
<td>30.0 to 1</td>
<td>18.36</td>
</tr>
</tbody>
</table>

End of Alpha Pinene Fraction

<table>
<thead>
<tr>
<th>Time in Hours</th>
<th>Reflux Ratio</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.11</td>
<td>30.0 to 1</td>
<td>25.29</td>
</tr>
</tbody>
</table>

End of Alpha Pinene Beta Pinene Midfraction

<table>
<thead>
<tr>
<th>Time in Hours</th>
<th>Reflux Ratio</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.95</td>
<td>30.0 to 1</td>
<td>5.30</td>
</tr>
<tr>
<td>23.60</td>
<td>15.0 to 1</td>
<td>6.12</td>
</tr>
<tr>
<td>24.58</td>
<td>30.0 to 1</td>
<td>4.89</td>
</tr>
</tbody>
</table>

End of Beta Pinene Fraction

<table>
<thead>
<tr>
<th>Time in Hours</th>
<th>Reflux Ratio</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.09</td>
<td>30.0 to 1</td>
<td>34.27</td>
</tr>
</tbody>
</table>

End of Beta Pinene Delta-3-Carene Midfraction

<table>
<thead>
<tr>
<th>Time in Hours</th>
<th>Reflux Ratio</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.72</td>
<td>30.0 to 1</td>
<td>22.84</td>
</tr>
<tr>
<td>43.80</td>
<td>15.0 to 1</td>
<td>22.44</td>
</tr>
<tr>
<td>47.39</td>
<td>10.0 to 1</td>
<td>11.01</td>
</tr>
<tr>
<td>48.60</td>
<td>5.0 to 1</td>
<td>4.08</td>
</tr>
<tr>
<td>48.85</td>
<td>10.0 to 1</td>
<td>.81</td>
</tr>
<tr>
<td>48.94</td>
<td>15.0 to 1</td>
<td>.81</td>
</tr>
<tr>
<td>49.07</td>
<td>30.0 to 1</td>
<td>1.22</td>
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</tbody>
</table>

End of Delta-3-Carene Fraction

<table>
<thead>
<tr>
<th>Time in Hours</th>
<th>Reflux Ratio</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>49.45</td>
<td>30.0 to 1</td>
<td>15.09</td>
</tr>
</tbody>
</table>

End of Delta-3-Carene Dipentene Midfraction

<table>
<thead>
<tr>
<th>Time in Hours</th>
<th>Reflux Ratio</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>54.13</td>
<td>30.0 to 1</td>
<td>6.52</td>
</tr>
<tr>
<td>56.15</td>
<td>15.0 to 1</td>
<td>8.56</td>
</tr>
<tr>
<td>57.52</td>
<td>10.0 to 1</td>
<td>5.71</td>
</tr>
<tr>
<td>58.15</td>
<td>5.0 to 1</td>
<td>16.32</td>
</tr>
<tr>
<td>59.13</td>
<td>10.0 to 1</td>
<td>.81</td>
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<td>59.22</td>
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<td>.81</td>
</tr>
<tr>
<td>59.35</td>
<td>30.0 to 1</td>
<td>2.04</td>
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</table>

End of Dipentene Fraction

Pounds of Bottoms 66.09

<table>
<thead>
<tr>
<th>Time of Run</th>
<th>Gross Profit per Run</th>
<th>Per Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>59.98</td>
<td>20.97</td>
<td>1048.52</td>
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</table>

End of Run
<table>
<thead>
<tr>
<th>Product</th>
<th>Amount in Pounds</th>
<th>Average Purity</th>
<th>Average Reflux Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Pinene Fraction</td>
<td>146.88</td>
<td>95.0</td>
<td>8.6 to 1</td>
</tr>
<tr>
<td>Alpha Pinene Beta Pinene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Midfraction</td>
<td>25.29</td>
<td>--</td>
<td>30.0 to 1</td>
</tr>
<tr>
<td>Beta Pinene Fraction</td>
<td>16.32</td>
<td>80.0</td>
<td>24.3 to 1</td>
</tr>
<tr>
<td>Beta Pinene Delta-3-Carene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Midfraction</td>
<td>34.27</td>
<td>--</td>
<td>30.0 to 1</td>
</tr>
<tr>
<td>Delta-3-Carene Fraction</td>
<td>63.24</td>
<td>95.0</td>
<td>19.1 to 1</td>
</tr>
<tr>
<td>Delta-3-Carene Dipentene</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Midfraction</td>
<td>15.09</td>
<td>--</td>
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<td>Dipentene Fraction</td>
<td>40.80</td>
<td>50.0</td>
<td>13.3 to 1</td>
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</tr>
<tr>
<td>Fraction</td>
<td>Amount</td>
<td>Reflux Ratio</td>
<td></td>
</tr>
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<td>-------------------------------</td>
<td>--------</td>
<td>--------------</td>
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</tr>
<tr>
<td>Alpha Pinene Fraction</td>
<td>120.5</td>
<td>5 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>10 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>15 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.5</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td>Average Purity</td>
<td>95.6</td>
<td>147.0 Average 8.55 to 1</td>
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<td>Alpha-Beta-Mid-fraction</td>
<td>25.5</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td>Beta Pinene Fraction</td>
<td>5.5</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>15 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td>Average Purity</td>
<td>82.9</td>
<td>16.0 Average 24.9 to 1</td>
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<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td>Delta-3-Carene Fraction</td>
<td>23.0</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21.0</td>
<td>15 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.0</td>
<td>10 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>5 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>10 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>15 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>30 to 1</td>
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<tr>
<td>Average Purity</td>
<td>98.0</td>
<td>62.0 Average 19.2 to 1</td>
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</tr>
<tr>
<td>Delta-3-Dipentene Mid-fraction</td>
<td>15.0</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td>Dipentene Fraction</td>
<td>6.0</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>15 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>10 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.0</td>
<td>5 to 1</td>
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<td>.5</td>
<td>10 to 1</td>
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</tr>
<tr>
<td></td>
<td>1.0</td>
<td>15 to 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>30 to 1</td>
<td></td>
</tr>
<tr>
<td>Average Purity</td>
<td>55.1</td>
<td>40.0 Average 12.8 to 1</td>
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</tr>
<tr>
<td>Bottoms</td>
<td>60.0</td>
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<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td>399.5</td>
<td></td>
</tr>
</tbody>
</table>
TABLE XXV

KEY TO SYMBOLS USED IN FIGURES 10-22

(See Page 136)
FIGURES 1-22
Corad Condenser Head

3-inch Outer Cylinder

Taper Joint-Ball Joint Adapter

1-inch Inner Cylinder, Penske Ring Packing

Two-liter Distillation Flask (stillpot)

Fiberglass and Aluminum Foil Insulation

FIG. 1 Experimental Distillation Apparatus
FIG. 2 Pilot Plant Distillation Equipment
FIG. 3 Schematic Of A Batch Distillation Column
FIG. 4 Schematic Of Input Requirements For Mathematical Model
FIG. 5  A Typical Multi-stage Process
FIG. 6  A Simple Proof For The Principle Of Optimality By Means Of
A Line Diagram.
FIG. 7 General Scheme Of Dynamic Programming Computation
ENTRY

Reads In Necessary Data

MAIN LINE

Calculates Optimum Conditions

DPMOD

Calculates Ave. Reflux Ratio

RROPT

Sort And Stores Optimum Decisions

SORT

Prints Out Optimum Cond.

EDIT

EXIT

FIG. 8 Overall Flow Chart Of Optimization Program
FIG. 9 Schematic Input Of Requirements For Optimization Program
### TABLE XXV

**KEY TO SYMBOLS USED IN FIGURES 10-22**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Alpha Pinene</td>
</tr>
<tr>
<td>O</td>
<td>Beta Pinene</td>
</tr>
<tr>
<td>▼</td>
<td>Delta-3-Carene</td>
</tr>
<tr>
<td>□</td>
<td>Dipentene</td>
</tr>
</tbody>
</table>
FIGURE 10: DISTILLATION DATA

POTLATCH IND. CRUDE-SIMULATION
5 TO 1 REFLUX RATIO
FIGURE 11 DISTILLATION DATA

POTLATCH INC. CRUDE
5 TO 1 REFLUX RATIO

PERCENT PURITY
100
90
80
70
60
50
40
30
20
10
0

PERCENT DISTILLED
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
FIGURE 12 DISTILLATION DATA

POTLATCH INC. CRUDE
10 TO 1 REFLUX RATIO
FIGURE 13 DISTILLATION DATA

POTLATCH INO. CRUDE
15 TO 1 REFLUX RATIO-EST.
FIGURE 14 DISTILLATION DATA

POTLATCH INC. CRUDE
30 TO 1 REFLUX RATIO

PERCENT PURITY

PERCENT DISTILLED
FIGURE 15 DISTILLATION DATA

SOUTHWEST FOREST INC CRUDE
5 TO 1 REFLUX RATIO
FIGURE 16 DISTILLATION DATA

SOUTHWEST FOREST INC. CRUDE
10 TO 1 REFLUX RATIO

PERCENT PURITY

PERCENT DISTILLED
FIGURE 10 DISTILLATION DATA

SOUTHWEST FOREST IND CRUDE
30 TO 1 REFLUX RATIO

PERCENT PURITY

PERCENT DISTILLED
FIGURE 19 DISTILLATION DATA

HOERNER WALDOFF CRUDE
5 TO 1 REFLUX RATIO

PERCENT PURITY

PERCENT DISTILLED
FIGURE 20 DISTILLATION DATA

HOERNER WALDORF CRUDE
10 TO 1 REFLUX RATIO
FIGURE 21 DISTILLATION DATA

HOERNER WALDORF CRUDE
15 TO 1 REFLUX RATIO EST.
FIGURE 22 DISTILLATION DATA

HOERNER WALDORF CRUDE
30 TO 1 REFLUX RATIO
NOMENCLATURE

Mathematical Model

\[ A_{j,i} = \text{Absorption factor for component } i \text{ and plate } j \]
\[ c = \text{Total number of components.} \]
\[ d_i = \text{Total molal flow rate of component in the distillate.} \]
\[ E_{j,i} = \text{Instantaneous value of vapor efficiency on plate } j \text{ for component } i. \]
\[ g_j(\theta_{-1,j} \ldots \theta_n) = \text{The } j\text{th function of } \theta_{-1,j} \ldots \theta_n. \]
\[ h_j = \text{Enthalpy per mole of liquid leaving plate } j. \]
\[ H_j = \text{Enthalpy per mole of vapor leaving plate } j. \]
\[ H_D = \text{Total enthalpy of the distillate.} \]
\[ \lambda_{j,i} = \text{Molal flow rate at which component } i \text{ in the liquid phase leaves plate } j. \]
\[ L_j = \text{Total molal flow rate at which liquid leaves plate } j. \]
\[ Q_c = \text{Condenser heat duty.} \]
\[ t = \text{Time in consistent units, } t_n \text{ is used to denote the time at which increment } t_{n+1} \text{ begins and } t_n + \Delta t \text{ at the time the interval ends.} \]
\[ T_j = \text{Temperature of liquid leaving plate } J. \]
\[ u_{j,i} = \text{Liquid holdup in moles of } i \text{ on plate } j \text{ when the vapor holdups are neglected.} \]
\[ U_j = \text{Total molal holdup of liquid on plate } j \text{ when the vapor holdup is neglected.} \]
\[ v_{j,i} = \text{Molal flow rate at which component } i \text{ in vapor phase leave plate } j. \]
\[ V_j = \text{Total molal flow rate at which vapor leaves plate } j. \]
(Nomenclature)

\( x_{j,i} \) = Mole fraction component \( i \) in the liquid leaving plate \( j \).

\( y_{j,i} \) = Mole fraction of component \( i \) in the vapor phase leaving plate \( j \).

Greek Letters

\( \theta \) = A multiplier associated with plate \( j \).

\( \mu \) = A weight factor used in the evaluation of an integral in terms of the value of the function at times \( t_n \) and \( t_n + t \).

\( \tau \) = Dimensionless time factor for plates.

Subscripts

Cal = Calculated value.

Cor = Corrected value.

i = Component number.

j = Plate number.

n = Trial number.

Superscripts

\( 0 \) = Value of a variable at the beginning of the time increment under consideration.

Dynamic Programming, Optimization Method

Amount = Pounds of product.

Bottoms = Pounds of material remaining in still pot at the end of the distillation.

Boil-up Rate = Liquid flow rate in 1bs/hr.
(Nomenclature)

Cost = Operating cost in $/hr of operating time.

Cost of Bottoms = Cost of disposing of bottoms product. Negative value indicates a profit.

Midfraction = Pounds of overhead not reaching desireable purity between cuts.

Percent Distilled = Weight percent distilled preceding of following the cut.

Price = Selling price of product in $/lb.

RR = Reflux ratio.

Subscripts

Average = The average value over the stage in consideration.
LITERATURE CITED


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<th>D378</th>
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<td>Optimization of the batch distillation of terpenes</td>
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