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 turpentines 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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A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree

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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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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.[8] Dynamic programming was developed by Richard Bellman in the 1950's.[2] 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.[4] Maximum principle was first hypothesized by the Russiam mathematician Pontryagin in 1956 and like dynamic programming takes advantage of the serial structure of the problem.[8]

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.[14] 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.[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]

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

RESEARCH OBJECTIVES

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

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

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

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

EQUIPMENT

Experimental Distillation Equipment

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

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

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

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

Pilot Plant Distillation Equipment

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

The packing selected for this column was one-half inch ceramic Berl saddles. This particular packing was chosen because it has a high-void space (63 percent), resists corrosion and can be readily cleaned by many solvents. Calibration with a toluene-methlcyclohexane 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[5] 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' oxydiproylnitrite on a 60/80 acid washed chromosorb P support. The chromatograph was operated at 75-80°C with a carrier gas-flow rate of 50-60 cc/min for 1 - 2 microliter samples. Chromatographic peaks were recorded on a Sargent Model SR recorder and the chromatograms were converted into percentage compositions by using a compensating polar planimeter.

Operating Procedure - Experimental

In obtaining both experimental data for optimization and

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

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

Operating Procedure - Verification Runs

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

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

MATHEMATICAL MODEL

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

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

In simulation of the packed column, it was broken into the calibrated number of theoretical stages and simulated as a tray column with the efficiency on each plate equal to one. In addition to this assumption, the following well-tested assumptions for continuous columns have been used.[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[9]

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

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

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

$$[\mu\,(v_{J+1,i} + \ell_{J-1,i} - v_{J,i} - \ell_{J,i}) - (1-\mu)(v^0_{J+1,i} + \ell^0_{J-1,i} - v^0_{J,i} - \ell_{J,i}]\Delta t = u_{J,i} - u^0_{J,i} \qquad (2)$$

Holland defines the liquid flow rate in terms of the vapor flow rates by use of the relationship:[6]

$$\ell_{j,i} = A_{j,i}\, v_{j,i} \qquad (3)$$

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

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

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

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

or

$$A\ X = B$$

where

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

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

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

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

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

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

$$P_{j,i} = \sigma[v^0_{j+1,i} + \ell^0_{j-1,i} - v^0_{j,i} - \ell^0_{j,i}] + \frac{u^0_{j,i}}{\mu\Delta\ t} \quad ;$$

$$P_{n+1,i} = \sigma[\ell^0_{n,i} - v^0_{n+1,i}] + \frac{u^0_{n+1,i}}{\mu\Delta t}$$

For any set values of Δt, μ, 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 algorthim developed by Holland.[6]

$$f_o = Co/Bo \qquad g_o = Do/Bo$$

$$f_k = \frac{C_k}{B_k - A_k F_{k-1}} \qquad k = 1, \ldots N \tag{6}$$

$$g_k = \frac{D_k - A_k\, g_{k-1}}{B_k - A_k\, f_{k-1}} \qquad k = 1, \ldots N+1 \tag{7}$$

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

$$v_{N+1} = g_{N+1} \tag{8}$$

and

$$v_k = g_k - f_k\, v_{k+1} \qquad k = N, N-1, N-2, \ldots 0 \tag{9}$$

where

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

B_j = diagonal elements of matrix A

C_j = super diagonal elements of matrix A

D_j = elements in the N+2 component vector B(J=0, . . . 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_o . . . U_N along with the distillation rate D are specified, the formulas for the θ method of convergence are as follows:

$$\left(\frac{u_{n+1,i}}{d_i}\right)_{cor} = \theta_{-1} \left(\frac{u_{n+1,i}}{d_i}\right)_{cal} \tag{10}$$

$$\left(\frac{u_{j,i}}{d_i}\right)_{cor} = \theta_j \left(\frac{u_{j,i}}{d_i}\right)_{cal} \tag{11}$$

$$j = 0, \ldots N$$

The desired set of θ's is that set of positive numbers

that make $g_{-1} = g_o \ldots = g_N = 0$ simultaneously. Where

$$g_{-1}\ (\theta_{-1},\ \theta_o,\ \theta_1 \ldots \theta_N) = \sum_{i=1}^{c} (d_i)_{cor} - D \qquad (12)$$

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

$$j = 0, \ldots N \ .$$

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

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

where

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

This process is repeated until a set of θ'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.

$$\left(\frac{u_{j,i}}{d_i}\right)_{cal} = \frac{(U_j/L_j)\, A_{j,i}\, v_{j,i}}{d_i} \qquad (15)$$

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

and

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

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

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

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:

$$y_{j,i} = E_{j,i} K_{j,i} x_{j,i} \tag{18}$$

and defining

$$\alpha_{j,i} = K_{j,i}/K_{j,B} \tag{19}$$

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

$$y_{j,i} = E_{j,i} K_{j,B} \alpha_{j,i} x_{j,i} \tag{20}$$

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

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

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

$$K_{j,i} = \frac{P_{j,i}}{\pi} \tag{22}$$

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

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

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

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

Enthalpy Balance: j^{th} plate

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

$$= U_jh_j \Big|_{t_n+\Delta t} - U_jh_j \Big|_{t_n} \qquad (24)$$

Condensor duty

$$\int_{t_n}^{t_n+\Delta t} [V_1H_1 - L_oh_o - DH_o - Q_c]dt$$

$$= U_oh_o \Big|_{t_n+\Delta t} - U_oh_o \Big|_{t_n} \qquad (25)$$

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

$$[V_1H_1 - L_oh_o - DH_D - Q_c] + (\sigma)[V_1^0H_1^0 - L_o^0h_o^0 - D^0H_D^0 - Q_c^0]$$

$$= (1/\mu\,\Delta t)[U_oh_o - U_o^0h_o^0] \qquad (26)$$

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

$$V_1H_1 = \sum_{i=1}^{c} H_{1,i}v_{1,i} \tag{27}$$

$$= \sum_{i=1}^{c} H_{1i}[\ell_{oi} + d_i + \sigma(\ell^0_{oi} + d^0_i - v^0_{1i}) + (1/\mu\Delta t)(u_{oi} - u^0_{oi})]$$

Thus,

$$V_1H_1 = L_oH(x_o)_1 + DH(x_D)_1 + \sigma[L^0_oH(x^0_o)_1 + D^0H(x^0_D)_1$$

$$- V^0_1H(y^0_1)_1] + (1/\mu\Delta t)[U_oH(x_o)_1 - U^0_oH(x^0_o)_1] \tag{28}$$

where

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

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

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

Elimination of V_1H_1 from Equation 27 followed by rearrangement yields the following for condenser heat duty

$$Q_c = L_o[H(x_o)_1 - h_o] + D[H(x_D)_1 - H_D] + \sigma[L^0_o(H(x^0_o)_1 - h^0_o]$$

$$+ D^0[H(x^0_D)_1 - H^0_D] - V^0_1[H(y^0_1)_1 - H^0_1) - Q^0_c] \tag{32}$$

$$+ (U_o/\mu\Delta t)[H(x_o)_1 - h_o] - (U^0_o/\mu\Delta t)[H(x^0_o)_1 - h^0_o]$$

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:

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

$$+ \frac{-L^0_j[H(x^0_j)_{j+1} - h^0_j] - D^0[H(x^0_D)_{j+1} - H^0_D] + Q^0_c)}{(H(x_j)_{j+1} - h_j)} \qquad (33)$$

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

Total Material Balance

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

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

$$V_{j+1} - L_j - D + \sigma(V^0_{j+1} - L^0_j - D^0) = (1/\mu\Delta t) \sum_{k=0}^{j} [U_k - U^0_k] \qquad (35)$$

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

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

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

Description of Computer Program for Mathematical Model

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

The calculation procedure is as follows:

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

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

3. θ 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:

CARD TYPE	DESCRIPTION
1	Number of Plates and Component Card The integer number of plates in

(CARD TYPE)	(DESCRIPTION)
	columns 1-2 and integer number of components columns 3-4.
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 preceeding 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 Boilup rate in moles/hr in columns 1-10. Weight factor for solution of differential Eq. Columns 11-20. Reflux ratio for evaluation, columns 21-30. Percent of total charge to be distilled, columns 31-40.
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

(CARD TYPE)	(DESCRIPTION)
	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.
7	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.

DYNAMIC PROGRAMMING -- BASIC THEORY

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.[4] 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:[2]

> 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.[4] 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

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

$$F_n(X_n) = \max_{D_n} [R_n(X_n,D_n) + F_{n-1}(x_{n-1})] \quad (36)$$

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 nth 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.

$$X_{n-1} = T_n(X_n,D_n) \quad (37)$$

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. Ouput 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

$$R_n = R_n(X_n, D_n) \tag{38}$$

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

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

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

.

.

.

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

Similarly the return from stage n is dependent only on X_N and D_N, D_{n+1}, . . . D_n.

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

$$R_n = R_n(X_N,D_N,\ldots D_n)$$

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:

$$f_n(X_n) = \underset{D_n \ldots D_1}{\text{Max}} [R_n(X_n,D_n) + R_{n-1}(X_{n-1},D_{n-1}) \ldots R(X_1,D_1)] \quad (39)$$

Since stage n return does not depend on decisions n-1 . . . 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:

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

But by definition of $f_n(X_n)$, it follows that

$$f_{n-1}(X_{n-1}) = \underset{D_{n-1},\ldots D_1}{\text{Max}} [R_{n-1}(X_{n-1},D_{n-1}) + \ldots$$

$$+ R_1(X_1,D_1)].$$

Thus the result is the objective function

$$f_n(X_n) = \underset{D_n}{\text{Max}} [R_n(X_n,D_n) + f_{n-1}(X_{n-1})] \qquad (40)$$

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.[14]

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:

Stage Number	Component
1	dipentene
2	delta-3-carene
3	beta-pinene
4	alpha-pinene

In the general case, stage number 1 is the least volatile major compent 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 co t for producing the product of that particular stage. The equations defining the return for each stage are as follows:

Stage 1:

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

Stage 2 . . . N :

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

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 sequencially 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:

$$\text{AMOUNT } (X_n, D_n) = (\text{PERCENT DISTILLED AT } RR_{X_n}, \text{ PURITY}_{X_n} - \text{PERCENT DISTILLED at } RR_{D_n}, \text{ PURITY}_{X_n}) \cdot \text{TOTAL} \tag{43}$$

$$\text{MID-FRACTION } (X_n, D_n) = (\text{PERCENT DISTILLED at } RR_{D_n}, \text{PURITY}_{X_n} - \text{PERCENT DISTILLED at } RR_{D_n}, \text{PURITY}_{D_n}) \cdot \text{TOTAL} \tag{44}$$

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,[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:

TYPE	DESCRIPTION
No. 1	Sentinel Card Positive number in column 1-3 indicates a new job. Blank is sentinel for the end of job.
No. 2	Input Data Description Card or Cards 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.
No. 3	Index Card 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.
No. 4	Input Data Description Card or Cards Same as card type No. 2.
No. 5	Total Charge Card Total charge of turpentine in pounds. Columns 1-10 with decimal.

(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)	(DESCRIPTION)
	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 alpha-numeric 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 θ 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-

ing the tolerances. 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 turpentines 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

10. Property tax.

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 preceeding 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.[10] 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 XVIII). 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 accuratly 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 tolerences 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 turpentines 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.[6] 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

TABLES I THROUGH XXV

TABLE I

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

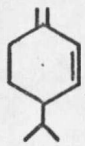
Alpha Pinene	
Camphene	
Beta Pinene	
Delta-3-Carene	
Myrcene	
Dipentene	
Beta Phellandrene	
Terpinolene	

TABLE II

TYPICAL COMPOSITION OF CRUDE SULFATE TURPENTINE

	Hoerner Waldorf Missoula, Montana	Southwest Forest Ind. Snowflake, Arizona	Potlatch Forests Lewiston, Idaho	Boiling Point °C
Alpha Pinene	37.7%	47.5%	56.5%	155.0
Camphene	1.1	.4	2.80	160.5
Beta Pinene	8.0	.9	7.40	158.3
Delta-3-Carene	39.2	40.5	16.1	170.2
Myrcene	1.3	--	.4	171.5
Dipentene	5.2	6.3	8.5	174.6
Beta Phellandrene	4.5	--	1.9	174.8
Terinolene	3.6	4.8	5.9	185.0

TABLE III

VAPOR PRESSURE EQUATION FOR TERPENES*

$\text{Log } P = A - B/(T + 240)$

P = mmHg

T = ^{o}C

A = 14.47981 + 0.0157748 (TB)

B = 1466.280 + 16.76439 (TB)

TB = Atmospheric boiling point, ^{o}C

Compound	A	B
Alpha Pinene	7.3495	1768.4714
Camphene	7.3755	1796.1192
Beta Pinene	7.3888	1810.3070
Delta-3-Carene	7.4494	1874.6973
Myrcene	7.4429	1867.7854
Dipentene	7.4645	1890.7039
Beta Phellandiene	7.4617	1887.7936
Terpinolene	7.5507	1982.3782

*Courtesy of: The Glidden Company
Organic Chemical Division
Jacksonville, Florida

TABLE IV

ENTHALPY EQUATIONS FOR TERPENES*

Vapor

$$h_V = W + U(t^{\circ}F + 460) \text{ BTU/Lb. mole}$$

Liquid

$$h_L = L + K(t^{\circ}F + 460) \text{ BTU/Lb. mole}$$

Molal heat of vaporization

$$H_V = (N)(1-Tr)^{0.38} \text{ BTU/Mole}$$

Tr is any reduced temperature.

Compound	W	U	L	K	N	Tc°K
Alpha Pinene	-10,881.5	61.768	-34,776	75.6	23,467.0	669.1
Camphene	- 8,720.2	61.915	-31.226	68.2	25,892.8	670.1
Beta Pinene	-11,436.0	68.038	-37,536	81.6	24 383.9	650.1
Delta-3-Carene	- 8,688.5	59.488	-30,932	65.46	24,388.9	648.6
Myrcene	-11,570.8	60.833	-37,720	82.0	25,806.6	638.7
Dipentene	- 9,327.1	66.899	-36,938	80.3	25,892.8	636.1
Beta Phellandrene	- 6,561.2	61.460	-35,190	76.5	26,280.6	646.9
Terpinoline	- 9,673.8	60.312	-31.240	66.1	23,467.0	634.7

*Courtesy of: Hercules Incorporated
Hattiesburg, Mississippi

TABLE V

SELLING PRICE OF TERPENES

Compound	Purity	Selling Price (bulk) $/lb.
Alpha Pinene*	95%	.0792
Beta Pinene*	80%	.1500
Dipentene**	55%	.0761
	33%	.0485
Delta-3-Carene***	95%	.1390

*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          10
C     PROCESSES WITH APPLICATIONS IN MULTICOMPONENT DISTILLATION-              20
C                                                                              30
C     PROGRAM IS WRITTEN IN FORTRAN II                                         40
C     LIBRARY SUBROUTINES HAVE BEEN MODIFIED TO ENABLE USE OF                  50
C     UNIVAC 1108, SEPTEMBER 1967, ALSO I/O STATEMENTS                         60
C                                                                              70
      DIMENSION XK(54,8),O(54),P(54),UCO(54,8),X(8),UCA(54,8),USUM(54),        80
     1G(54),PSUM(54),AP(54),GP(54,54),DELO(54),ON(54),UA(54),UO(54),           90
     2CX(54,8),F(54,8),T(54),AT(54),V(54),Z(54),SL(54,8),Y(54,8),             100
     3SV(54,8),TO(54),ZO(54),VO(54),XCO(54,8),Y O (54,8),ABF(54,8),           110
     4TOU(54),AV(54),BV(54),CV(54),DV(54),FV(54),GV(54),SD(9),A(9)            120
      DIMENSION  B(9) ,YEN(8), SDO(8), UL(8), WL(8),VL(8),VK(8)               130
     1,XLHV(8),T2O(54),V2O(54),TC(8),XN(8),        PTOT(54),SZ(54,8)         140
     2,PCO(54,8),D(8),PD(8),IMT(8),XO(8)                                      150
      COMMON YEN,WL,UL,VL,VK,NCMPS                                            160
C     READ IN  NECESSARY DATE  FOR  SIMULATON OF BATCH DISTILLATION COL.       170
C     READ - NUMBER OF PLATES - NUMBER OF COMPONENTS                           180
  200 READ 901,NPLTS,NCMPS                                                    190
      IF (NPLTS) 201,201,202                                                  200
  202 NC1 = NCMPS                                                             210
      NN=NPLTS+1                                                              220
      N2=NPLTS+2                                                              230
      AMOUNT = 0.0                                                            240
C     READ - MOLES TOTAL CHARGE - TOTAL MOLES OF EACH COMPONENT                250
      READ 900, UF,(X(I),I=1,NCMPS)                                           260
C     READ - HOLD-UP ON EACH PLATE-ASSUMED TEMPERATURE PROFILE AND EFF.        270
      DO 1 I=1,N2                                                             280
    1 READ 900,UA (I),AT(I)                                                   290
      DO 400 J = 1,N2                                                         300
      DO 400 I = 1,NCMPS                                                      310
  400 E(J,I) = 1.0                                                            320
C     READ - V RPOR  PRESSURE  EQUATION IN THE FORM LOGP=A/T+B                 330
      DO 2 I=1, NC1                                                           340
    2 READ 900, B(I),A(I)                                                     350
```

```
C     READ - INTIAL BOIL-UP-RATE,DIFFERENTIAL EQUATION WEIGHT FACTOR
C     ,REFLUX RATIO, PERCENT TO BE DISTILLED
C
      READ 900, BUR, XMU, RR, PCDT
C     READ - CONSTANTS FOR ENTHALPY EQUATIONS - H=A+ B*T
C     VAPOR - LIQUID - CONSTANTS FOR LATENT HEAT - CRITICAL TEMP
C
      DO 3 I=1,NCMPS
    3 READ 900,UL(I),WL(I), VK(I),VL(I),XN(I),TC(I)
C     READ - PRESSURE ON EACH PLATE
C
      READ900,(PTOT(J),J=1,N2)
C     BEGIN CALCULATION FOR STARTUP, STEADY STATE
C     CALCULATE  U(J,I)/U(0,I) - WHERE U IS  LIQUID HOLD UP IN MOLES
C     OF COMPONENT I ON PLATE -VAPOR HOLD-UP IS NEGLECTED
C     CALCULATE EQUIBRUM COEFFICIENTS - RAOULTS LAW
C     INDEX J= PLATE NUMBER, 1=CONDENSER,2...N+1,PLATE,
C     N+2 REBOILER
C     INDEX I= COMPONENT NUMBER
C     UCA = CALCULATED RATIO OF MOLAR HOLDUP ON PLATE J TO
C     CONDENSOR - EQUATION  8-38
      ISNT= 1
      UFO=UF
      DO 5 I = 1, NCMPS
    5 IMT(I) = 1
    6 DO 4 J = 1,N2
    4 T(J) = AT(J)
      DO 10 J = 1,N2
   10 O(J) = 1.0
   37 DO 8 I=1, NC1
      XM=1.
      DO 9 J=2,N2
      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(1)
    8 XK(1,I)=(10.0    **(A(I)/(T(1)-33.)+B(I)))/PTOT(1)
  110 DO 11 J=1,N2
   11 P(J)= .5*O(J)*10.E-4
```

```
C     CALCULATION OF THE CORRECTED MOLAR HOLD UP AT PLATE ZERO                740
C     UCO = CORRECTED MOLAR HOLDUP ON PLATE J OF COMPONENT I                  750
C     UCO(1,I) CALCULATED BY EQUATION  8-41                                   760
C                                                                             770
      DO 13 I=1,NCMPS                                                         780
      SUM=0.0                                                                 790
      DO 12 J=2,N2                                                            800
   12 SUM=SUM+O(J)*UCA(J,I)                                                   810
   13 UCO(1,I)=(UF*X(I))/(1.+SUM)                                             820
      DO 14 I=1, NCMPS                                                        830
      DO 14 J=2,NN                                                            840
   14 UCO(J,I)=O(J)*UCA(J,I)*UCO(1,I)                                         850
      DO 253 I = 1,NCMPS                                                      860
      SUM = 0.0                                                               870
      DO 252 J = 1,NN                                                         880
  252 SUM = SUM + UCO(J,I)                                                    890
  253 UCO(N2,I) = UF*X(I) -SUM                                                900
C     CALCULATION OF G-S FOR THE DELTA CONVERENCE METHOD                      910
C     FILL MATRIX G(J) FOR NEWTON RAPHSON CONVERENCE                          920
C     SUCH THAT ALL G-S ARE ZERO SIMULTANEOUSLY                               930
C                                                                             940
      DO 15 J=1,NN                                                            950
      USUM (J)= 0.0                                                           960
      DO 16 I=1, NCMPS                                                        970
   16 USUM (J)=USUM(J) +UCO (J,I)                                             980
   15 G(J)= UA(J) -USUM(J)                                                    990
      USUM(N2) = 0.0                                                         1000
      DO 255I = 1,NCMPS                                                      1010
  255 USUM(N2) = USUM(N2) +UCO(N2,I)                                         1020
      DO 17 JD=1,NN                                                          1030
      DO 17 JK =1,NN                                                         1040
C     CALCULATE THE PARTIAL DERIVATIVE OF G(JK) WITH                         1050
C     RESPECT TO O(JD)                                                       1060
C                                                                            1070
      RO = O(JK+1)                                                           1080
      O(JK+1)=O(JK+1)+P(JK+1)                                                1090
      DO98 I=1,NCMPS                                                         1100
```

```
      SUM=0.0                                                          1110
      DO 7 J=2,N2                                                      1120
    7 SUM=SUM+O(J)*UCA(J,I)                                            1130
   98 PCO(1,I)=(UF*X(I))/(1.+SUM)                                      1140
      DO 18 I=1,NCMPS                                                  1150
      DO 18 J=2, N2                                                    1160
   18 PCO(J,I)=O(J)* UCA(J,I)*PCO(1,I)                                 1170
      DO 19 J=1,NN                                                     1180
      PSUM(J)=0.0                                                      1190
      DO 20 I=1,NCMPS                                                  1200
   20 PSUM(J)=PSUM(J)+PCO(J,I)                                         1210
   19 AP(J)=PSUM(J)-UA(J)                                              1220
      GP(JD,JK)=(AP(JD  )+G(JD)  )/P(JK+1)                             1230
   17 O(JK+1)=RO                                                       1240
      CALL M TRIX (NN,GP,G ,DELO)                                      1250
      ON(1) = O(1)                                                     1260
      DO 21 J=1,NN                                                     1270
   21 ON(J+1)=O(J+1)+DELO(J)                                           1280
      DO 22 J=1,N2                                                     1290
C     TEST FOR CONVERGENCE                                             1300
C                                                                      1310
      IF (ABS(O(J)-ON(J))-.001) 22,22,23                               1320
   22 CONTINUE                                                         1330
      GO TO 24                                                         1340
   23 DO 242 J = 1, NN                                                 1350
      IF (ON(J+1))240, 241, 241                                        1360
  240 O(J+1) = O(J+1)/2.                                               1370
C     NEGATIVE O(J) IS SET TO 1/2 LAST POSITIVE VALVE                  1380
C                                                                      1390
      GO TO 242                                                        1400
  241 O(J+1) = ON(J+1)                                                 1410
  242 CONTINUE                                                         1420
      GO TO 37                                                         1430
   24 DO 26 J=1,N2                                                     1440
      DO 26 I=1,NCMPS                                                  1450
C     CALCULATE MOL FRACTION ON PLATE J OF COMPONENT I                 1460
C                                                                      1470
```

```
   26 CX (J,I) = UCO(J,I)/USUM(J)                                    1480
      XCMPS = NCMPS                                                  1490
C     CALCULATE TEMPERATURES BY KB METHOD,KB=1,NUMBER COMPS          1500
C                                                                    1510
      DO 31 J=1,N2                                                   1520
      DUM = 0.0                                                      1530
      DO 29 IB = 1,NCMPS                                             1540
      SUM=0.0                                                        1550
      DO 32 I=1,NCMPS                                                1560
   32 SUM=SUM+E(J,I)*CX(J,I)*XK(J,I)/XK(J,IB)                        1570
      R=1./SUM                                                       1580
      PV=R*(PTOT(J))                                                 1590
      T(J) = A(IB)/(ALOG10(PV)-B(IB)) + 33.0                         1600
   29 DUM = DUM +T(J)                                                1610
   31 T(J) = DUM/XCMPS                                               1620
      DO 33 J = 1,N2                                                 1630
C     CHECK TEMPERATURES FOR CONVERVENCE                             1640
C                                                                    1650
      IF(ABS (T(J)-AT(J))- .5)33,33,34                               1660
   33 CONTINUE                                                       1670
      GO TO 35                                                       1680
   34 DO 36 J = 1,N2                                                 1690
   36 AT(J) = T(J)                                                   1700
      GO TO 37                                                       1710
   35 DO 39 I =1,NCMPS                                               1720
      DO 39 J= 1,NN                                                  1730
      V(J)=BUR                                                       1740
      Z(J)=BUR                                                       1750
      SL(J,I)=Z(J)*CX(J,I)                                           1760
      Y(J,I)=E(J+1,I)*XK(J+1,I)*CX(J+1,I)                            1770
   39 SZ(J,I)=V(J)*Y(J,I)                                            1780
C     SET VALUE FOR CALCULATIONS OF PRODUCT PERIOD                   1790
      DO 209  I=1, NCMPS                                             1800
      DO 209 J= 1,N2                                                 1810
      XCO(J,I)=CX(J,I)                                               1820
  209 YO(J,I)=Y(J,I)                                                 1830
      DO 210 J=1,NN                                                  1840
```

```
      UO(J)=UA(J)                                                        1850
      ZO(J)=Z(J)                                                         1860
      VO (J)= V(J)                                                       1870
  210 TO (J)=AT(J)                                                       1880
      TO (N2)=AT(N2)                                                     1890
      UO(N2)=UA(N2)                                                      1900
      DRO=0.0                                                            1910
      QCO=0.0                                                            1920
C     CALCULATE LATENT HEATS OF OVERHEAD PRODUCT                         1930
C                                                                        1940
      DO 213 I = 1,NCMPS                                                 1950
  213 XLHV(I) = XN(I)*(1.-  T(1) /TC(I))**.38                            1960
C     CALCULATE CONDENSER HEAT DUTY -STEADY STATE                        1970
C                                                                        1980
      DO 211 I=1, NCMPS                                                  1990
  211 QCO=QCO+XLHV(I)* CX(1,I)*BUR                                       2000
      SIG= (1.-XMU)/XMU                                                  2010
      TIME = 0.0                                                         2020
C     PRINT- OVERHEAD COMPOSITION - STEADY STATE                         2030
C                                                                        2040
      PRINT 801                                                          2050
      PRINT 800, TIME,(CX(1,I),I=1,NCMPS)                                2060
      DR=BUR/(RR+1.)                                                     2070
      DT=UF/(DR* 50.)                                                    2080
      DO 214 I = 1,NCMPS                                                 2090
      XO(I) = X(I)                                                       2100
  214 SDO(I)=0.0                                                         2110
      UFP = UF                                                           2120
      PRINT 701                                                          2130
      DO 61 J = 1,N2                                                     2140
   61 O(J) = 1.                                                          2150
C     CALCULATE ABSORBTION FACTOR ON PLATE J OF COMPONENT I              2160
C                                                                        2170
  162 DO 40 I=1,NCMPS                                                    2180
      DO 41 J=2,NN                                                       2190
   41 ABF(J,I)=Z(J)/(V(J-1)*E(J,I)*XK(J,I))                              2200
```

```
   40 ABF(1,I)=Z(1)/DR                                                    2210
      DO 42 J=1,NN                                                        2220
   42 TOU(J)=UA(J)*DT/Z(J)                                                2230
      DO 52 I=1,NCMPS                                                     2240
C     CALCULATE A, B, C D OF TRIDIAGONAL MATRIX SOLUTION                  2250
C                                                                         2260
      BV(1)=-1.-ABF(1,I)*(1.+TOU(1)/XMU)                                  2270
      AV(1)=0.0                                                           2280
      CV(1)=1.0                                                           2290
      DV(1) = -SIG*(SZ(1,I)-SL(1,I)-SDO (I))-UCO(1,I)/(XMU*DT)            2300
      DO 53 J=2,NN                                                        2310
      AV(J)=ABF(J-1,I)                                                    2320
      BV(J)= -1.0-ABF(J,I)*(1.+TOU(J)/XMU)                                2330
      CV(J)=1.0                                                           2340
   53 DV(J)=-SIG*(SZ(J,I)+SL(J-1,I)-SZ(J-1,I)-SL(J,I))-UCO                2350
     1(J,I)/(XMU*DT)                                                      2360
      AV(N2)=ABF(NN,I)                                                    2370
      BV(N2)= -1.-(UA(N2)/V(NN))/(XMU*DT*XK(N2,I))                        2380
      CV(N2)=0.0                                                          2390
      DV(N2)=-SIG*(SL(NN,I)-SZ(NN,I))-UCO(N2,I)/(XMU*DT)                  2400
C     SOLVE TRIDIAGONAL MATRIX FOR COMPONENT VAPORRATE                    2410
C     LEAVING PLATE J                                                     2420
C                                                                         2430
      FV(1)=CV(1)/BV(1)                                                   2440
      GV(1)=DV(1)/BV(1)                                                   2450
      DO 54 J=2,NN                                                        2460
      FV(J)=CV(J)/(BV(J)-AV(J)*FV(J-1))                                   2470
   54 GV(J)=(DV(J)-AV(J)*GV(J-1))/(BV(J)-AV(J)*FV(J-1))                   2480
      GV(N2)=(DV(N2)-AV(N2)*GV(NN))/(BV(N2)-AV(N2)*FV(N2-1))              2490
      SV(N2,I)=GV(N2)                                                     2500
      K=NN                                                                2510
   56 SV(K,I)=GV(K)-FV(K)*SV(K+1,I)                                       2520
      K=K-1                                                               2530
      IF(K) 57,57,56                                                      2540
   57 SD(I)=SV(1,I)                                                       2550
C     CHECK TO SEE IF COMPONENT HAS BEEN DISTILLED OFF.                   2560
C                                                                         2570
```

```
      IF ( IMT(I)) 563,563,562                                          2580
  563 DO 564 J = 1,N2                                                   2590
  564 UCA(J,I) = 0.0                                                    2600
      GO TO 52                                                          2610
  562 SUM = 0.0                                                         2620
C     CALCULATE RATIO OF COMPONENT MOLARHOLD-UP TO THE                  2630
C     DISTILLATION RATE - EQUATION ON PAGE 77                           2640
C                                                                       2650
      DO 58 J = 1,NN                                                    2660
      IF (SV(J,I)) 998,998,999                                          2670
  998 UCA(J,I) = 0.0                                                    2680
      GO TO 58                                                          2690
  999 IF (SD(I)) 560,560,561                                            2700
  560 SD(I) = SV(J,I)                                                   2710
  561 UCA(J,I) = (UA(J)*ABF(J,I)*SV(J,I))/(Z(J)*SD(I))                  2720
   58 SUM = SUM + UCA(J,I)                                              2730
      UCA(N2,I) = UFP*X(I)/SD(I) - SUM                                  2740
   52 CONTINUE                                                          2750
  620 DO 62 J=1,N2                                                      2760
   62 P(J)=.5 *O(J)*10.E-4                                              2770
      DO 64 I=1, NCMPS                                                  2780
      SUM=UFP*X(I)                                                      2790
      CUM=0.0                                                           2800
      DO 63 J=1,NN                                                      2810
   63 CUM=CUM+O(J+1)*UCA(J,I)                                           2820
      CUM=CUM+O(1)*UCA(N2,I)                                            2830
      IF ( IMT(I))641,641,642                                           2840
  641 D(I) = 0.0                                                        2850
      GO TO 64                                                          2860
C     CALCULATE CORRECTED  COMPONENT DISTILLATION RATE                  2870
C     EQUATION  8-47                                                    2880
C                                                                       2890
  642 D  (  I)=(-SIG*SDO(I)+1./(XMU*DT) *SUM)/(1. +  1.                 2900
     1/(XMU*DT) *CUM)                                                   2910
   64 CONTINUE                                                          2920
      DO 650I=1,NCMPS                                                   2930
      DO 65 J=1,NN                                                      2940
```

```
 65 UCO(J,I)=O(J+1)*UCA(J,I)*D   (   I)                                  2950
650 UCO(N2,I)=O(1)*UCA(N2,I)*D(I)                                       2960
    DO 67 J=2, N2                                                       2970
    USUM(J)=0.0                                                         2980
    DO 68 I=1,NCMPS                                                     2990
 68 USUM(J)=USUM(J)+UCO(J-1,I)                                          3000
C   CALCULATE NEWTON-RAPHSON MATRIX - G(J)                              3010
C                                                                       3020
 67 G(J)=UA(J-1)-USUM(J)                                                3030
    USUM(1)=0.0                                                         3040
    DO 69 I=1,NCMPS                                                     3050
 69 USUM(1)=USUM(1)+D(I)                                                3060
    G(1)=DR-USUM(1)                                                     3070
    DO 70 JD=1,N2                                                       3080
    DO 70 JK= 1,N2                                                      3090
    RO= O(JK)                                                           3100
    O(JK)=O(JK)+P(JK)                                                   3110
    DO 640 I=1, NCMPS                                                   3120
    SUM=UFP*X(I)                                                        3130
    CUM=0.0                                                             3140
    DO 630 J=1,NN                                                       3150
630 CUM=CUM+O(J+1)*UCA(J,I)                                             3160
    CUM=CUM+O(1)*UCA(N2,I)                                              3170
    IF (IMT(I)) 643,643,644                                             3180
643 PD(I) = 0.0                                                         3190
    GO TO 640                                                           3200
644 PD (   I)=(-SIG*SDO(I)+1./(XMU*DT) *SUM)/(1. +   1.                 3210
   1/(XMU*DT) *CUM)                                                     3220
640 CONTINUE                                                            3230
    DO 71 I=1,NCMPS                                                     3240
    DO 72 J=1,NN                                                        3250
 72 PCO(J,I)=O(J+1)*UCA(J,I)*PD (   I)                                  3260
 71 PCO(N2,I)=O(1)*UCA(N2,I)*PD(    I)                                  3270
    DO 74 J=2,N2                                                        3280
    PSUM(J)=0.0                                                         3290
    DO 73 I=1,NCMPS                                                     3300
```

```
   73 PSUM(J)=PSUM(J)+PCO(J-1,I)                                        3310
   74 AP(J)=PSUM(J)-UA(J-1)                                             3320
      PSUM(1)=0.0                                                       3330
      DO 75 I=1,NCMPS                                                   3340
   75 PSUM(1)=PSUM(1)+PD (   I)                                         3350
      A P(1)=PSUM(1)-DR                                                 3360
C     CALCULATE THE PARTIAL DERIVATIVE OF G(JK) WITH                    3370
C     RESPECT TO O(JD)                                                  3380
C                                                                       3390
      G P(JD,JK)=(AP(JD)+G(JD))/P(JK)                                   3400
   70 O(JK)=RO                                                          3410
C     SOLVE MATRIX GP*X = G FOR X,WHICH EQUALS DELTA O                  3420
C                                                                       3430
      CALL M TRIX(N2,GP,G,DELO)                                         3440
      DO 76 J=1,N2                                                      3450
   76 ON(J)=O(J)+DELO(J)                                                3460
      DO 77 J=1,N2                                                      3470
C     CHECK FOR CONVERGENCE                                             3480
C                                                                       3490
      IF (ABS(O(J)-ON(J))-.001) 77,77,78                                3500
   77 CONTINUE                                                          3510
      GO TO 79                                                          3520
   78 DO 80 J=1,N2                                                      3530
C     NEGATIVE O IS SET TO 1/2 LAST POSITIVE VALVE                      3540
C                                                                       3550
      IF (ON(J))280, 280, 281                                           3560
  280 O(J) = O(J)/2.                                                    3570
      GO TO 80                                                          3580
  281 O(J) = ON(J)                                                      3590
   80 CONTINUE                                                          3600
      GO TO 620                                                         3610
   79 DO 81 J =1,N2                                                     3620
      UA(J) = 0.0                                                       3630
      DO 81 I = 1,NCMPS                                                 3640
   81 UA(J) = UA(J) + UCO(J,I)                                          3650
C     CALCULATE MOL FRACTION ON PLATE J OF COMPONENT I                  3660
C                                                                       3670
```

```
      DO 82 J = 1,N2                                                    3680
      DO 82 I = 1,NCMPS                                                 3690
      IF (IMT(I)) 821,821,822                                           3700
  821 CX(J,I) = 0.0                                                     3710
      GO TO 82                                                          3720
  822 CX(J,I) = UCO(J,I)/UA(J)                                          3730
   82 CONTINUE                                                          3740
C     CALCULATE TEMPERATURES ON EACH PLATE                              3750
C                                                                       3760
      DO 86 J=1,N2                                                      3770
      XCMPS = NCMPS                                                     3780
      DUM = 0.0                                                         3790
      DO 84 IB = 1,NCMPS                                                3800
C     CHECK TO SEE IF COMPONENT HAS BEEN DISTILLED OFF                  3810
C                                                                       3820
      IF(IMT(IB)) 840,840,841                                           3830
  840 T(J) = 0.0                                                        3840
      XCMPS = XCMPS     -1.0                                            3850
      GO TO 84                                                          3860
  841 SUM = 0                                                           3870
      DO 85 I=1,NCMPS                                                   3880
   85 SUM=SUM+E(J,I)*CX(J,I)*XK(J,I)/XK(J,IB)                           3890
      R=1./SUM                                                          3900
      PV=R*(PTOT(J))                                                    3910
      T(J) = A(IB)/(ALOG10(PV)-B(IB)) + 33.0                            3920
   84 DUM = DUM +  T(J)                                                 3930
   86 T(J) = DUM/XCMPS                                                  3940
      DO 830 J=1,N2                                                     3950
      DO 830 I=1,NCMPS                                                  3960
  830 XK(J,I)=(10.0**(A(I)/(T(J)-33.0)+B(I)))/PTOT(J)                   3970
   89 Z(1)=DR*RR                                                        3980
      DO 500 I=1,NCMPS                                                  3990
C     ENTHALPY BALANCE                                                  4000
C                                                                       4010
  500 YEN(I) = CX (1,I)                                                 4020
      HX01 = ENTHPY (T(2), 2)                                           4030
```

```
      DO 501 I=1,NCMPS                                                    4040
  501 YEN(I)=CX(1,I)                                                      4050
      SH = ENTHPY(T(1),1)                                                 4060
      DO 502 I=1,NCMPS                                                    4070
  502 YEN(I) = XCO(1,I)                                                   4080
      HXO1O= ENTHPY(T(2),2)                                               4090
      DO 503 I=1,NCMPS                                                    4100
  503 YEN(I)=XCO(1,I)                                                     4110
      SHO=ENTHPY(TO(1),1)                                                 4120
      DO 504 I=1,NCMPS                                                    4130
  504 YEN(I) = YO(1,I)                                                    4140
      HYO1 = ENTHPY(T(2), 2)                                              4150
       HYOO = ENTHPY(TO(2), 2)                                            4160
      QC = Z(1) * (HXO1-SH) + DR *(HXO1-SH) + SIG*(ZO(1)*(H               4170
     1XO1O - SHO) +DRO*(HXO1-SHO) -VO(1)*(HYO1-HYOO)- QCO)                4180
     2+ UA(1)/(XMU*DT) * (HXO1-SH) -UO(1)/(XMU*DT) *(HXO1O-SHO)           4190
      DO 401 J=2,NN                                                       4200
      DO 505 I=1, NCMPS                                                   4210
  505 YEN(I) = CX(1,I)                                                    4220
      HXDJ=ENTHPY(T(J+1),2)                                               4230
      DO 506 I=1,NCMPS                                                    4240
  506 YEN(I) = YO(J  ,I)                                                  4250
      HYJ = ENTHPY(T(J+1),2)                                              4260
      HYJO = ENTHPY (TO(J+1),2)                                           4270
      DO 507 I=1,NCMPS                                                    4280
  507 YEN(I) = XCO(J  ,I)                                                 4290
      HXJO = ENTHPY(T(J+1),2)                                             4300
      SHJO = ENTHPY(T(J+1), 1)                                            4310
      DO 508 I=1,NCMPS                                                    4320
  508 YEN(I) = XCO(1,I)                                                   4330
      HXDJO = ENTHPY(T(J+1),2)                                            4340
      DO 509 I=1,NCMPS                                                    4350
  509 YEN(I) = CX(J  ,I)                                                  4360
      HXOJ = ENTHPY (T(J+1),2)                                            4370
      SHJ = ENTHPY(T(J),1)                                                4380
      DIV = HXO J-SHJ                                                     4390
      SUM=0.0                                                             4400
```

```
      NJ=J                                                              4410
      DO 402 K=1,NJ                                                     4420
      DO 520 I=1,NCMPS                                                  4430
  520 YEN(I)=CX(K,I)                                                    4440
      HE1=ENTHPY(T(J+1),2)                                              4450
      HE2=ENTHPY(T(K),1)                                                4460
      DO 521 I=1,NCMPS                                                  4470
  521 YEN(I)=XCO(K,I)                                                   4480
      HE3=ENTHPY(T(J+1),2)                                              4490
      HE4=ENTHPY(TO(K),1)                                               4500
  402 SUM=SUM+UA(K)*(HE1-HE2)-UO(K)*(HE3-HE4)                           4510
C     CALCULATE LIQUID FLOW RATES BY ENTHALPY BALANCE                   4520
C                                                                       4530
  401 Z(J)=(-DR*(HXDJ-SH) +QC + SIG* (VO(J)*(HYJ -HYJO)))/              4540
     1DIV + (-ZO(J)*( HXJO -SHJO) -DRO * (HXDJO - SHO) +QCO)/DI         4550
     2V-SUM/(XMU*DT*DIV)                                                4560
C     TOTAL MATERIAL BALANCE                                            4570
      SUM=0.0                                                           4580
      DO 99 J=1,NN                                                      4590
      SUM=SUM+UA(J)-UO(J)                                               4600
C     CALCULATE TOTAL VAPOR FLOW RATES BY TOTAL MATERIAL BALANCE        4610
C                                                                       4620
   99 V(J)=Z(J)+DR -SIG* (VO(J)- ZO(J)-DRO)+SUM/(XMU*DT)                4630
      DO 100 I=1,NC1                                                    4640
      DO 100 J=1,NN                                                     4650
      Y(J,I) = SV(J+1,I)/V(J)                                           4660
      SZ(J,I) = SV(J+1,I)                                               4670
  100 SL(J,I)=Z(J)*CX(J,I)                                              4680
      DO 87 J=1,N2                                                      4690
C     CHECK FOR CONVERGENCE ON TEMPERATURES                             4700
C                                                                       4710
  163 IF (ABS (T(J)-AT(J))-.4)87,87,88                                  4720
   87 CONTINUE                                                          4730
      GO TO 189                                                         4740
   88 DO 90 J=1,N2                                                      4750
   90 AT(J)=T(J)                                                        4760
      GO TO 162                                                         4770
```

```
  189 DO 212 I=1,NCMPS                                                  4780
      SD (I)=CX(1,I)*DR                                                 4790
      UA(N2) = UO(N2)- DR*DT                                            4800
      IF ( IMT(I) ) 221,221,222                                         4810
  222 UFP= 0.0                                                          4820
      DO 223 J = 1,N2                                                   4830
  223 UFP= UFP+ UA(J)                                                   4840
C     CALCULATE OVERALL COLUMN COMPOSITION                              4850
C                                                                       4860
      X(I) =(UF*XO(I) -DR*CX(1,I)*DT)/UFP                               4870
      GO TO 212                                                         4880
  221 X(I) = 0.0                                                        4890
  212 CONTINUE                                                          4900
      TIME = TIME + DT                                                  4910
C     PRINT - TIME, OVERHEAD COMPOSITION AND AMOUNT                     4920
C                                                                       4930
      PRINT 800, TIME,(CX(1,I),I=1,NCMPS)                               4940
      AMOUNT = DR*DT*136.42 +AMOUNT                                     4950
      PRINT 802, AMOUNT                                                 4960
  408 DO 409 J = 1,N2                                                   4970
  409 UO(J) = UA(J)                                                     4980
  308 DO 310 J=1,NN                                                     4990
      T2O (J)=TO(J)                                                     5000
      V2O(J)=VO(J)                                                      5010
      TO (J)=AT(J)                                                      5020
      AT(J)= T(J)                                                       5030
      ZO(J)=Z(J)                                                        5040
  310 VO(J)=V(J)                                                        5050
      T2O(N2)=TO(N2)                                                    5060
      TO(N2)=AT(N2)                                                     5070
      AT(N2) = T(N2)                                                    5080
  314 DO 309 I=1,NCMPS                                                  5090
      DO 309 J = 1,N2                                                   5100
      YO(J,I)=Y(J,I)                                                    5110
  309 XCO(J,I)=CX(J,I)                                                  5120
      QCO=QC                                                            5130
      DRO=DR                                                            5140
```

```
      UF = UFP                                                          5150
C     CHECK FOR END OF RUN                                              5160
C                                                                       5170
      IF ((UFO-UF)/UFO-PC DT) 311,311,312                               5180
  311 DO 330 I=1,NCMPS                                                  5190
      XO(I) = X(I)                                                      5200
C     CHECK TO SEE IF COMPONENT HAS BEEN DISTILLED OFF                  5210
      IF (X(I)-.001) 320,321,321                                        5220
  320 IF(IMT(I)) 322,322,323                                            5230
  322 SDO(I) = 0.0                                                      5240
  323 IMT(I) = 0                                                        5250
      X(I) = 0.0                                                        5260
      SDO(I) = SD(I)                                                    5270
      GO TO 330                                                         5280
  321 SDO(I) = SD(I)                                                    5290
  330 CONTINUE                                                          5300
      DT = UFO/(DR* 50.)                                                5310
      GO TO 162                                                         5320
C     PRINT - BOTTOMS COMPOSITION                                       5330
C                                                                       5340
  312 WRITE (6,803)                                                     5350
      WRITE (6,800) TIME,(X(I),I=1,NCMPS)                               5360
      GO TO 200                                                         5370
  201 CALL EXIT                                                         5380
  700 FORMAT (1H ,7E14.8)                                               5390
  701 FORMAT  (21H START PRODUCT PERIOD)                                5400
  800 FORMAT (9F14.3)                                                   5410
  801 FORMAT(32H ANSWER-TIME AND TOP COMPOSITION)                       5420
  802 FORMAT (9H AMOUNT =,F10.3)                                        5430
  803 FORMAT (16H END COMPOSITION)                                      5440
  900 FORMAT (8F10.0)                                                   5450
  901 FORMAT (2I2)                                                      5460
      END                                                               5470
```

```
      FUNCTION ENTHPY( T,IVAP)                                          10
C     THIS ROUTINE CALCULATES THE ENTHALPY OF A VAPOR OR LIQUID         20
C     AT TEMPERATURE T IN DEGREES K, BY THE SUM OF ENTHALPIES OF        30
C     THE PURE COMPONENT TIMES THE MOLE FRACTION                        40
C                                                                       50
      DIMENSION UL(8),WL(8),VL(8),VK(8),YEN(8)                          60
      COMMON YEN,WL,UL,VL,VK,NCMPS                                      70
      Q =T*1.8                                                          80
      ENTHPY=0.0                                                        90
      IF (IVAP-1) 2,2,1                                                100
    1 DO 3 I=1,NCMPS                                                   110
    3 ENTHPY=ENTHPY+(WL(I)+UL(I)*Q)*YEN(I)                             120
      RETURN                                                           130
    2 DO 4 I=1, NCMPS                                                  140
    4 ENTHPY=ENTHPY+(VL(I)+VK(I)*Q)*YEN(I)                             150
      RETURN                                                           160
      END                                                              170
```

```
      SUBROUTINE M TRIX (N,A,B,X)                                          10
C     THIS ROUTINE SOLVES THE MATRIX AX=B FORX                             20
C     WHERE A IS N BY N AND  B IS N BY 1                                   30
C     GAUSSIAN ELIMINATION IS USED WITH PIVOTAL COMPENSATION               40
C                                                                          50
      DIMENSION A(54,54),B(54),X(54)                                       60
      K = 1                                                                70
    4 I = K +1                                                             80
      L=K                                                                  90
   99 IF(ABS (A(I,K))-ABS (A(L,K)))100,100,101                            100
  101 L=I                                                                 110
  100 IF(I-N) 102,103,103                                                 120
  102 I= I+1                                                              130
      GO TO 99                                                            140
  103 IF(L-  K) 104,104,105                                               150
  104 J=K                                                                 160
  108 CON = A(K,J)                                                        170
      A(K,J) = A(L,J)                                                     180
      A(L,J) = CON                                                        190
      IF(J-  N) 106,107,107                                               200
  106 J=J+1                                                               210
      GO TO 108                                                           220
  107 CON = B(K)                                                          230
      B(K) = B(L)                                                         240
      B(L) = CON                                                          250
  105  I=K+1                                                              260
    5 Y = A(I,K)/A(K,K)                                                   270
      A(I,K) = 0.0                                                        280
      J = K +1                                                            290
   80 A(I,J) = A(I,J) -Y*A(K,J)                                           300
      IF (J-N) 8,9,9                                                      310
    8 J = J + 1                                                           320
      GO TO 80                                                            330
    9 B(I) = B(I) -Y*B(K)                                                 340
      IF(I-N) 10,11,11                                                    350
```

```
10 I =I +1                                                    360
   GO TO 5                                                    370
11 IF ( K-(N-1)) 12,13,13                                     380
12 K = K+1                                                    390
   GO TO 4                                                    400
13 X(N) = B(N)/A(N,N)                                         410
   I = N-1                                                    420
19 J = I +1                                                   430
   S = 0.0                                                    440
16 S = S+A(I,J)*X(J)                                          450
   IF(J-N) 14,15,15                                           460
14 J = J+1                                                    470
   GO TO 16                                                   480
15 X(I) =(B(I)-S)/A(I,I)                                      490
   IF (I-1) 17,17,18                                          500
18 I = I-1                                                    510
   GO TO19                                                    520
17 RETURN                                                     530
   END                                                        540
```

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.

DELTO(J) = Jth incremental change in 0:Δ0.

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 0's.

GP(JK,JD)= The partial derivative of G(JK) with respect to 0(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) = Total molal flow rate of vapor leaving plate J.

VK(J) = Constant for calculation of the enthalpy of component I in vapor phase.

VL(I) = Constant for calculation of the enthalpy of component I in vapor phase.

VO(J) = Value at the beginning of the time increment of the total molal flow rate of vapor leaving plate J.

WL(I) = Constant for calculation of the enthalpy of component I in liquid phase.

X(I) = Total mole fraction of component I, in the column.

XCO(J,I) = Value at the beginning of time increment of mole fraction of component I on plate J.

XK(J,I) = Equilibrium constant for component I on plate J.

XLHV(I) = Latent heat of vaporization of component I.

Y(J,I) = Mole fraction of component I in vapor leaving plate J.

YO(J,I) = Value at the beginning of the time increment of the mole fraction of component I in vapor leaving plate J.

Z(J) = Total molal flow rate of liquid leaving plate J.

ZO(J) = 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
 1
  HOERNER WALDORF CRUDE                    INPUT DATA

1 NUMBER OF COMPOUNDS,PURITIES PER COUMPOUND,NUMBER OF REFLUX RATIOS
  4  1  1  1  1  4
1 TOTAL CHARGE
   408.
  PERCENT DISTILLED PRECEEDING THE CUT AT PURITY 1
1   30 TO 1   15 TO 1   10 TO 1    5 TO 1
   .738       .754       .775       .789      DIPENTENE
   .546       .602       .657       .684       DELTA 3 CARENE
   .422       .435      -1.        -1.         BETA PINENE
  .0         .0         .0         .0          ALPHA PINENE
  PERCENT DISTILLED SUCCEEDING THE CUT IT PURITY 1
1   30 TO 1   15 TO 1   10 TO 1    5 TO 1
   .838       .833       .831       .829      DIPENTENE
   .701       .698       .696       .694       DELTA 3 CARENE
   .462       .450      -1.        -1.         BETA PINENE
   .360       .315       .300       .295       ALPHA PINENE
1 REFLUX RATIOS
 30.        15.0       10.0       5.0
1 PRICE DATA IN DOLLARS PER POUND
 .076          DIPENTENE
 .1359         DELTA 3 CARENE
 .150          BETA PINENE
 .079          ALPHA PINENE
1 PURITIES OF EACH COUMPOUND
 50.0          DIPENTENE
 95.0          DELTA 3 CARENE
 80.0          BETA PINENE
 95.0          ALPHA PINENE
```

TABLE (CONTINUED)

COST DATA INCLUDES OPERATING COST,BOIL UP RATE,COST OF BOTTOMS AND
1 NUMBER OF RUNS PER YEAR

.10	100.0	-.0185	50.

BOTTOMS PRODUCT
DIPENTENE FRACTION
DELTA 3 CARENE DIPENTENE MIDFRACTION
DELTA 3 CARENE FRACTION
BETA PINENE DELTA 3 CARENE MIDFRACTION
BETA PINENE FRACTION
ALPHA PINENE BETA PINENE MIDFRACTION
ALPHA PINENE FRACTION

TABLE IX

TYPICAL OUTPUT OF SIMULATION PROGRAM

TABLE

* SEE TABLE 1 FOR KEY TO NUMBERS

* CMP. NO.	1	2	3	4	5	6	7	8
ANSWER-TIME AND TOP COMPOSITION								
0.000	.978	.010	.012	.001	0.000	0.000	0.000	0.000
START PRODUCT PERIOD								
AMOUNT =	15.998							
2.422	.970	.013	.016	.001	0.000	0.000	0.000	0.000
AMOUNT =	31.996							
4.844	.972	.012	.015	.001	0.000	0.000	0.000	0.000
AMOUNT =	47.994							
7.266	.976	.011	.013	.001	0.000	0.000	0.000	0.000
AMOUNT =	63.992							
9.689	.963	.015	.020	.001	0.000	0.000	0.000	0.000
AMOUNT =	79.990							
12.111	.973	.012	.014	.001	0.000	0.000	0.000	0.000
AMOUNT =	95.988							
14.533	.961	.016	.021	.001	0.000	0.000	0.000	0.000
AMOUNT =	111.986							
16.955	.973	.012	.014	.001	0.000	0.000	0.000	0.000
AMOUNT =	127.984							
19.377	.956	.017	.023	0.000	0.000	0.000	0.000	0.000
AMOUNT =	143.982							
21.799	.971	.013	.016	.001	0.000	0.000	0.000	0.000
AMOUNT =	159.980							
24.221	.954	.018	.026	.002	0.000	0.000	0.000	0.000
AMOUNT =	175.978							
26.643	.968	.014	.017	.001	0.000	0.000	0.000	0.000
AMOUNT =	191.976							
29.066	.950	.020	.028	.002	0.000	0.000	0.000	0.000

TABLE CONTINUED

AMOUNT =	207.974							
31.488	.966	.015	.018	.001	0.000	0.000	0.000	0.000
AMOUNT =	223.972							
33.910	.944	.021	.031	.002	0.000	0.000	0.000	0.000
AMOUNT =	239.970							
36.332	.962	.016	.020	.001	0.000	0.000	0.000	0.000
AMOUNT =	255.968							
38.754	.956	.019	.024	.001	0.000	0.000	0.000	0.000
AMOUNT =	271.966							
41.176	.946	.021	.030	.002	0.000	0.000	0.000	0.000
AMOUNT =	287.964							
43.598	.947	.022	.029	.002	0.000	0.000	0.000	0.000
AMOUNT =	303.962							
46.021	.941	.022	.029	.002	0.000	.001	0.000	0.000
AMOUNT =	319.960							
48.443	.938	.025	.034	.002	0.000	0.000	0.000	0.000
AMOUNT =	335.958							
50.865	.931	.026	.039	.003	0.000	.001	0.000	0.000
AMOUNT =	351.956							
53.287	.926	.030	.041	.002	0.000	0.000	0.000	0.000
AMOUNT =	367.954							
55.709	.880	.043	.070	.005	0.000	.001	0.000	0.000
AMOUNT =	383.952							
58.131	.924	.031	.043	.002	0.000	0.000	0.000	0.000
AMOUNT =	399.950							
60.553	.836	.057	.098	.008	0.000	.002	0.000	0.000
AMOUNT =	415.948							
62.975	.890	.042	.063	.003	0.000	.001	0.000	0.000
AMOUNT =	431.946							

END OF RUN

TABLE X

PROGRAM LIST OF OPTIMIZATION PROGRAMS

```
C      MAINLINE                                                          10
C      THIS ROUTINE SERVES AS AN EXECUTIVE ROUTINE, READS DATA AND SETS  20
C      INDEXS                                                            30
C                                                                        40
       DIMENSION IPT(10),IORIN(4,4),PDT(16,4,2),XMID(16,4,4),RR(4   ),PP(  50
      14,4), PUR(4,4),FX(16,16),DMAX(16),IORD(16,16),AMOT(8),RSR(8),OPER1  60
      2(8, 8),OPER2(8,8),ANS(5,5),IE(40,8),ICM(4)                        70
       DIMENSION TMOT(8) ,TSR(8)                                         80
       DIMENSION H(20)                                                   90
       COMMON ISENT,ICMP,IPT,IRR,TOTAL,IORIN,PDT, XMID, RR,PP,PUR,OC,   100
      1BUR,CB,CDBR,AMOUNT,AVERR,RTN,FX,DMAX,IORD,FMAX,INP,AMOT,RSR,OPER1,  110
      2 OPER2,ANS,IE,ICM,IMD,RYEAR,IPM                                  120
  102 READ 851,ISENT                                                    130
       DEFINE DISK(20,2000)                                             140
C                                                                       150
C      SPACEING OF THE PAGE FOR PRINTING OUT INPUT DATA                 160
C      READ- ISENT - BLANK = END OF JOB, POSTIVE NUMBER= NEW  JOB       170
C                                                                       180
       PRINT 800                                                        190
       DO 1000 I = 1,10                                                 200
 1000  PRINT 804                                                        210
       IF(ISENT)100,100,101                                             220
C      DECP  PRINTS HEADINGS  FOR INPUT  DATA                           230
  101  CALL DECP                                                        240
C      READ  -   NUMBER OF STAGES- ICMP                                 250
C            -   NUMBER OF PURITIES PER STAGE-IPT(I)                    260
C            -   NUMBER OF REFLUX RATIOS - IRR                          270
C                                                                       280
       READ 851,ICMP,(IPT(I),I=1,ICMP),IRR                             290
       PRINT851,ICMP,(IPT(I),I=1,ICMP),IRR                             300
       CALL DECP                                                        310
C      READ   -   TOTAL POUND OF CHARGE                                 320
C                                                                       330
       READ 802, TOTAL                                                  340
       PRINT 802, TOTAL                                                 350
C      SORT FOR MAXIMUM PURITIES ON ALL STAGES                          360
```

```
C                                                                       370
      IPMX=1                                                            380
      DO 2 I=1,ICMP                                                     390
      IF (IPT(I)-IPMX) 2,2,3                                            400
    3 IPMX=IPT(I)                                                       410
    2 CONTINUE                                                          420
C     GENERATE INDEX FOR PURITY AND REFLUX RATIO                        430
C                                                                       440
      IANT=0                                                            450
      DO 6 IP=1,IPMX                                                    460
      DO 7 I=1,IRR                                                      470
    7 IORIN(IP,I) =I+IANT                                               480
      IANT=IANT+IRR                                                     490
    6 CONTINUE                                                          500
C     READ - DISTILLATION  DATA - PDT (J,IK, 1) = PERCENTAGE PRIOR      510
C                               - PDT (J,IK, 2) = PERCENTAGE FOLLOWIN   520
      DO 1 K=1,2                                                        530
      CALL DECP                                                         540
C     IK = STAGE NUMBER, J = REFLUX RATIO-PURITY INDEX                  550
C                                                                       560
      DO 1 IK=1,ICMP                                                    570
      IPM=IPT(IK)                                                       580
      DO 1 IP=1,IPM                                                     590
      NBF=IORIN(IP,1)                                                   600
      NBG=IORIN(IP,IRR )                                                610
      READ 802,(PDT(J,IK,K),J=NBF,NBG),(H(M),M = 1,20)                 620
    1 PRINT802,(PDT(J,IK,K),J=NBF,NBG),(H(M),M = 1,20)                  630
C     DETERMINE AMOUNT OF MIDFRACTION FOR EACH INPUT AND DECISION       640
C                                                                       650
      DO 4 IS = 1,ICMP                                                  660
      DO 4 IK=1,IRR                                                     670
      IPM=IPT(IS)                                                       680
      DO 4 IP=1,IPM                                                     690
      I=IORIN(IP,IK)                                                    700
      DO 4 IPP=1,IPM                                                    710
      ID=IORIN(IPP,IK)                                                  720
      IF(PDT(ID,IS,2)) 12,13,13                                         730
```

```
   13 IF(IS-1) 14,14,15                                                  740
   14 XMID (I,IPP,IS)=(1.00-PDT(ID,IS,2))*TOTAL                          750
      GO TO 4                                                            760
   15 IF(PDT(I,IS-1,1)) 16,17,17                                         770
   17 XMID(I,IPP,IS)=(PDT(I,IS-1,1)-PDT(ID,IS,2))*TOTAL                  780
      GO TO 4                                                            790
   16 ISM= IS                                                            800
  160 ISM = ISM-1                                                        810
      IF(ISM-1) 18,18,19                                                 820
   18 XMID(I,IPP,IS)= (1.00-PDT(ID,IS,2))*TOTAL                          830
      GO TO 4                                                            840
   19 IF(PDT(I,ISM-1,1))160,21,21                                        850
   21 XMID(I,IPP,IS)=(PDT(I,ISM-1,1)-PDT(ID,IS,2))*TOTAL                 860
      GO TO 4                                                            870
   12 XMID(I,IPP,IS)=0.0                                                 880
    4 CONTINUE                                                           890
      CALL DECP                                                          900
C     READ-VALUES FOR THE REFLUX RATIOS TO BE EVALUATED                  910
C                                                                        920
      READ 802,(RR(I),I=1,IRR)                                           930
      PRINT 802,(RR(I),I=1,IRR)                                          940
      CALL DECP                                                          950
C     READ-PRICES AT VARIOUS PURITIES FOR EACH STAGE                     960
C                                                                        970
      DO 10 IK=1,ICMP                                                    980
      IPM=IPT(IK)                                                        990
      READ 801,(PP(I,IK),I=1,IPM)   ,(H(M),M=1,20)                      1000
   10 PRINT801,(PP(I,IK),I=1,IPM)   ,(H(M),M=1,20)                      1010
      CALL DECP                                                         1020
C     READ-PURITIES OF COMPOUNDS TO BE EVALUATED                        1030
C                                                                       1040
      DO 11 IK=1,ICMP                                                   1050
      IPM=IPT(IK)                                                       1060
      READ 801,(PUR(I,IK), I=1,IPM),(H(M),M=1,20)                       1070
   11 PRINT801,(PUR(I,IK), I=1,IPM),(H(M),M=1,20)                       1080
      CALL DECP                                                         1090
```

```
C      READ-COST DATA-HOURLY OPERATING COST-OC                          1100
C                        -   BOIL UP RATE          - BUR                1110
C                        -   COST OF BOTTOMS   -  CB                    1120
C                        -   NUMBER OF RUN/YEAR    - R YEAR             1130
C                                                                       1140
       READ 802,OC,BUR,CB ,RYEAR                                        1150
       PRINT802,OC,BUR,CB ,RYEAR                                        1160
       PRINT 901                                                        1170
       NQ = ICMP*2                                                      1180
C      READ-HEADING CARDS - 2 PER STAGE  - 40 COLUMNS/CARD              1190
C          -IE(J,1) = BOTTOMS -                                         1200
C          -IE(J,2) = STAGE 1 -                                         1210
C          -IE(J,3) = MIDFRACTION BETWEEN STAGE 1 AND 2-                1220
C          -  .  .  .                .  .  .    -                      1230
C          -  .  .  .                .  .  .    -                      1240
C          -IE(J,2N-1) = MID FRACTION BETWEEN STAGE N-1 AN N-           1250
C          -IE(J,2N) = STAGE N-                                         1260
C                                                                       1270
       DO 5 I = 1,NQ                                                    1280
     5 READ 900,(IE(J,I),J=1,20)                                        1290
       PRINT 800                                                        1300
C      CALL ROUTINES FOR OPTIMIZATION                                   1310
C                                                                       1320
       CALL DPMOD                                                       1330
       CALL SORT                                                        1340
       CALL EDIT                                                        1350
       GO TO 102                                                        1360
   800 FORMAT(1H1)                                                      1370
   802 FORMAT(4F10.4,20A2)                                              1380
   801 FORMAT( F10.3,20A2)                                              1390
   804 FORMAT(1H )                                                      1400
   851 FORMAT ( 6I 3)                                                   1410
   901 FORMAT(15H  END  OF  DATA)                                       1420
   902 FORMAT(15H  END  OF  RUN )                                       1430
   100 PRINT902                                                         1440
   900 FORMAT(20A2)                                                     1450
       CALL EXIT                                                        1460
       END                                                              1470
```

```
      SUBROUTINE DPMOD                                                  10
C     SUBROUTINE DPMOD-DYNAMIC PROGRAMMING MODEL                        20
C     THIS ROUTINE DETERMINES THE VALUES OF THE OBJECTIVE               30
C     FUNCTION,SORTS AND DETERMINES OPTIMUM DECISIONS                   40
C                                                                       50
      DIMENSION IPT(10),IORIN(4,4),PDT(16,4,2),XMID(16,4,4),RR(4   ),PP(60
     14,4), PUR(4,4),FX(16,16),DMAX(16),IORD(16,16),AMOT(8),RSR(8),OPER1 70
     12(8, 8),OPER2(8,8),ANS(5,5),IE(40,8),ICM(4)                       80
      DIMENSION TMOT(8) ,TSR(8)                                         90
      DIMENSION H(20)                                                   100
      COMMON ISENT,ICMP,IPT,IRR,TOTAL,IORIN,PDT, XMID, RR,PP,PUR,OC,    110
     1BUR,CB,CDBR,AMOUNT,AVERR,RTN,FX,DMAX,IORD,FMAX,INP,AMOT,RSR,OPER1,120
     2 OPER2,ANS,IE,ICM,IMD,RYEAR,IPM                                   130
      CDBR=OC/BUR                                                       140
      IZ = 1                                                            150
C     CYCLE THROUGH ALL THE STAGES, NUMBER OF COMPONENTS                160
C                                                                       170
      DO 2IS=1,ICMP                                                     180
C     SET NUMBER OF PURITIES FOR THE COMPOUND                           190
      IPM=IPT(IS)                                                       200
C     CYCLE THROUGH ALL INPUTS-REFLUX RATIOS-PURITIES                   210
C                                                                       220
      DO 1IR=1,IRR                                                      230
      DO 1IP=1,IPM                                                      240
C     SET INDEX FOR INPUT COMBINATION-I                                 250
C                                                                       260
      I=IORIN(IP,IR)                                                    270
C     CHECK TO SEE IF PRODUCT AT INPUT CONDITIONS                       280
C                                                                       290
      IF (PDT(I,IS,1))21,19,22                                          300
   19 I = IORIN(IP,IRR)                                                 310
      GO TO 22                                                          320
   21 ISM=IS                                                            330
C     CYCLE THOUGH ALL DECISIONS-WITH NO SUITABLE INPUT                 340
```

```
C
      DO 111 IDD=1,IRR                                                    350
      DO 111 IPS=1, IPM                                                   360
      IO = IORIN(IPS,IR)                                                  370
      ID = IORIN(IP,IR)                                                   380
C     SORT TO SEE IF THIS IS TO BE CONSIDERED A STAGE                     390
C                                                                         400
      IF(PDT(I,IS+1,2))23,26,26                                           410
   23 RTN = 0.0                                                           420
      IF(IS-1)200,200,201                                                 430
  200 FX(I,IO) = RTN                                                      440
      GO TO 110                                                           450
   26 IF(ISM-1)28,28,29                                                   460
   29 IF(PDT(I,ISM-1,1)) 24,25,25                                         470
   24 ISM = ISM - 1                                                       480
      GO TO 26                                                            490
C     DETERMINE RETURN FOR STAGE 1                                        500
C                                                                         510
   28 RTN=-XMID(ID,IPS ,IS)*CB                                            520
      FX(I,IO )=RTN                                                       530
      GO TO 110                                                           540
C     DETERMINE FOR STAGE 2....N                                          550
C                                                                         560
   25 RTN=-XMID(ID,IPS,IS)*CDBR*(RR(IR)+1.0                               570
C     FIND INDEX FOR OPTIMUM DECISION FOR STAGE IS-1,INPUT IO             580
C                                                                         590
  201 K = IORD(IO,IS-1)                                                   600
C     FIND LOCATION OF DECISION ON DISK FILE                              610
C                                                                         620
      IFF = (IS-2) * (IPM*IRR*IPM*IRR) +(IO-1)*IPM*IRR +K                 630
      FIND(IFF)                                                           640
C     FETCH OPTIMUM DECISION STAGE IS-1, INPUT IO                         650
C                                                                         660
      FETCH(IFF) FOFX,TMOUNT,TVERR,IW,IX,IMB,(TMOT(J),TSR(J),J=1,IMB)     670
      FX(I,IO )=FOFX+RTN                                                  680
                                                                          690
```

```
  110 IMD = 1                                                              700
      AMOUNT = 0.                                                          710
      AVERR = RR(IR)                                                       720
      AMOT(1) = 0.                                                         730
      RSR(1) = RR(IR)                                                      740
C     RECORD OPTIMUM DECISION STAGE IS, INPUT I                            750
C                                                                          760
      RECORD (IZ) FX(I,IO),AMOUNT,AVERR,IR,IP,IMD,(AMOT(J),RSR(J),J=1,IM   770
     1D)                                                                   780
  111 PRINT 900,I,IS ,ID,IO,FX(I,IO ),RTN                                  790
      GO TO 1                                                              800
C     CYCLE THROUGH ALL DECISIONS WITH SUITABLE INPUT                      810
C                                                                          820
   22 DO 10IDD=1,IRR                                                       830
      DO 10IPS=1,IPM                                                       840
C     SET INDEX ON DECISION-FINIAL REFLUX RATIO-AND                        850
C     INPUT PURITY STAGE IS-1                                              860
C                                                                          870
      IO= IORIN(IPS,IDD)                                                   880
      ID=IORIN(IP ,IDD)                                                    890
C     CHECK TO SEE IF DECISION IS VALID FOR INPUT                          900
C                                                                          910
      IF(PDT(ID,IS,2))30,30,31                                             920
   30 AVERR = RR(IDD)                                                      930
      ISM = IS                                                             940
      AMOUNT = 0.0                                                         950
      IMD = 1                                                              960
      AMOT(1) = 0.0                                                        970
      RSR(1) = RR(IR)                                                      980
  300 ISM = ISM+ 1                                                         990
C     SORT TO SEE IF COMPOUND SHOUD BE CONSIDERED A STAGE                 1000
C                                                                         1010
      IF(PDT(ID,ISM,2)) 300,300,301                                       1020
  301 ISN = IS                                                            1030
  304 IF(PDT(ID,ISN,1))302,302,303                                        1040
  302 ISN = ISN -1                                                        1050
      IF (ISN) 305,305,304                                                1060
```

```
  305 XMID(IO,IP,ISN+1) = XMID(IO,IP,ISM)-TOTAL*(PDT(I,IS,1)-PDT(ID,ISM,     1070
     12))                                                                    1080
C     DETERMINE RETURN FOR IMPROPER DECISION                                1090
C                                                                           1100
      RTN = -CB*XMID(IO,IP,ISN+1)                                           1110
      FX(I,IO) = RTN                                                        1120
      GO TO 121                                                             1130
  303 XMID(IO,IP,IS) =XMID(IO,IP,ISM) -TOTAL*(PDT(I,IS,1)-PDT(ID,ISM,2))    1140
      GO TO 32                                                              1150
   31 CALL RROPT (I,ID,IS,IR,IP)                                            1160
      ISZ = IS                                                              1170
  311 ISZ = ISZ-1                                                           1180
      IF(ISZ) 11,11,312                                                     1190
  312 IF(PDT(ID,ISZ,1))311,311,12                                           1200
   32 IF(IS-1)11,11,12                                                      1210
C     RETURN FOR STAGE 1                                                    1220
C                                                                           1230
   11 RTN = PP(IP,IS)*AMOUNT-CDBR*AMOUNT*(AVERR+1.)-XMID(IO,IP,IS)*CB       1240
      FX(I,IO ) =RTN                                                        1250
      GO TO 121                                                             1260
C     RETURN FOR STAGE 2....N                                               1270
C                                                                           1280
   12 RTN = PP(IP,IS)*AMOUNT- CDBR*AMOUNT*(AVERR+1.)-XMID(IO,IP,IS)*(       1290
     1RR(IDD)+1.)*CDBR                                                      1300
C     DETERMINE INDEX FOR OPTIMUM DECISION STAGE IS-1, INPUT IO             1310
C                                                                           1320
  203 K=IORD(IO,IS-1)                                                       1330
C     FIND LOCATION OF DECISION ON DISK FILE                                1340
C                                                                           1350
      IFF = (IS-2) * (IPM*IRR*IPM*IRR) +(IO-1)*IPM*IRR +K                   1360
C     FETCH OPTIMUM DECISION STAGE IS-1, INPUT ID                           1370
C                                                                           1380
      FETCH(IFF) FOFX,TMOUNT,TVERR,IW,IX,IMB,(TMOT(J),TSR(J),J=1,IMB)       1390
      FX(I,IO )= FOFX   + RTN                                               1400
  121 PRINT 900,I,IS ,ID,IO,FX(I,IO ),RTN                                   1410
C     RECORD OPTIMUM DECISION DECISION STAGE IS, INPUT I                    1420
C                                                                           1430
```

```
   10 RECORD (IZ) FX(I,IO),AMOUNT,AVERR,IDD,IP,IMD,(AMOT(J),RSR(J),J=1,      144C
     1IMD)                                                                   145C
      1 CONTINUE                                                             146C
C       SORT FOR MAXIMUM VALVE OF OBJECTIVE FUNCTION FOR EACH I              147C
C                                                                            148C
        DO 3 IR=1,IRR                                                        149C
        DO 3 IPS=1,IPM                                                       150C
        IF(IS-ICMP)51,50,50                                                  151C
   50   I = IORIN(IPS,IRR)                                                   152C
        GO TO 52                                                             153C
   51   I= IORIN(IPS,IR)                                                     154C
   52   IF (PDT(I,IS,1))40,41,41                                             155C
   40   IORD(I,IS) =I                                                        156C
        DMAX(I) = FX(I,I)                                                    157C
        GO TO 3                                                              158C
C       STORE MAXIMUM VALVE OF FX(I,IO) FOR ALL I IN DMAX(I)                 159C
C                                                                            160C
   41   DMAX(I) = FX(I,1)                                                    161C
        IORD(I,IS)=1                                                         162C
        IKK=IRR*IPM     -1                                                   163C
        DO 3 ID=1, IKK                                                       164C
        IF(FX(I,ID+1)-DMAX(I)) 3,3,4                                         165C
      4 IORD(I,IS)=ID+1                                                      166C
        DMAX(I)= FX(I,ID+1)                                                  167C
      3 CONTINUE                                                             168C
      2 CONTINUE                                                             169C
C       SORT FOR OPTIMUM INPUT TO STAGE N AND STORE IN FMAX                  170C
C                                                                            171C
        INP= IRR                                                             172C
        FMAX = DMAX(INP)                                                     173C
        IPM=IPT(ICMP)                                                        174C
        IF(IPM-1) 7,7,8                                                      175C
      8 DO 5 IP=2,IPM                                                        176C
```

```
      IW=IORIN(IP,IRR)                                                  177C
      IF(FMAX-DMAX(IW))5,5,6                                            178C
    6 INP=IW                                                            179C
      FMAX=DMAX(IW)                                                     180C
    5 CONTINUE                                                          181C
    7 RETURN                                                            182C
  900 FORMAT(1H ,4I2,2F10.2)                                            183C
      END                                                               184C
```



```
      SUBROUTINE SORT                                                     1C
C     SUBROUTINE SORT                                                     2C
C     THIS ROUTINE RETURNS OPTIMUM DECISIONS FROM DISK FILE               3C
C     STARTING WITH OPTIMUM INPUT TO STAGE N, PROCEDING TO 1              4C
C     DECISION ARE STORED IN ANS, OPER1 AND OPER2 ARRAYS                  5C
C                                                                         6C
```

```
      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 TMOT(8) ,TSR(8)          \
      DIMENSION H(20)
      COMMON ISENT,ICMP,IPT,IRR,TOTAL,IORIN,PDT, XMID, RR,PP,PUR,OC,
     1BUR,CB,CDBR,AMOUNT,AVERR,RTN,FX,DMAX,IORD,FMAX,INP,AMOT,RSR,OPER1,
     2 OPER2,ANS,IE,ICM,IMD,RYEAR,IPM
      IS=ICMP
C     INDEX ON OPTIMUM DECISION WITH OPTIMAL INPUT-INP
C
    3 K=IORD(INP,IS)
      IFF = (IS-1) * (IPM*IRR*IPM*IRR) +(INP-1)*IPM*IRR +K
      FETCH(IFF) FOFX,AMOUNT,AVERR,IR,IX,IMD,(AMOT(I),RSR(I),I=1,IMD)
      ANS(1,IS)=AMOUNT
      ANS(2,IS)=AVERR
      ANS( 3,IS)= XMID(K,IX,IS)
      ANS(5,IS) = RR(IR)
      ANS(4,IS)= PUR(IX,IS)
      ICM(IS)=IMD
      DO 100 M=1,IMD
      OPER1(IS,M) = AMOT(M)
  100 OPER2 (IS,M)=RSR (M)
C     CHECK TO SEE IF STAGE 1 HAS BEEN COMPLETED
C     YES-RETURN TO MAIN LINE
C     NO-DECREASE STAGE COUNT BY 1, CONTINUE
C
      IF (IS-1) 1, 1, 2
    2 IS= IS-1
      INP = K
      GO TO 3
    1 RETURN
      END
```

```
      SUBROUTINE DECP                                                   1C
C     SUBROUTINE DECP-DECRIPTION-                                       2C
C     THIS ROUTINE PRINTS HEADING CARDS FOR INPUT DATA                  3C
C     1 IN COLUMN ONE RETURNS CONTROL TO MAINLINE                       4C
C                                                                       5C
      DIMENSION A(20)                                                   6C
    1 READ 900,IA,(A(I),I=1,20)                                         7C
      PRINT 901, (A(I), I=1,20)                                         8C
      IF (IA) 1,1,2                                                     9C
    2 RETURN                                                           10C
  900 FORMAT (I1,A3,19A4)                                              11C
  901 FORMAT (A3,19A4)                                                 12C
      END                                                              13C
```

```
      SUBROUTINE EDIT                                                    1(
C     SUBROUTINE EDIT                                                    2(
C     THIS ROUTINE EDITS BOTH THE SUMMARY AND OVERALL SUMMARY            3(
C     OF OPTIMUM OPERATING CONDITIONS                                    4(
C                                                                        5(
C     HEADINGS ARE READ IN MAIN LINE ROUTINE (IE(J,I))                   6(
C                                                                        7(
      DIMENSION IPT(10),IORIN(4,4),PDT(16,4,2),XMID(16,4,4),RR(4  ),PP(  8(
     14,4), PUR(4,4),FX(16,16),DMAX(16),IORD(16,16),AMOT(8),RSR(8),OPER1 9(
     22(8, 8),OPER2(8,8),ANS(5,5),IE(40,8),ICM(4)                       10(
      DIMENSION TMOT(8) ,TSR(8)                                         11(
      DIMENSION H(20)                                                   12(
      COMMON ISENT,ICMP,IPT,IRR,TOTAL,IORIN,PDT, XMID, RR,PP,PUR,OC,    13(
     1BUR,CB,CDBR,AMOUNT,AVERR,RTN,FX,DMAX,IORD,FMAX,INP,AMOT,RSR,OPER1, 14(
     2 OPER2,ANS,IE,ICM,IMD,RYEAR,IPM                                   15(
      TIME = 0.0                                                        16(
C     PRINT OUT SUMMARY                                                 17(
C                                                                       18(
      PRINT 900                                                         19(
      DO 10 I = 1, 10                                                   20(
   10 PRINT 902                                                         21(
      PRINT 901                                                         22(
      PRINT 902                                                         23(
      PRINT 9002                                                        24(
      I=ICMP                                                            25(
    3 II =2*I                                                           26(
   30 PRINT 903, (IE(J,II),J=1,20), ANS(1,I), ANS(4,I), ANS(2,I)        27(
   40 IF(I-1) 2,2,1                                                     28(
    1 II=II-1                                                           29(
      PRINT 905,(IE(J,II),J=1,20), ANS(3,I),ANS(5,I)                    30(
      I=I-1                                                             31(
      GO TO 3                                                           32(
    2 PRINT 906,(IE(J,I),J=1, 20), ANS(3,I)                             33(
C     PRINT OUT DETAILED SUMMARY                                        34(
```

```
C                                                                       35C
      PRINT 900                                                         36C
      DO 11 I= 1,10                                                     37C
   11 PRINT 902                                                         38C
      PRINT 907                                                         39C
      TIME=0.0                                                          40C
      PRINT 908                                                         41C
      PRINT 902                                                         42C
      IS=ICMP                                                           43C
   50 NN = ICM(IS)                                                      44C
      DO 5 N=1,NN                                                       45C
   51 TIM=OPER1(IS,N)/(BUR/(OPER2(IS,N)+1.))                            46C
      PRINT 909,TIME,OPER2(IS,N),OPER1(IS,N)                            47C
    5 TIME=TIME+TIM                                                     48C
   60 NQ = 2 * IS                                                       49C
      PRINT 910, (IE(I,NQ),I=1,20)                                      50C
      IF (IS-1) 6,6,7                                                   51C
    7 TIM=ANS(3,IS)/(BUR/(ANS(5,IS)+1.))                                52C
      PRINT 909,TIME,ANS(5,IS),ANS(3,IS)                                53C
      TIME=TIME+TIM                                                     54C
      NQ=NQ-1                                                           55C
      PRINT 910,(IE(I,NQ),I=1,20)                                       56C
      IS=IS-1                                                           57C
      GO TO 50                                                          58C
    6 PRINT 911, ANS(3,IS),TIME                                         59C
      GYEAR=FMAX* RYEAR                                                 60C
      PRINT 912,FMAX,GYEAR                                              61C
  900 FORMAT (1H1)                                                      62C
  901 FORMAT (38H SUMMARY OF OPTIMUM RUNNING CONDITIONS)                63C
  902 FORMAT (1H )                                                      64C
 9002 FORMAT (16X,7HPRODUCT,19X,16HAMOUNT IN POUNDS,5X,35HAVERAGE PURITY 65C
     1 AVERAGE REFLUX RATIO)                                            66C
  903 FORMAT (20A2, F13.2,15X,F6.1,13X,F6.1,5H TO 1)                    67C
  905 FORMAT(20A2,F13.2,15X,4H****,13X,F6.1,5H TO 1)                    68C
  906 FORMAT(20A2,F13.2,15X,4H****,13X,10H**********)                   69C
  907 FORMAT(47H DETAILED SUMMARY OF OPTIMUM RUNNING CONDITIONS)        70C
```

```
  908 FORMAT( 3X,13HTIME IN HOURS,8X,12HREFLUX RATIO,12X,6HAMOUNT)          71C
  909 FORMAT( F12.2,16X,F6.1,5H TO 1,8X,F7.2)                               72C
  910 FORMAT( 8H END OF ,20A2)                                              73C
  911 FORMAT (14H   END OF RUN , F13.2,32H POUNDS OF BOTTOMS   TIME OF R    74C
     1UN,F13.2)                                                             75C
  912 FORMAT(21H GROSS PROFIT PER RUN,F13.2,9HPER YEAR ,F14.2)              76C
      RETURN                                                                77C
      END                                                                   78C


      SUBROUTINE  RROPT( L,M,N,IRI,IPI)                                      1C
      DIMENSION IPT(10),IORIN(4,4),PDT(16,4,2),XMID(16,4,4),RR(4  ),PP(      2C
     14,4), PUR(4,4),FX(16,16),DMAX(16),IORD(16,16),AMOT(8),RSR(8),OPER1     3C
     2(8, 8),OPER2(8,8),ANS(5,5),IE(40,8),ICM(4)                             4C
      DIMENSION TMOT(8) ,TSR(8)                                              5C
      DIMENSION H(20)                                                        6C
      COMMON ISENT,ICMP,IPT,IRR,TOTAL,IORIN,PDT, XMID, RR,PP,PUR,OC,         7C
     1BUR,CB,CDBR,AMOUNT,AVERR,RTN,FX,DMAX,IORD,FMAX,INP,AMOT,RSR,OPER1,     8C
     2 OPER2,ANS,IE,ICM,IMD,RYEAR,IPM                                        9C
C     SUBOUTINE PROPT-REFLUX RATIO OPERATOR-                                10C
C                                                                           11C
C     THIS ROUTINE DETERMINES AMOUNT AND FOR A GIVEN INPUT                  12C
C     (L) AND DECISION(M)                                                   13C
C                                                                           14C
C     REFLUX RATIO CHANGES BETWEEN INPUT AND DECISION ARE                   15C
C     DETERMINE AND STORED IN THE RSR ARRAY                                 16C
C                                                                           17C
C     THE AMOUNT OF PRODUCT FOR INTERMEDIATE REFLUX RATIO                   18C
C     CHANGE IS CALCULATED AND STORED IN THE AMOT ARRAY                     19C
C                                                                           20C
C     IMD IS THE NUMBER OF CHANGES OCCURING IN EACH                         21C
C     FRACTION                                                              22C
C                                                                           23C
```

```
      I=L                                                              240
      ID=M                                                             250
      IS=N                                                             260
      TIME=0.0                                                         270
      IP = IPI                                                         280
      IMD = 0                                                          290
      IZ = IRI                                                         300
      IF (PDT(I,IS,1))11,11,12                                         310
   11 IZ = IRR                                                         320
   12 IF(I-IRR*IP )1,13,13                                             330
   13 K=I                                                              340
      KZ =IZ                                                           350
      GO TO 14                                                         360
    1 IF(PDT(I+1,IS,1)) 4,8,8                                          370
    8 AMT= (PDT(I+1,IS,1)-PDT(I,IS,1))*TOTAL                           380
      TIME1= AMT/(BUR/(RR(IZ)+1.))                                     390
      IMD = IMD +1                                                     400
      AMOT(IMD)= AMT                                                   410
      RSR(IMD) = RR(IZ)                                                420
      TIME=    TIME+TIME1                                              430
      IF (I-IRR*IP+1)2,3,3                                             440
    2 I= I+1                                                           450
      IZ = IZ +1                                                       460
      GO TO 1                                                          470
    3 K=I+1                                                            480
      KZ = IZ +1                                                       490
   14 IF(K-ID) 6,24,24                                                 500
    4 K=I                                                              510
      KZ = IZ                                                          520
   24 AMT = (PDT(K,IS,2)- PDT(K,IS,1))*TOTAL                          530
      TIME1 = AMT/(BUR / (RR(KZ)+1.))                                  540
      IMD = IMD + 1                                                    550
      AMOT(IMD) = AMT                                                  560
      RSR(IMD) = RR(KZ)                                                570
      TIME = TIME  +TIME1                                              580
    5 IF( K-ID) 6,6,7                                                  590
```

```
      7 K   =   K-1                                                      60(
        KZ = KZ - 1                                                      61(
        AMT = (PDT(K,IS,2)-PDT(K+1,IS,2))*TOTAL                          62(
        TIME1 = AMT/(BUR / (RR(KZ)+1.))                                  63(
        TIME = TIME + TIME1                                              64(
        IMD = IMD +1                                                     65(
        AMOT(IMD) = AMT                                                  66(
        RSR(IMD) = RR(KZ)                                                67(
        GO TO 5                                                          68(
C       CALCULATE AMOUNT                                                 69(
C                                                                        70(
      6 AMOUNT = 0.0                                                     71(
        DO 10 JJ = 1,IMD                                                 72(
     10 AMOUNT = AMOUNT + AMOT(JJ)                                       73(
C       CALCULATE THE TIME AVERAGED REFLUX RATIO                         74(
C                                                                        75(
        ARR = AMOUNT/(BUR*TIME)                                          76(
        ARR = 1./ARR                                                     77(
        AVERR = ARR -1.0                                                 78(
C       RETURN TO DPMOD                                                  79(
C                                                                        80(
        RETURN                                                           81(
        END                                                              82(
```

TABLE XI

DEFINITION OF SYMBOLS IN OPTIMIZATION PROGRAM

AMOT(I)	The amount of product obtained at I intermediate reflux ratio.
AMOUNT	Total pounds of product for the stage.
ANS(K,I)	Optimum decision I for stage K.
AVERR	Average reflux ratio for the stage.
BUR	Boil up rate -- pounds/hour.
CB	Cost of bottoms product -- $/pound.
CDBR	Operating cost divided by boil up rate.
DMAX(I)	Maximum value of objective function over all decisions with an input I.
FX(I,J)	Value of the objective function for input I and decision J.
ICM(K)	Number of intermediate reflux ratio changes for stage K.
ICMP	Number of stages to be considered.
IE(J,I)	Heading for editing of fraction I, J equals the word number.
INP	Optimum input for the stage.
IORIN(I,J)	Index associated with purity I and reflux ratio J.
IORD(I,K)	Index on optimum decision for input I and stage K.
IRR	Number of reflux ratios to be evaluated
ISENT	Sentinal indicating beginning or ending of a job.
OC	Hourly operating cost -- $/hour.

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 preceeding 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

TYPICAL INPUT DATA FOR SIMULATION OF A BATCH COLUMN

SOUTHWEST FOREST IND. CRUDE 17 THEORETICAL PLATES

```
**********) CARDS WITH * IN COLUMN 1 NOT INCLUDED IN DATA PACKAGE (**********
*  NUMBER OF PLATES-COMPOUNDS
15 6
*  TOTAL MOLES CHARGED-WEIGHT FRACTION OF EACH COMPOUND
5.86          .474      .0041      .0085      .404       .062       .0474
*  HOLDUP ON EACH PLATE - ASSUMED TEMPERATURE
.00075      430.0
.00075      430.5
.00075      431.0
.00075      431.5
.00075      432.0
.00075      432.5
.00075      433.0
.00075      433.5
.00075      434.0
.000825     434.5
.000825     435.0
.000825     435.5
.000825     436.0
.000825     436.5
.000825     437.0
.000825     437.5
5.84755     438.0
*  VAPOR PRESSURE CONSTANTS
7.3495      -1768.4714
7.3755      -1796.1192
7.3888      -1810.3070
7.4494      -1874.6973
7.4645      -1890.7039
7.5507      -1982.3783
```

TABLE (CONTINUED)

```
*  INTIAL DATA CARD
1.5000              .85       45.0          .9
*  ENTHALPY DATA
63.712      -8968.971 70.13375   -31826.82 26390.     669.13
61.915097 -8720.237 68.21432   -32226.82 25892.8    670.13
60.118034 -8471.403 66.294894  -32625.08 23190.     650.13
59.488839 -8688.546 65.455691  -30932.28 24383.9    648.63
61.80       -13550.    84.2        -38790.    22810.     636.13
60.311975 -9673.854 66.103149  -31240.79 23467.     634.7
*  PRESSURE ON EACH PLATE
759.88     761.95     764.02     766.09     768.02     770.09     772.16     774.25
776.36     778.43     780.50     782.57     784.64     786.71     788.78     790.85
792.92     794.99     797.06     799.13     801.20     803.27     805.34     807.41
```

TABLE XIII

INPUT FOR OPTIMIZATION USING
POTLATCH INDUSTRY'S CRUDE

Number of Compounds Purities per Compound Number of Reflux Ratios

4 1 1 1 1 4

Total Charge
388.0

Percent Distilled Preceeding the Cut at Purity 1

30 to 1	15 to 1	10 to 1	5 to 1	
.732	.746	.750	.755	Dipentene
.678	-1.0	-1.0	-1.0	Delta-3-Carene
.560	.571	.578	-1.0	Beta Pinene
.0	.0	.0	.0	Alpha Pinene

Percent Distilled Succeeding the Cut at Purity 1

30 to 1	15 to 1	10 to 1	5 to 1	
.831	.811	.800	.794	Dipentene
.720	-1.0	-1.0	-1.0	Delta-3-Carene
.601	.591	.583	-1.0	Beta Pinene
.519	.496	.493	.490	Alpha Pinene

Reflux 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

Time in Hours	Reflux Ratio	Amount
0.00	5.0 to 1	190.12
11.40	10.0 to 1	1.16
11.53	15.0 to 1	1.16
11.72	30.0 to 1	8.92
End of Alpha Pinene Fraction		
14.48	30.0 to 1	15.90
End of Alpha Pinene Beta Pinene Midfraction		
19.41	30.0 to 1	4.26
20.74	15.0 to 1	2.71
21.17	10.0 to 1	1.94
21.39	15.0 to 1	3.10
21.88	30.0 to 1	3.88
End of Beta Pinene Fraction		
23.08	30.0 to 1	29.87
End of Beta Pinene Delta-3-Carene Midfraction		
32.35	30.0 to 1	16.29
End of Delta-3-Carene Fraction		
37.40	30.0 to 1	4.65
End of Delta-3-Carene Dipentene Midfraction		
38.84	30.0 to 1	5.43
40.53	15.0 to 1	1.55
40.77	10.0 to 1	1.94
40.99	5.0 to 1	15.13
41.90	10.0 to 1	2.32
42.15	15.0 to 1	4.26
42.83	30.0 to 1	7.76
End of Dipentene Fraction		
End of Run	Pounds of Bottoms	65.57
Time of Run 45.98		
Gross Profit per Run 20.11	Per Year	1005.85
End of Run		

TABLE XV

OVERALL SUMMARY OF OPTIMUM CONDITIONS FOR POTLATCH INDUSTRY'S CRUDE

Product	Amount in Pounds	Average Purity	Average Reflux Ratio
Alpha Pinene Fraction	201.37	95.0	6.1 to 1
Alpha Pinene Beta Pinene Midfraction	15.90	--	30.0 to 1
Beta Pinene Fraction	15.90	80.0	22.0 to 1
Beta Pinene Delta-3-Carene Midfraction	29.87	--	30.0 to 1
Delta-3-Carene Fraction	16.29	95.0	30.0 to 1
Delta-3-Carene Dipentene Midfraction	4.65	--	30.0 to 1
Dipentene Fraction	38.31	50.0	15.6 to 1
Bottoms Product	65.57	--	--

TABLE XVI

EXPERIMENTAL VERIFICATION OF OPTIMUM CONDITIONS FOR POTLATCH CRUDE

	Amount		Reflux Ratio
Alpha Pinene Fraction	190.0		5 to 1
	1.5		10 to 1
	1.2		15 to 1
	9.0		30 to 1
Average Purity 95.9	201.7	Average	6.2 to 1
Alpha-Beta Mid-Fraction	16.0		30 to 1
Beta Pinene Fraction	4.0		30 to 1
	3.0		15 to 1
	2.0		10 to 1
	3.0		15 to 1
	4.0		30 to 1
Average Purity 81.9	16.0	Average	21.8 to 1
Beta-Delta-3 Mid-Fraction	29.5		30 to 1
Delta-3-Carene Fraction	16.0		30 to 1
Average Purity 95.2	16.0	Average	30 to 1
Delta-3-Dipentene Mid-Fraction	5.0		30 to 1
Dipentene Fraction	5.5		30 to 1
	1.5		15 to 1
	1.7		10 to 1
	14.0		5 to 1
	2.0		10 to 1
	4.5		15 to 1
	6.5		30 to 1
Average Purity 53.5	35.7	Average	16.1 to 1
Bottoms	64.0		
TOTAL	382.9		

TABLE XVII

INPUT FOR OPTIMIZATION USING SOUTHWEST FOREST INDUSTRY'S CRUDE

Number of Compounds Purities per Compound Number of Reflux Ratios

4 1 1 1 1 4

Total Charge
369.0000

Percent Distilled Preceeding the Cut at Purity 1

30 to 1	15 to 1	10 to 1	5 to 1	
.7790	.7793	.7796	.7800	Dipentene
.4270	.4730	-1.0000	-1.0000	Delta-3-Carene
-1.0000	-1.0000	-1.0000	-1.0000	Beta Pinene
0.0000	0.0000	0.0000	0.0000	Alpha Pinene

Percent Distilled Succeeding the Cut at Purity 1

30 to 1	15 to 1	10 to 1	5 to 1	
.8110	.8096	.8093	.8090	Dipentene
.7640	.7510	.7360	.7230	Delta-3-Carene
-1.0000	-1.0000	-1.0000	-1.0000	Beta Pinene
.3450	.3000	.2700	.2400	Alpha Pinene

Reflux Ratios

30.0000	15.0000	10.0000	5.0000

Price Data in Dollars Per Pound

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

Purities of Each Compound

50.0000	Dipentene
95.0000	Delta-3-Carene
80.0000	Beta Pinene
95.0000	Alpha Pinene

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

.1000	100.0000	-.0185	50.0000

End of Data

TABLE XVIII

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

Time in Hours	Reflux Ratio	Amount
0.00	5.0 to 1	88.56
5.31	10.0 to 1	11.07
6.53	15.0 to 1	11.07
8.30	30.0 to 1	16.60
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 Fracti n		
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 XIX

OVERALL SUMMARY OF OPTIMUM CONDITIONS FOR SOUTHWEST FOREST INDUSTRY'S CRUDE

Product	Amount in Pounds	Average Purity	Average Reflux Ratio
Alpha Pinene Fraction	127.30	95.0	9.5 to 1
Alpha Pinene Beta Pinene Midfraction	30.25	--	30.0 to 1
Beta Pinene Fraction	0.00	80.0	30.0 to 1
Beta Pinene Delta-3-Carene Midfraction	0.00	--	30.0 to 1
Delta-3-Carene Fraction	124.35	95.0	12.2 to 1
Delta-3-Carene Dipentene Midfraction	5.33	--	30.0 to 1
Dipentene Fraction	11.80	50.0	6.6 to 1
Bottoms Product	69.74	--	--

TABLE XX

EXPERIMENTAL VERIFICATION OF OPTIMUM CONDITIONS FOR SOUTHWEST FOREST INDUSTRY'S CRUDE

	Amount		Reflux Ratio
Alpha Pinene Fraction	88.0		5 to 1
	11.0		10 to 1
	11.0		15 to 1
	16.0		30 to 1
Average Purity 95.0	126.0	Average	9.5 to 1
Alpha-Beta-Midfraction	30.0		30 to 1
Beta Fraction	0.0		--
Average Purity 0.0	0.0	Average	--
Beta-Delta-3-Carene Midfraction	0.0		--
Delta-3-Carene	16.0		30 to 1
	18.5		15 to 1
	18.0		10 to 1
	56.0		5 to 1
	5.0		10 to 1
	5.0		15 to 1
	5.0		30 to 1
Average Purity 95.1	123.5	Average	12.1 to 1
Delta-3-Dipentene Midfraction	5.5		30 to 1
Dipentene Fraction	0.0		30 to 1
	0.0		15 to 1
	0.0		10 to 1
	11.0		5 to 1
	0.0		10 to 1
	0.0		15 to 1
	1.0		30 to 1
Average Purity 58.5	12.0	Average	7.1 to 1
Bottoms	73.0		
TOTAL	370.0		

TABLE XXI

INPUT FOR OPTIMIZATION USING
HOERNER WALDORF'S CRUDE

Number of Compounds Purities per Compound Number of Reflux Ratios
4 1 1 1 1 4

Total Charge
408.0000

Percent Distilled Preceeding the Cutaat Purity 1

30 to 1	15 to 1	10 to 1	5 to 1	
.7380	.7540	.7750	.7890	Dipentene
.5460	.6020	.6570	.6840	Delta-3-Carene
.4220	.4350	-1.0000	-1.0000	Beta Pinene
0.0000	0.0000	0.0000	0.0000	Alpha Pinene

Percent Distilled Succeeding the Cut at Purity 1

30 to 1	15 to 1	10 to 1	5 to 1	
.8380	.8330	.8310	.8290	Dipentene
.7010	.6980	.6960	.6940	Delta-3-Carene
.4620	.4500	-1.0000	-1.0000	Beta Pinene
.3600	.3150	.3000	.2950	Alpha Pinene

Reflux Ratios

30.0000	15.0000	10.0000	5.0000

Price Data in Dollars per Pound

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

Purities of Each Compound

50.0000	Dipentene
95.0000	Delta-3-Carene
80.0000	Beta Pinene
95.0000	Alpha Pinene

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

.1000	100.0000	-.0185	50.0000

End of Data.

TABLE XXII

DETAILED SUMMARY OF OPTIMUM RUNNING CONDITIONS FOR HOERNER WALDORF'S CRUDE

Time in Hours	Reflux Ratio	Amount
0.00	5.0 to 1	120.36
7.22	10.0 to 1	2.04
7.44	15.0 to 1	6.12
8.42	30.0 to 1	18.36
End of Alpha Pinene Fraction		
14.11	30.0 to 1	25.29
End of Alpha Pinene Beta Pinene Midfraction		
21.95	30.0 to 1	5.30
23.60	15.0 to 1	6.12
24.58	30.0 to 1	4.89
End of Beta Pinene Fraction		
26.09	30.0 to 1	34.27
End of Beta Pinene Delta-3-Carene Midfraction		
36.72	30.0 to 1	22.84
43.80	15.0 to 1	22.44
47.39	10.0 to 1	11.01
48.60	5.0 to 1	4.08
48.85	10.0 to 1	.81
48.94	15.0 to 1	.81
49.07	30.0 to 1	1.22
End of Delta-3-Carene Fraction		
49.45	30.0 to 1	15.09
End of Delta-3-Carene Dipentene Midfraction		
54.13	30.0 to 1	6.52
56.15	15.0 to 1	8.56
57.52	10.0 to 1	5.71
58.15	5.0 to 1	16.32
59.13	10.0 to 1	.81
59.22	15.0 to 1	.81
59.35	30.0 to 1	2.04
End of Dipentene Fraction		

Pounds of Bottoms 66.09 Time of Run 59.98

Gross Profit per Run 20.97 Per Year 1048.52

End of Run

TABLE XXIII

OVERALL SUMMARY OF OPTIMUM CONDITIONS FOR HOERNER WALDORF'S CRUDE

Product	Amount in Pounds	Average Purity	Average Reflux Ratio
Alpha Pinene Fraction	146.88	95.0	8.6 to 1
Alpha Pinene Beta Pinene Midfraction	25.29	--	30.0 to 1
Beta Pinene Fraction	16.32	80.0	24.3 to 1
Beta Pinene Delta-3-Carene Midfraction	34.27	--	30.0 to 1
Delta-3-Carene Fraction	63.24	95.0	19.1 to 1
Delta-3-Carene Dipentene Midfraction	15.09	--	30.0 to 1
Dipentene Fraction	40.80	50.0	13.3 to 1
Bottoms Product	66.09	--	--

TABLE XXIV

EXPERIMENTAL VERIFICATION RUN FOR HOERNER WALDORF CRUDE

	Amount	Reflux Ratio
Alpha Pinene Fraction	120.5	5 to 1
	2.0	10 to 1
	6.0	15 to 1
	18.5	30 to 1
Average Purity 95.6	147.0	Average 8.55 to 1
Alpha-Beta-Mid-fraction	25.5	30 to 1
Beta Pinene Fraction	5.5	30 to 1
	5.5	15 to 1
	5.0	30 to 1
Average Purity 82.9	16.0	Average 24.9 to 1
Beta-Delta-3 Mid-fraction	34.0	30 to 1
Delta-3-Carene Fraction	23.0	30 to 1
	21.0	15 to 1
	11.0	10 to 1
	4.0	5 to 1
	2.0	10 to 1
	1.0	15 to 1
	1.0	30 to 1
Average Purity 98.0	62.0	Average 19.2 to 1
Delta-3-Dipentene Mid-fraction	15.0	30 to 1
Dipentene Fraction	6.0	30 to 1
	8.5	15 to 1
	5.5	10 to 1
	17.0	5 to 1
	.5	10 to 1
	1.0	15 to 1
	1.5	30 to 1
Average Purity 55.1	40.0	Average 12.8 to 1
Bottoms 60.0		
TOTAL	399.5	

TABLE XXV

KEY TO SYMBOLS USED IN FIGURES 10-22

(See Page 136)

FIGURES 1-22

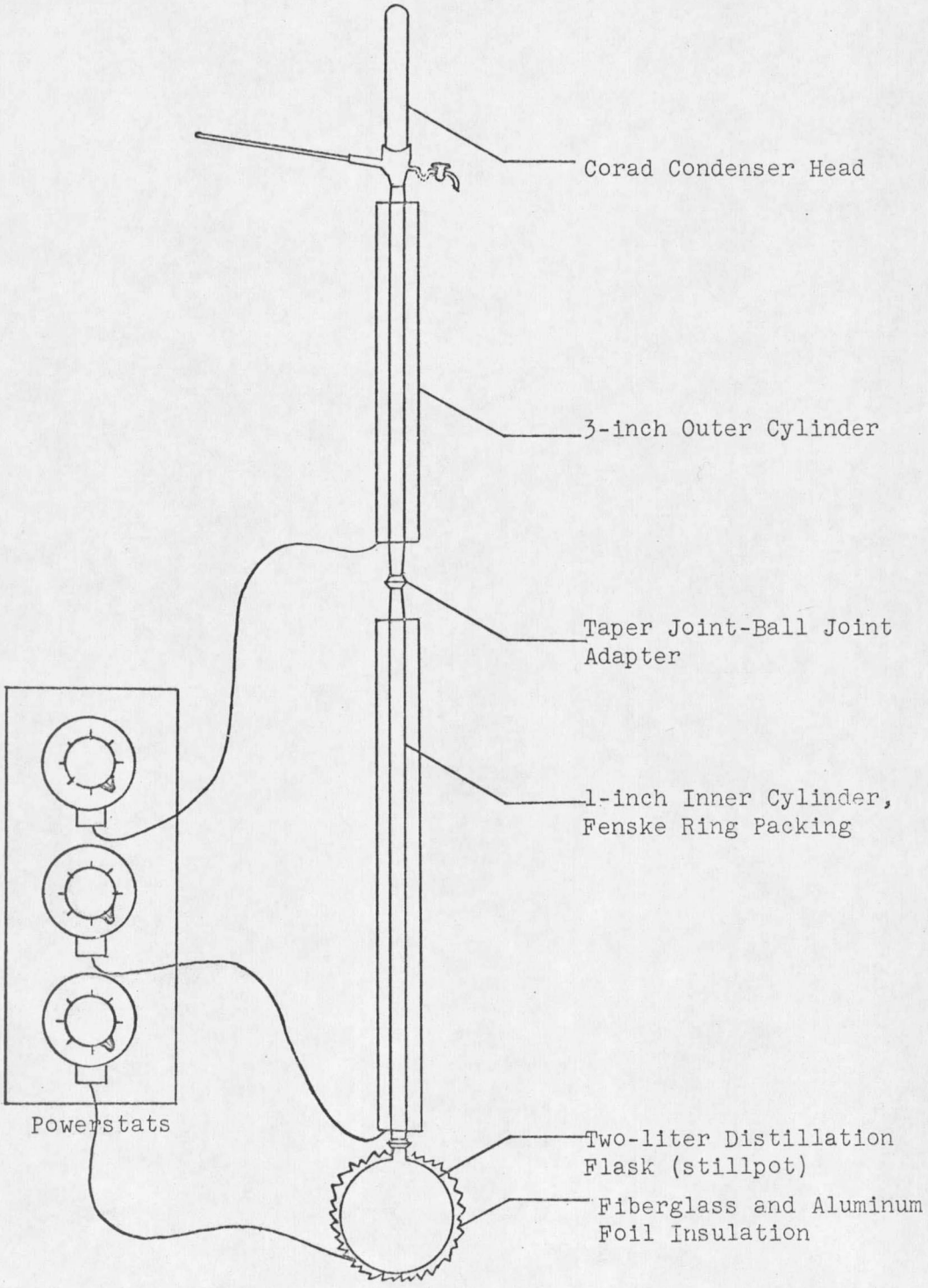


FIG. 1 Experimental Distillation Appratus

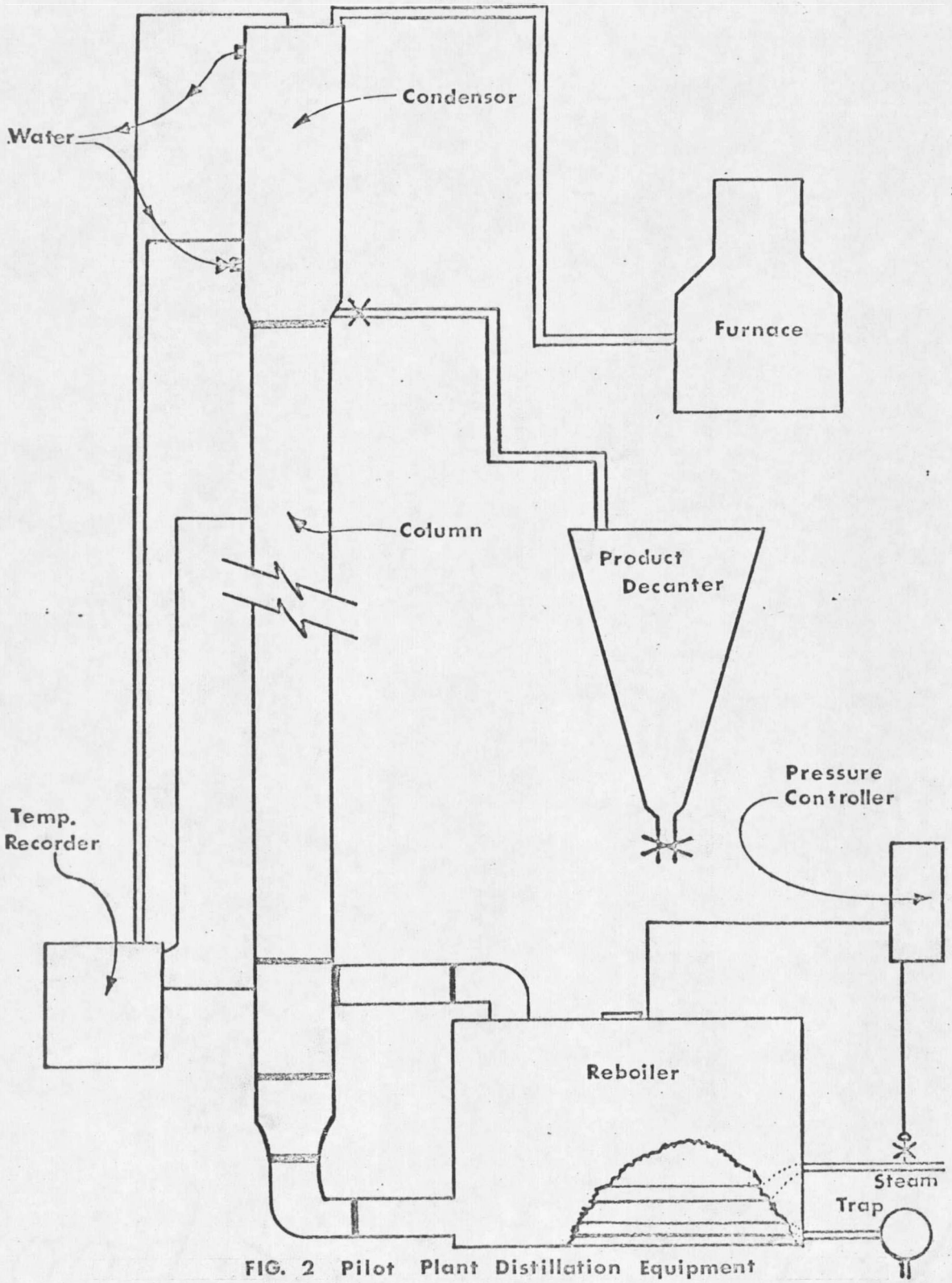


FIG. 2 Pilot Plant Distillation Equipment

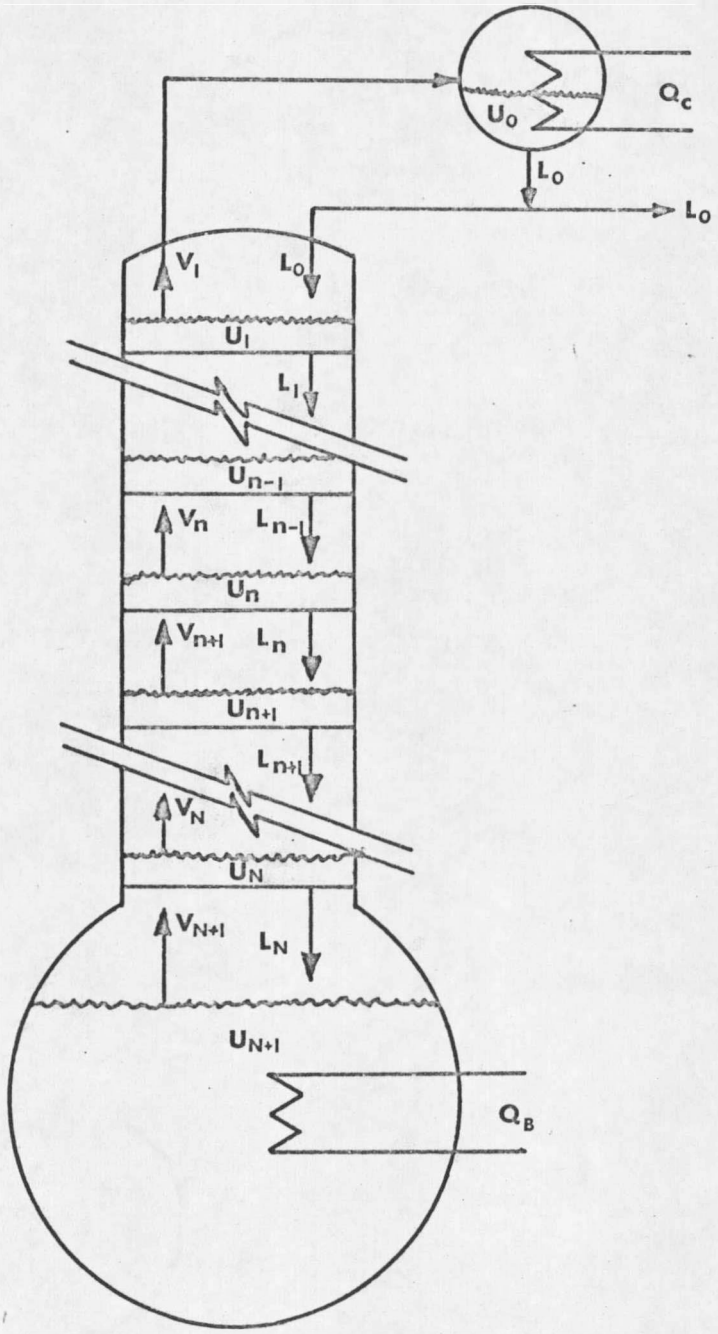


FIG. 3 Schematic Of A Batch Distillation Column

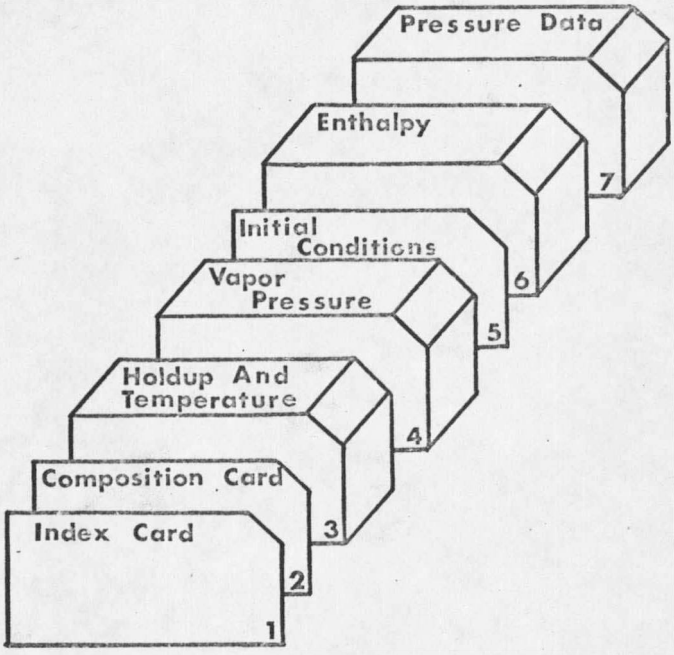


FIG. 4 Schematic Of Input Requirements For Mathematical Model

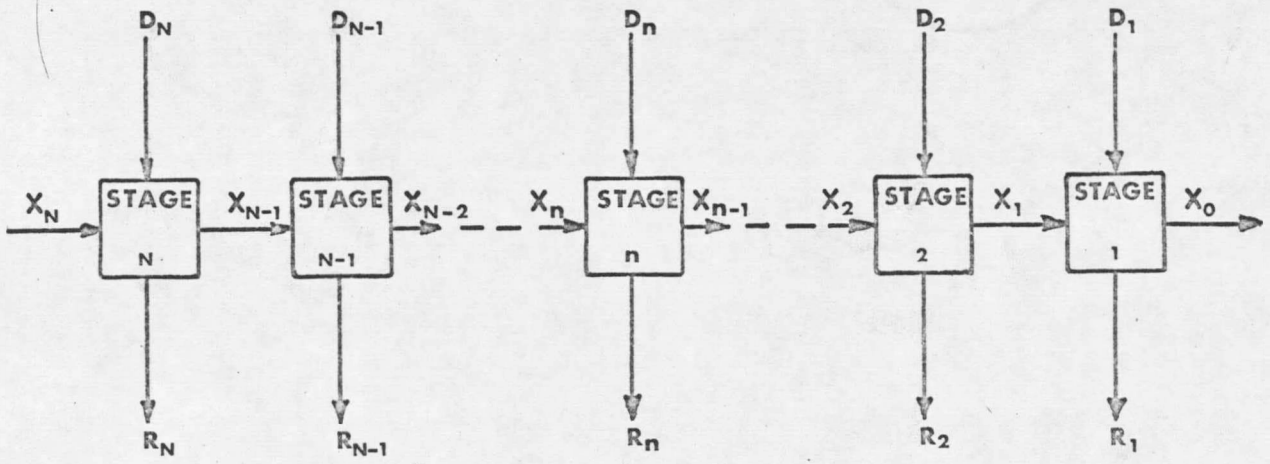


FIG. 5 A Typical Multi-stage Process

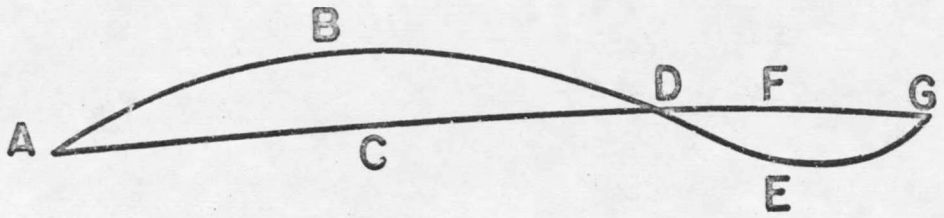


FIG. 6 A Simple Proof For The Principle Of Optimality By Means Of A Line Diagram.

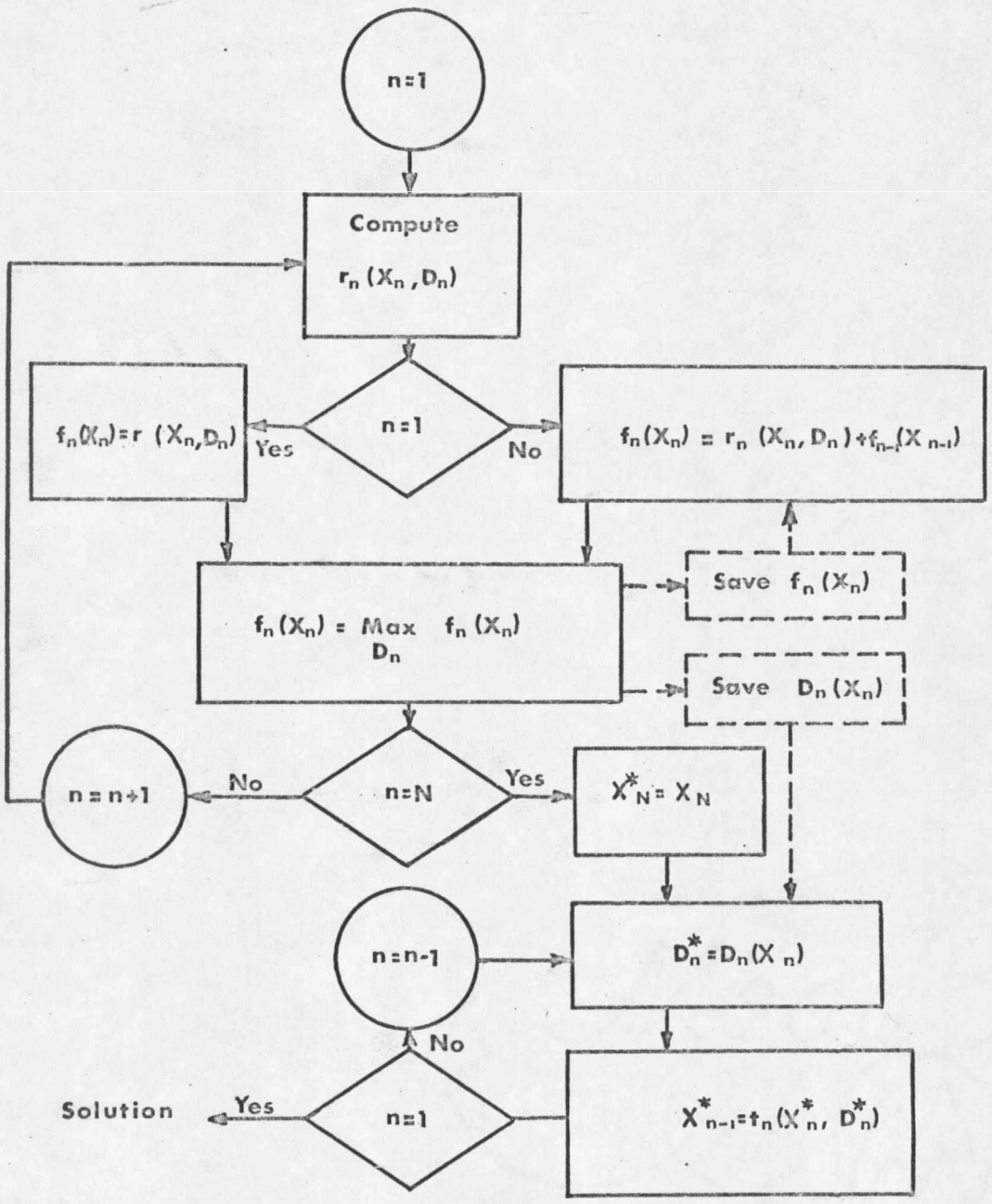


FIG. 7 General Scheme Of Dynamic Programing Computation

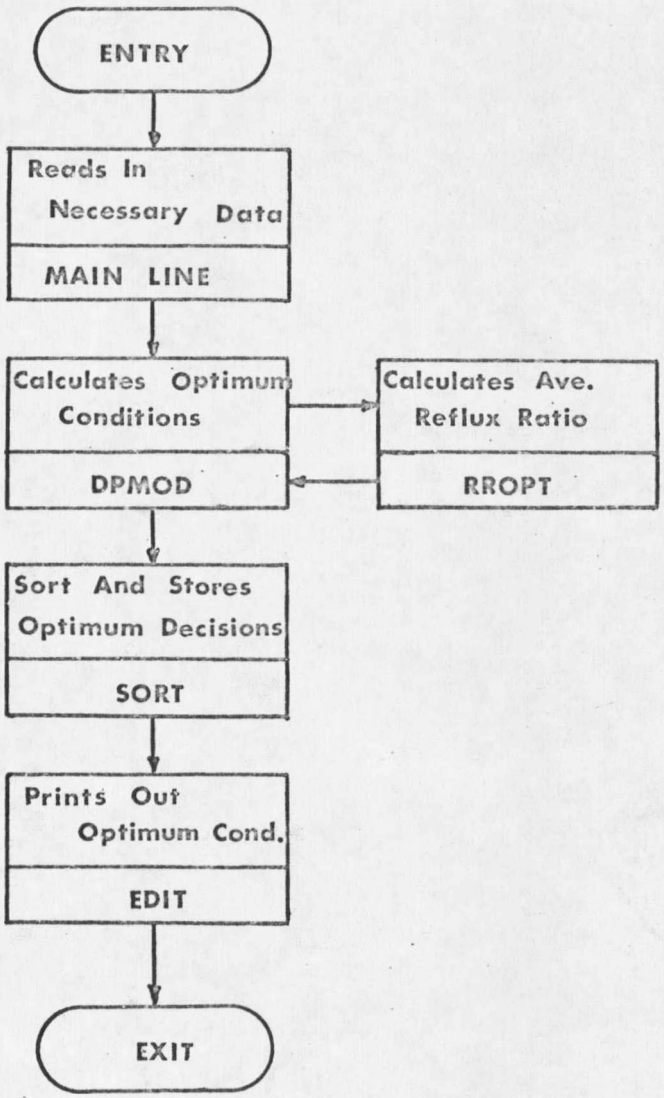


FIG. 8 Overall Flow Chart Of Optimization Program

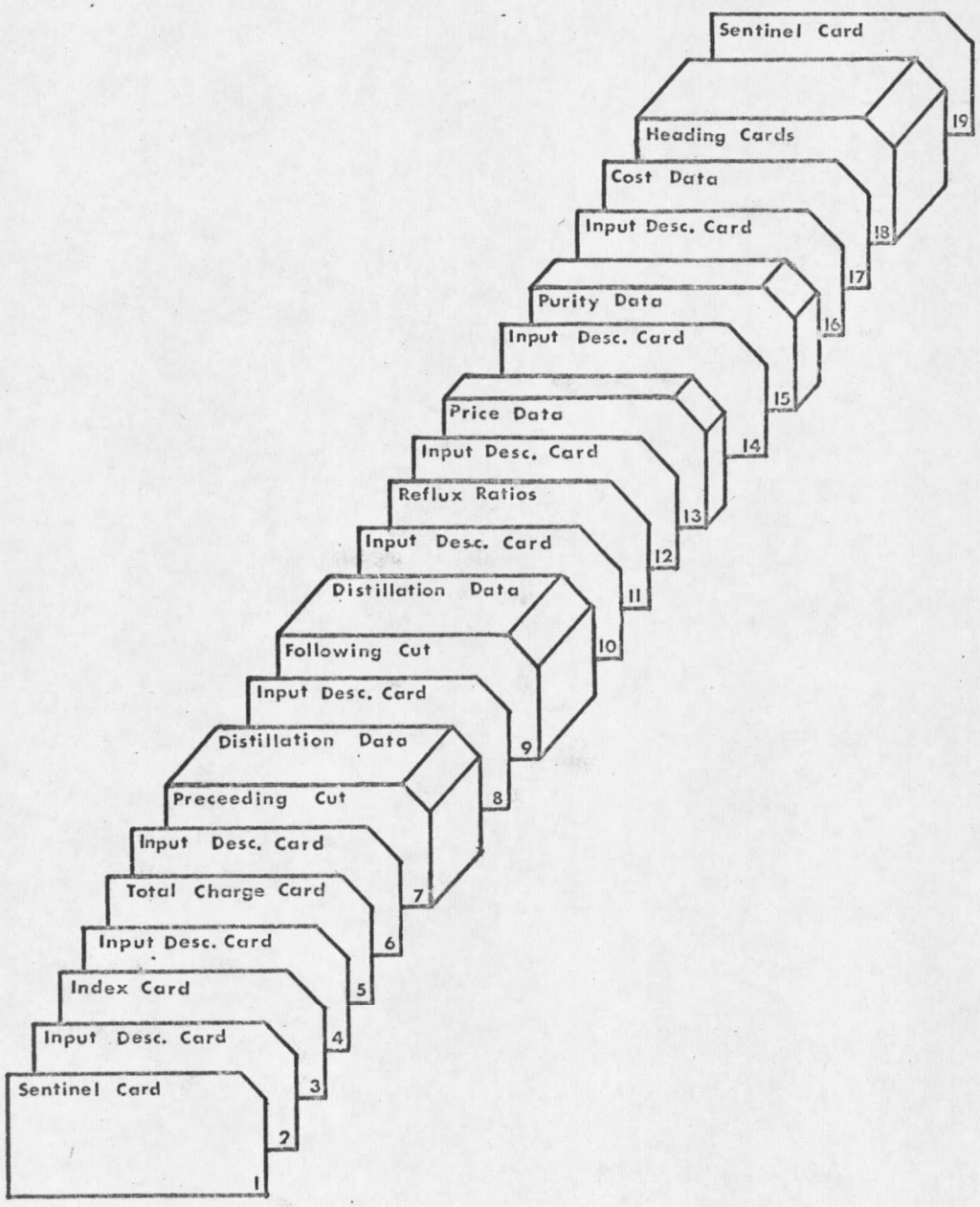


FIG. 9 Schematic Input Of Requirements For Optimization Program

TABLE XXV

KEY TO SYMBOLS USED IN FIGURES 10-22

⊙	Alpha Pinene
⬡	Beta Pinene
▽	Delta-3-Carene
□	Dipentene

FIGURE 10 DISTILLATION DATA

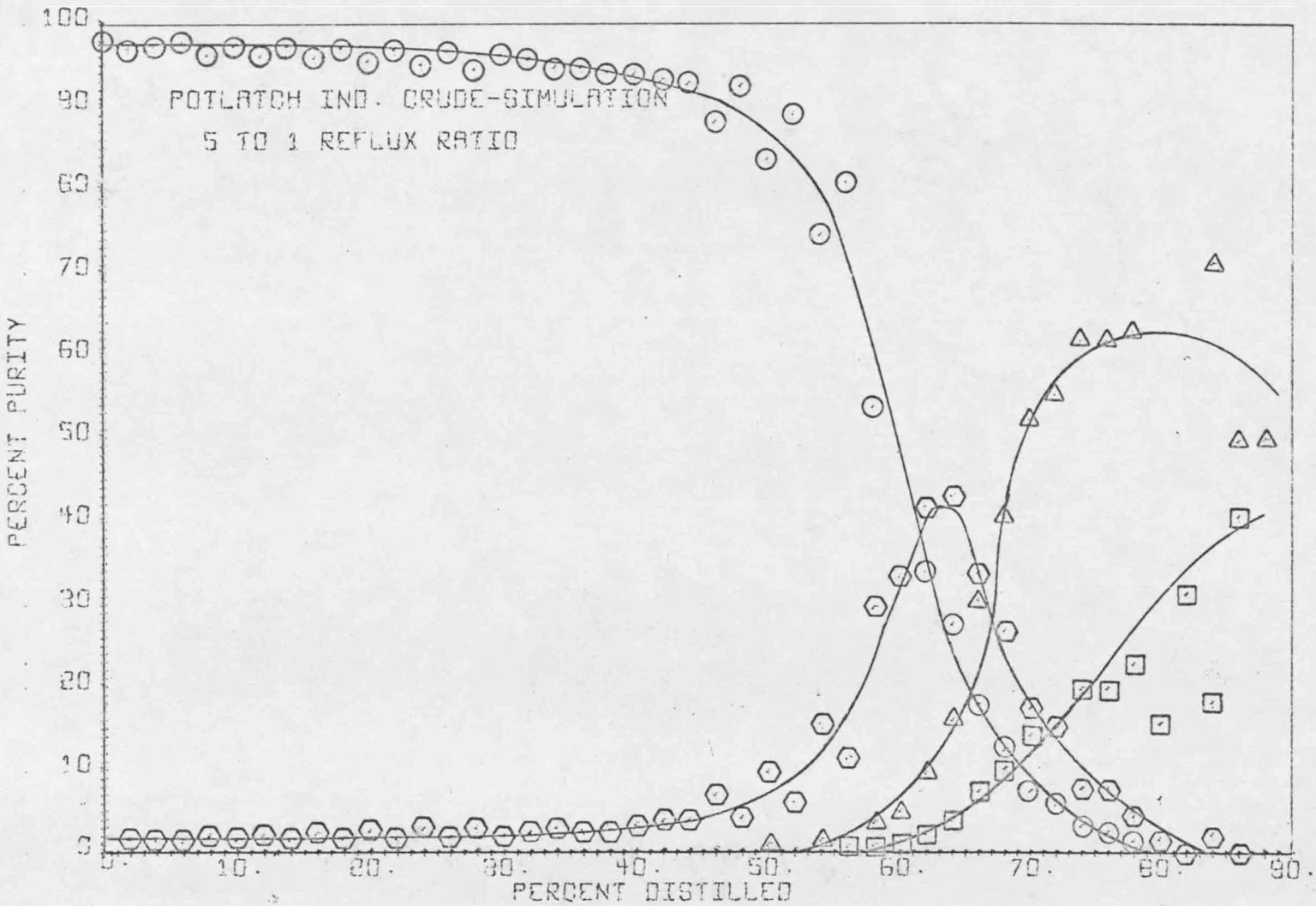


FIGURE 11 DISTILLATION DATA

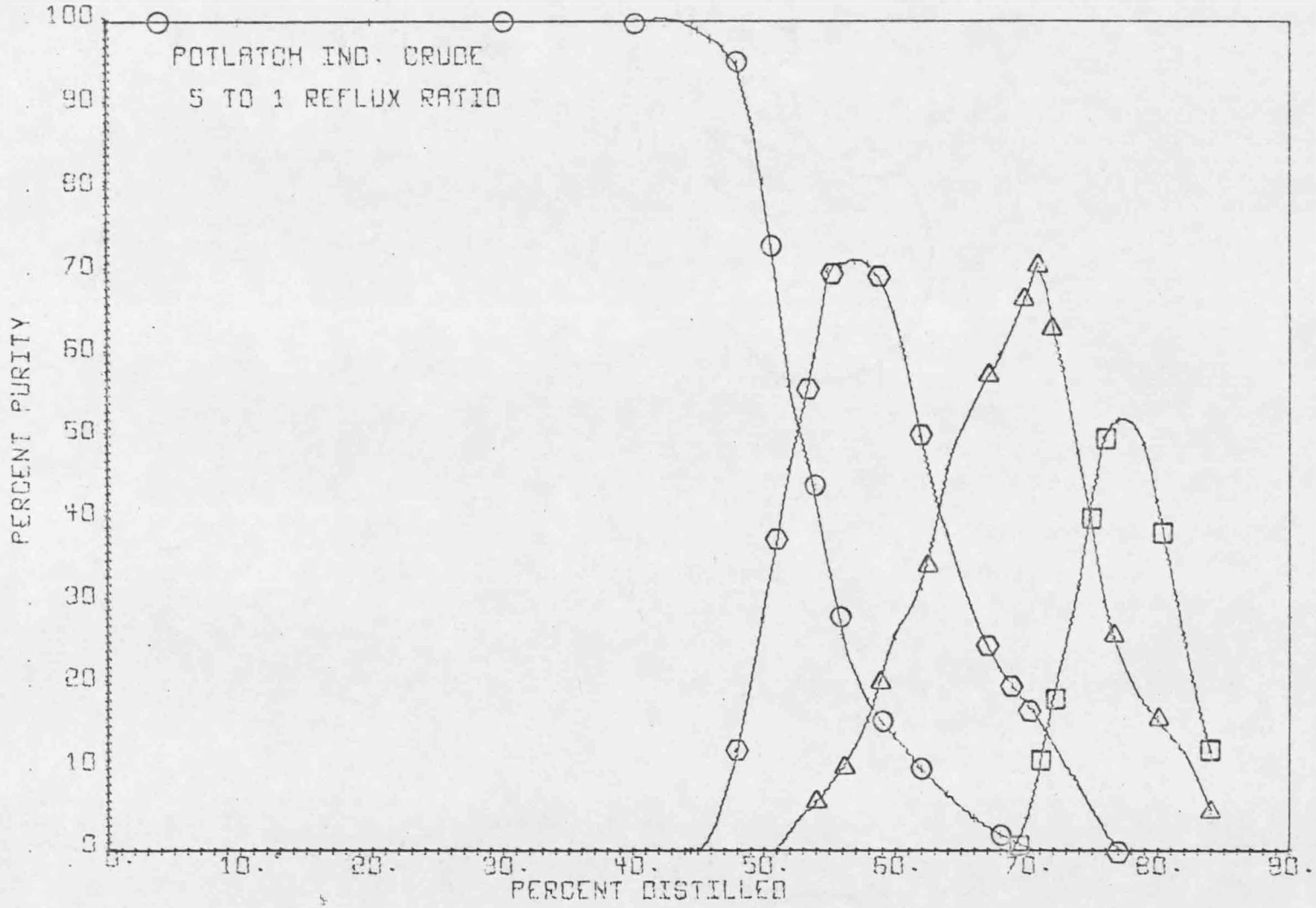


FIGURE 12 DISTILLATION DATA

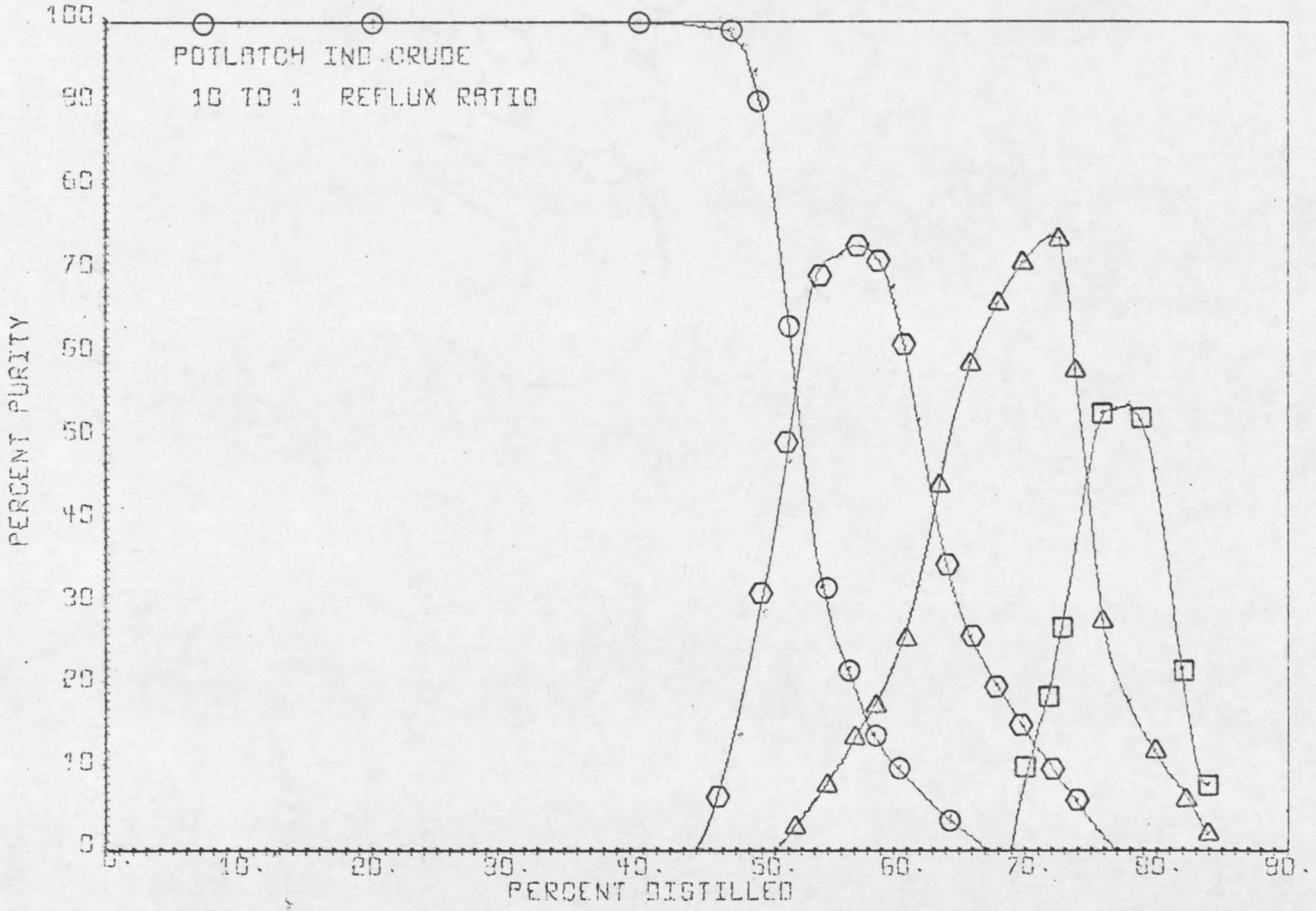


FIGURE 13 DISTILLATION DATA

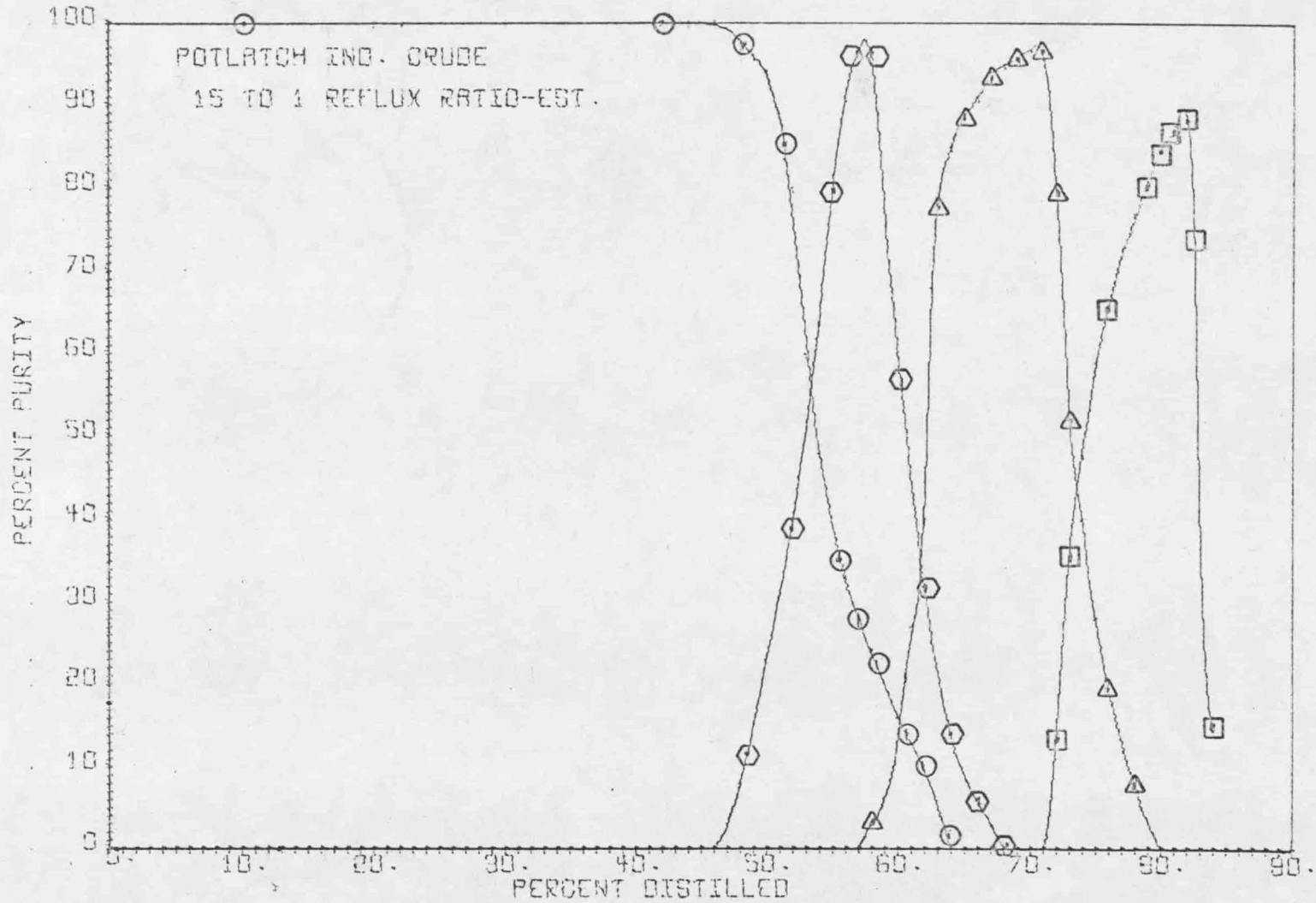


FIGURE 14 DISTILLATION DATA

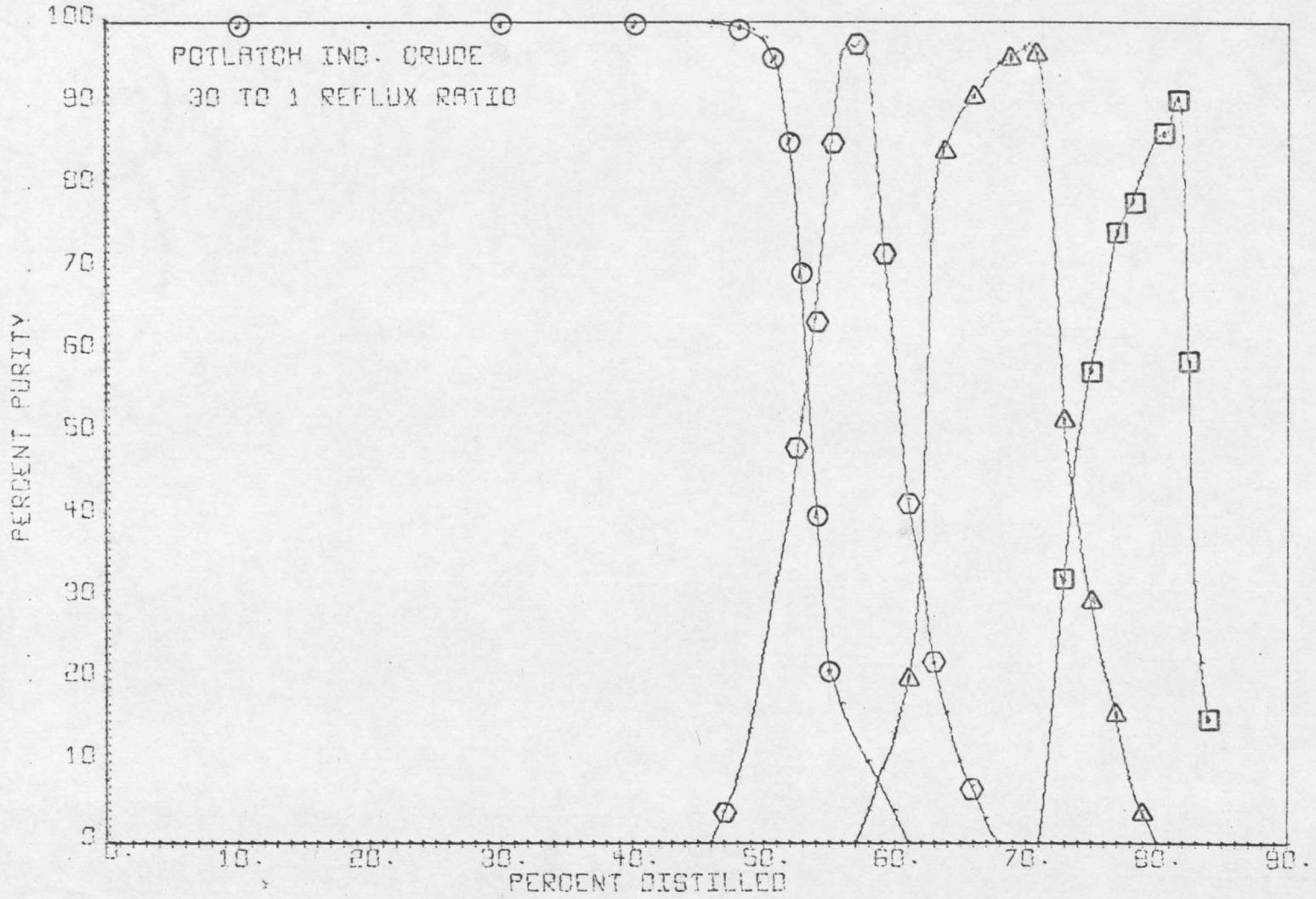


FIGURE 15 DESTILLATION DATA

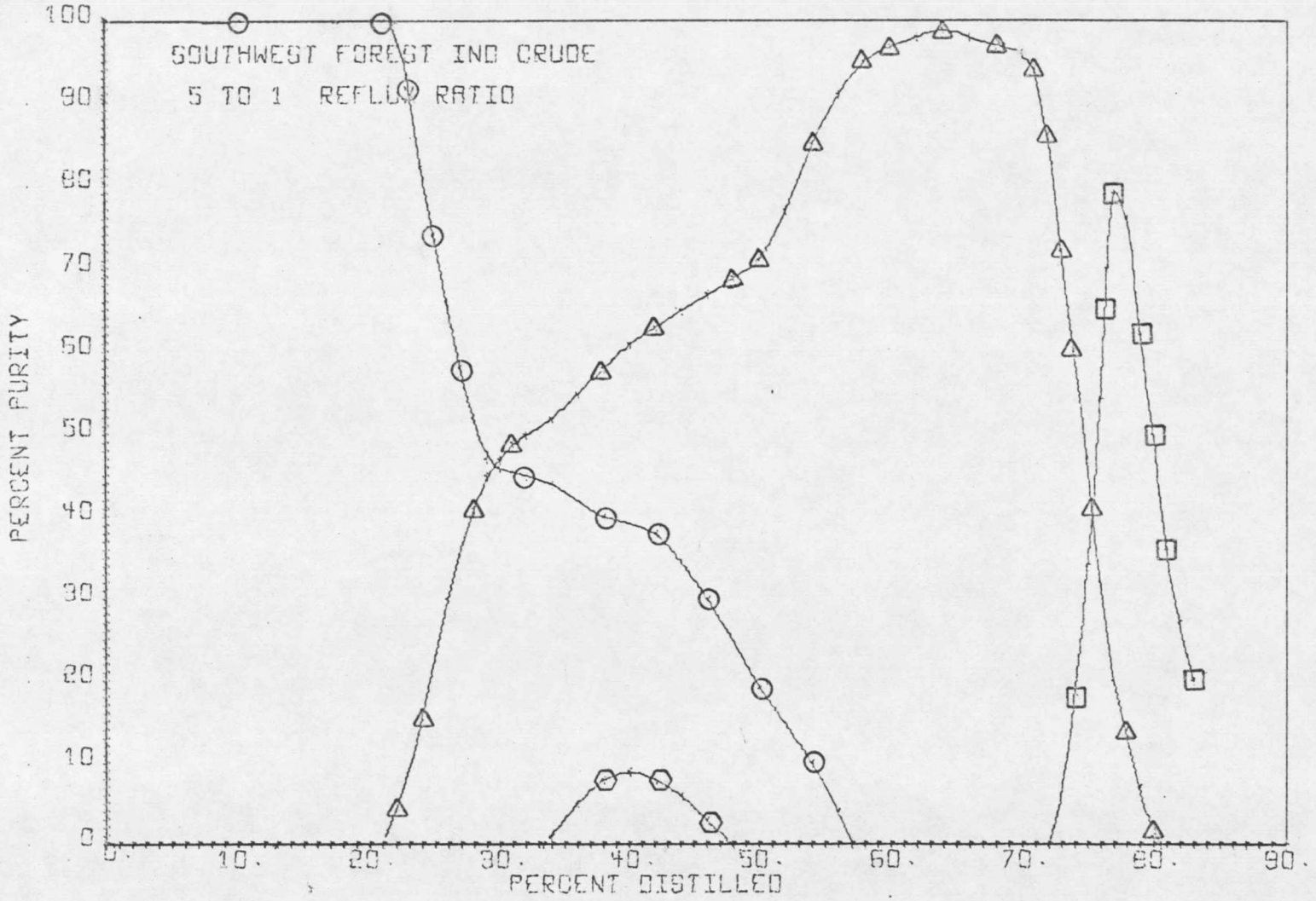


FIGURE 16 DISTILLATION DATA

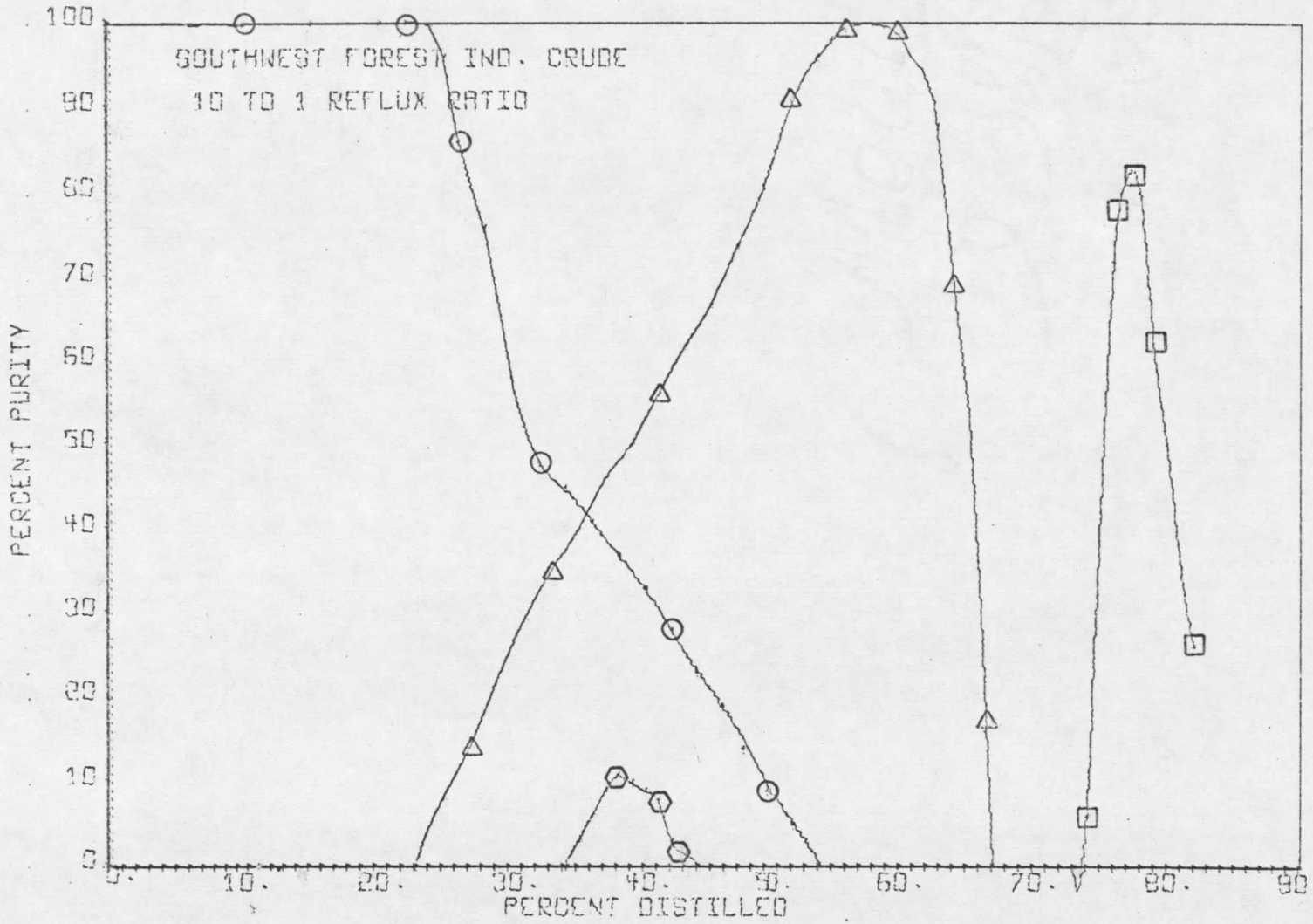


FIGURE 17 DISTILLATION DATA

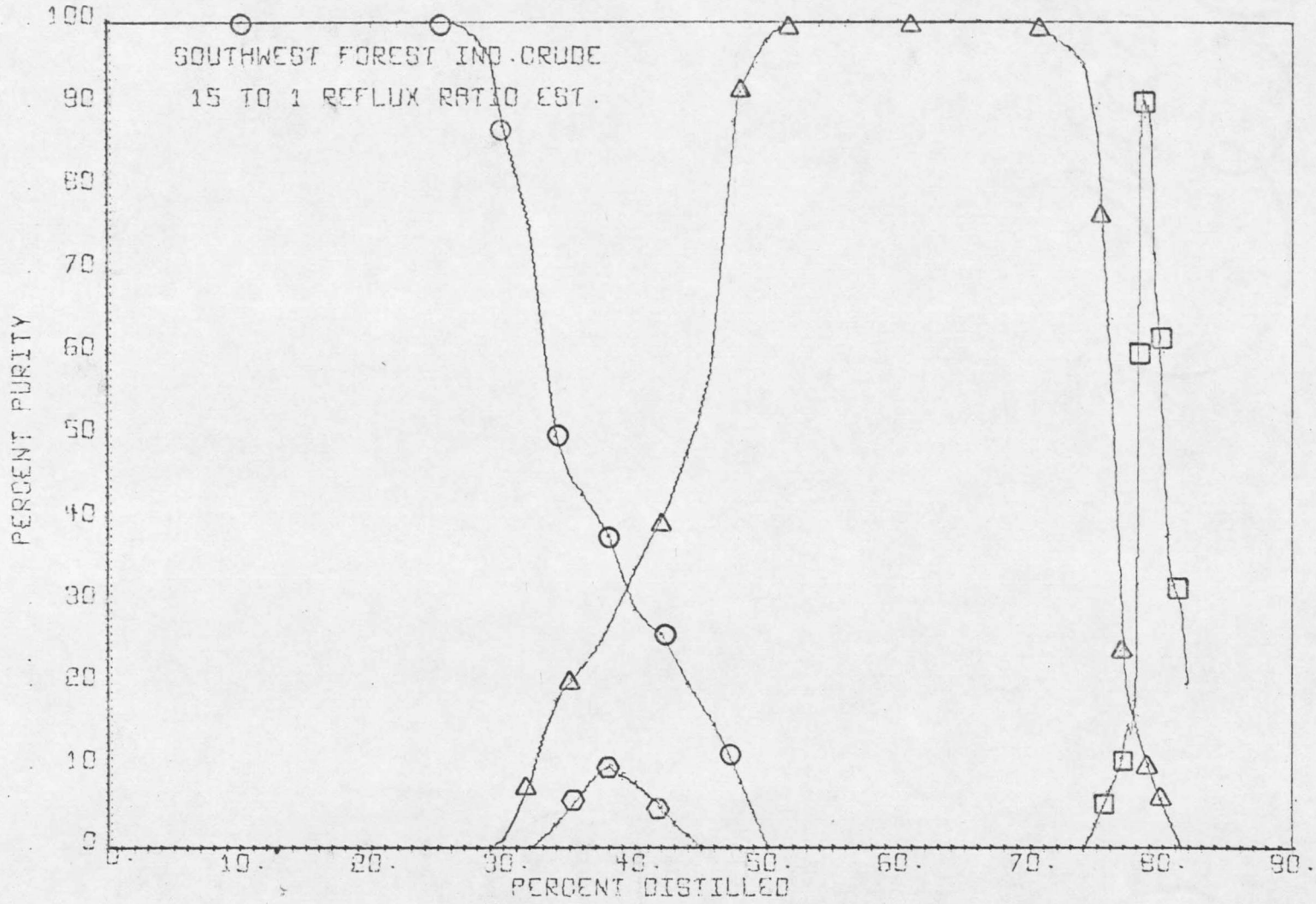


FIGURE 18 DISTILLATION DATA

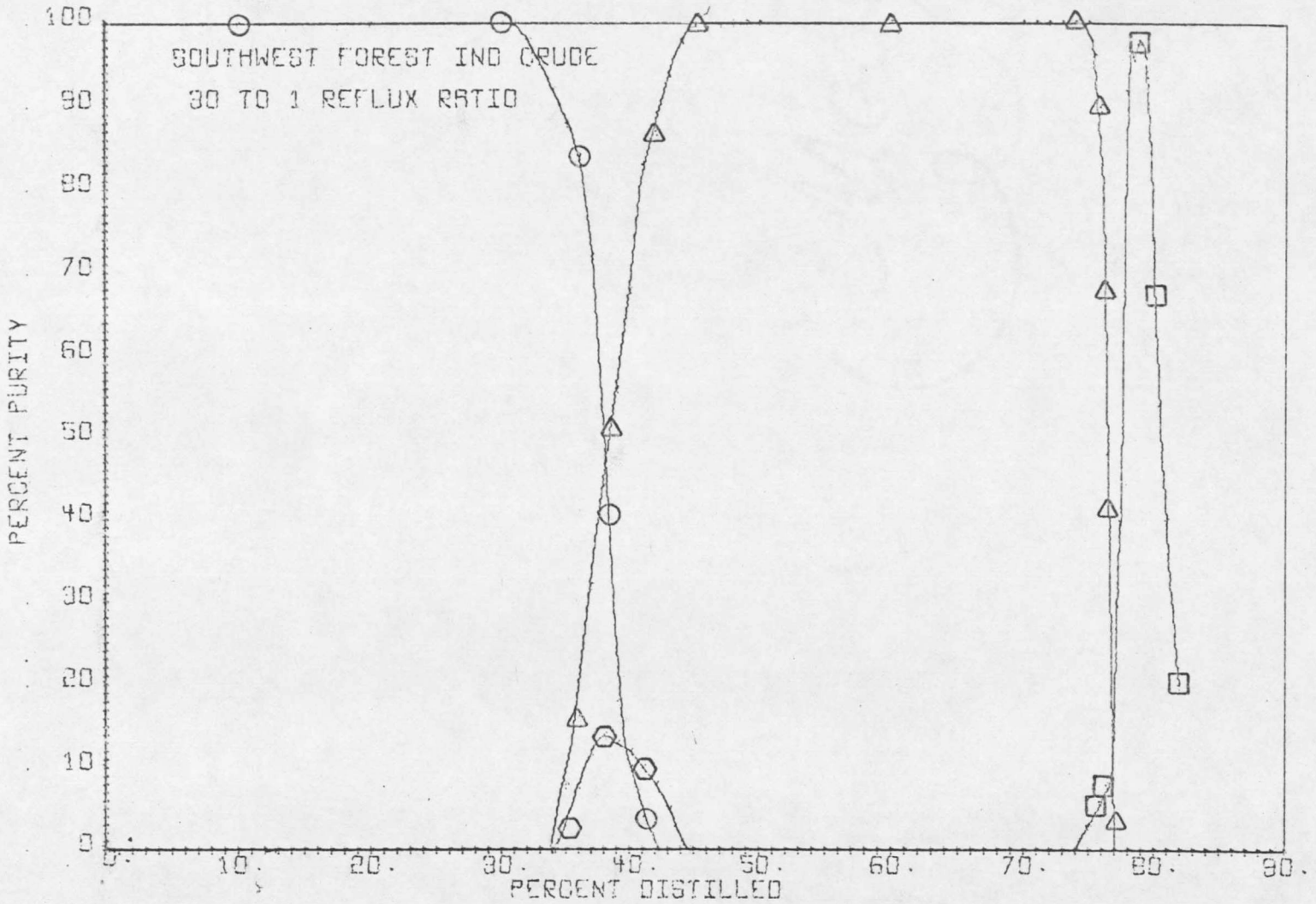


FIGURE 19 DISTILLATION DATA

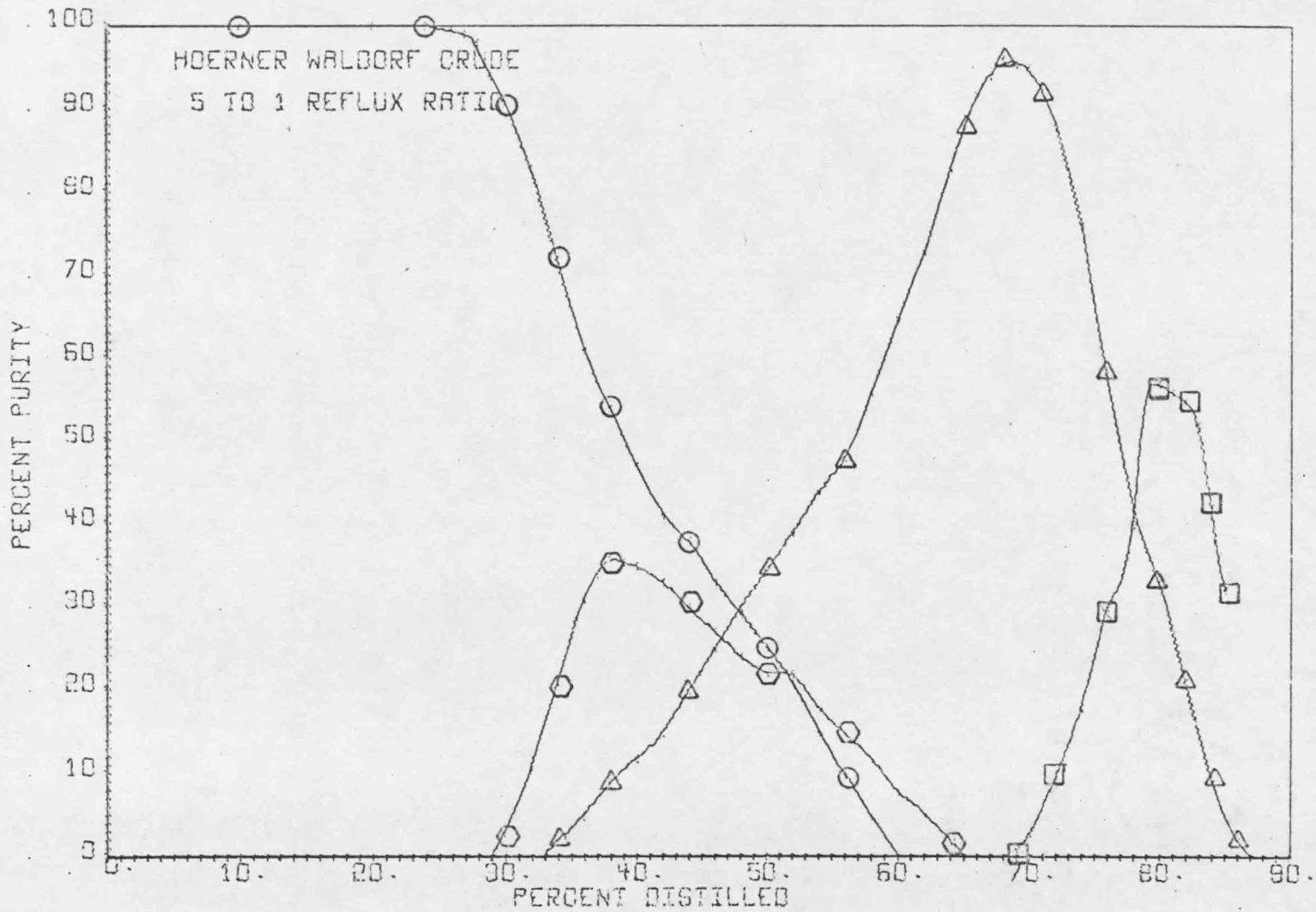


FIGURE 20 DISTILLATION DATA

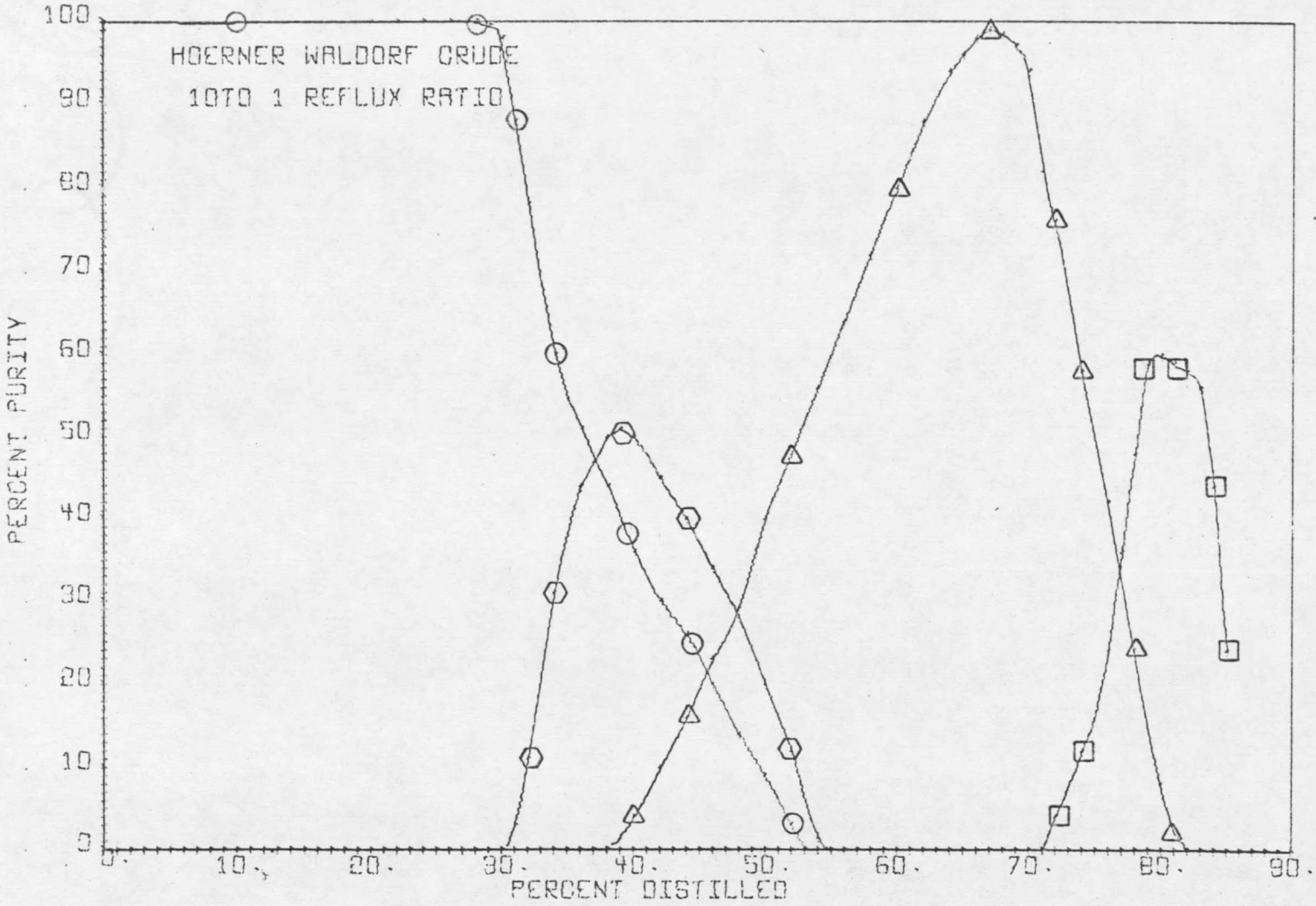


FIGURE 21 DISTILLATION DATA

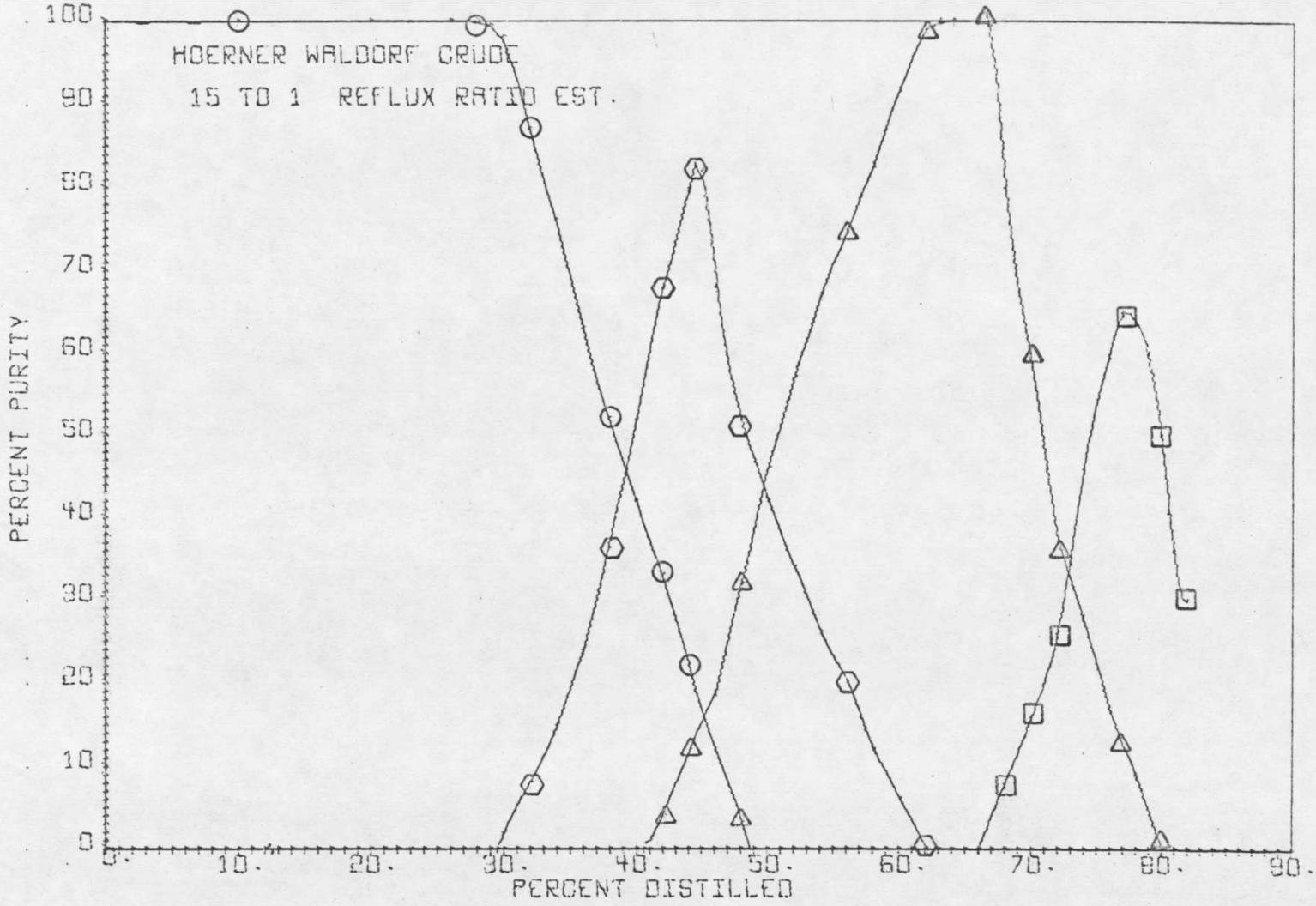
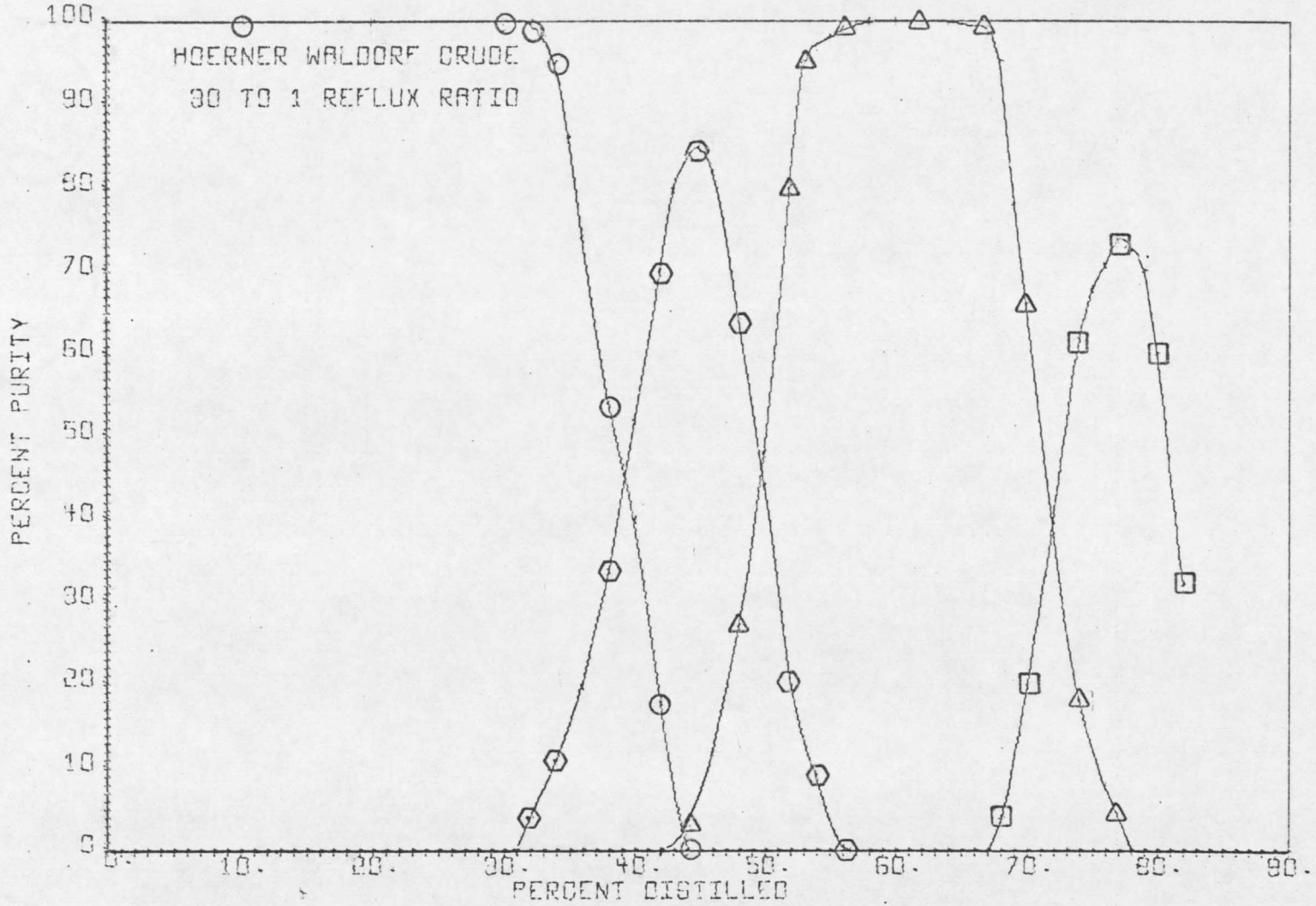


FIGURE 22 DISTILLATION DATA



NOMENCLATURE

NOMENCLATURE

Mathematical Model

$A_{j,i}$ = Absorption factor for component i and plate j

c = Total number of components.

d_i = Total molal flow rate of component in the distillate.

$E_{j,i}$ = Instantaneous value of vapor efficiency on plate j for component i.

$g_j(\theta_{-1,j} \ldots \theta_n)$ = The jth function of $\theta_{-1,j} \ldots \theta_n$.

h_j = Enthalpy per mole of liquid leaving plate j.

H_j = Enthalpy per mole of vapor leaving plate j.

H_D = Total enthalpy of the distillate.

$\ell_{j,i}$ = Molal flow rate at which component i in the liquid phase leaves plate j.

L_j = Total molal flow rate at which liquid leaves plate j.

Q_c = Condenser heat duty.

t = Time in consistent units, t_n is used to denote the time at which increment t_{n+1} begins and $t_n+\Delta t$ the time the interval ends.

T_j = Temperature of liquid leaving plate J.

$u_{j,i}$ = Liquid holdup in moles of i on plate j when the vapor holdups are neglected.

U_j = Total molal holdup of liquid on plate j when the vapor holdup is neglected.

$v_{j,i}$ = Molal flow rate at which component i in vapor phase leave plate j.

V_j = 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

θ = A multiplier associated with plate j.

μ = A weight factor used in the evaluation of an integral in terms of the value of the function at times t_n and $t_n + t$.

τ = 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 lbs/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 preceeding of following the cut.

Price = Selling price of product in $/lb.

RR = Reflux ratio.

Subscripts

Average = The average value over the stage in consideration.

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LITERATURE CITED

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