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Determination of distillation efficiencies for the water-methanol-acetone system

Chorng Shyong Wang

DETERMINATION OF DISTILLATION EFFICIENCIES FOR
THE WATER-METHANOL-ACETONE SYSTEM

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ABSTRACT

A pilot-scale, eight-plate, bubble-cap distillation tower with a multi-point temperature recorder and automatic sampling device was used to obtain operating data on temperatures and liquid phase compositions for distillation efficiency studies. The tower was run with a single feed, a total condenser, and a partial reboiler. At steady state, as indicated by constant temperatures, samples were taken and later analyzed by gas chromatography.

A digital program was developed to calculate component efficiencies on each plate according to Holland's modified Murphree plate efficiency, utilizing the operating data, and reflux rate, the input and output flows and compositions, and vapor-liquid equilibrium data.

The program was checked by use on data from independent distillation simulations and proved to be reliable. An extension of this method should be useful in periodically monitoring efficiencies in industrial distillation.

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I. INTRODUCTION AND OBJECTIVES

The purpose of this research is to develop and demonstrate a procedure which may be used to obtain a set of component efficiencies for a pilot plant distillation column.

The distillation tray is often called an equilibrium stage. This term is a misnomer. Because of its operation, equilibrium is never achieved. The contact time between the vapor and liquid on a distillation tray is insufficient to attain true equilibrium unless the vapor rate is exceedingly small.

Efficiency is a term used to describe this deviation from equilibrium in distillation operation. The approach to equilibrium which is attained on a specific tray is an indication of the degree of liquid mixing on that tray and of the mass transfer rates in both the liquid and vapor phases present.

Efficiency may vary for the same system from tray to tray because of the mechanical design such as the size of slots or spacing between trays. Differences in downcomer type and downcomer clearance can also affect the efficiency of the tray. The efficiency achieved on a particular tray may also vary from time to time as a result of changes in the physical properties of the vapor-liquid mixture on the tray. In this case the efficiency is affected by the viscosity, volatility, enthalpy, and equilibrium conditions of the streams on the trays. Overall operating conditions such as the total flow rate of liquid or vapor for a particular operation may also change the efficiency developed in a distillation.

True equilibrium compositions for outlet streams are not readily calculated. Thermodynamic effects are described by equations developed by data correlations based on temperature and sometimes compositions. When these correlations are applied to calculate a pseudo-equilibrium for a physical system, their results are approximate and in some cases these results deviate appreciably from the true equilibrium conditions.

A calculated efficiency value thus may account not only for the actual deviation encountered on the tray but also for the apparent deviations which arise from the calculational procedure used in the problem.

Pilot plant efficiency data for a particular system may be valuable for several reasons. These data may be used to predict performance characteristics of existing columns when these columns may not be released from service for test purpose. Indications of their adaptability to a new service could be obtained without interrupting the process now using the column. These efficiencies could also be used to point out locations where the deviation from theoretical operations is greatest, and thus where development could be most effective.

The data normally available from a pilot plant distillation operation may be sufficiently detailed to permit individual efficiencies to be calculated for each component on each stage. These individual component efficiencies would be of more value than a single number for column efficiency.

Column efficiency, used quite often for many years, described the separation behavior of an entire column. It would be an accurate value only when the identical system and column are used again. The individual component efficiency could be an accurate value whenever conditions are encountered which approximated those of the pilot plant tray for a given component.

Two forms have been suggested for component efficiencies: the modified Murphree plate efficiency which is expressed as the ratio of the actual change in vapor composition across a single stage to the change which would have occurred if a vapor had actually reached a state of equilibrium. It is described in Equation (1.1),

$$E_{ji}^{M} = \frac{y_{ji} - y_{j+1,i}}{Y_{ji} - y_{j+1,i}} \qquad (1.1)$$

This efficiency expression deviates from the original statement of the Murphree plate efficiency in that the equilibrium composition for tray j are calculated at the actual tray temperature and not at the bubble point for the equilibrium composition.

The vaporization efficiency is more readily adapted to distillation calculation. It is expressed as the ratio of the actual vapor composition on a stage to the ideal vapor composition which would be encountered on that stage if the vapor were in equilibrium with the liquid overflow and at the temperature of the stages.

II. LITERATURE REVIEW

The earliest definition for plate efficiency was given by Murphree(14) who described plate efficiency as a quantitative measurement of separation capability of an actual plate. This definition was developed from the absorption equation of interphase mass transfer. It is based on the assumption of constant molal flow rates along the column which is, seldom achieved. It was mathematically defined as the ratio of composition enrichment through an actual plate to that through an equilibrium plate, i.e. $E_{ji} = \frac{y_{ji} - y_{j+1,i}}{y^*_{ji} - y_{j+1,i}}$, where y^*_{ji} is a fictitious vapor composition which would be in equilibrium with the liquid leaving an equilibrium plate. It should be calculated at the bubble point of liquid leaving that equilibrium plate. In the fictitious vapor, the summation of compositions, y^*_{ji}, should be unity, the vapor was assumed to be a perfect gas, and the liquid was assumed to obey Raoult's Law, i.e. $y^*_{ji} = \frac{p_i}{P} = \frac{p^*_i\ x_i}{P}$.

McAdams(12) defined vaporization efficiency in the batch-steam distillation of a system containing one volatile (two phases) component. It is the ratio of actual partial pressure of the volatile component in the vapor to the equilibrium partial pressure of that component which would be in equilibrium with the charged liquid, $E^v = \frac{p_i}{p^*_i x_i}$, where p^*_i is vapor pressure of pure component i.

Holland and Welch(10) extended the McAdam's definition of vaporization efficiency to make it applicable for multi-component mixture. $E^{o}_{ji} = \frac{y_{ji}}{Y_{ji}}$

y_{ji} = Actual vapor composition of component i leaving plate j.

Y_{ji} = Fictitious composition of vapor which would be in equilibrium with liquid evaluated at actual plate temperature.

Holland(9) modified Murphree's definition of plate efficiency by considering actual operating conditions and permitting variation of molal overflow rates within the column. A fictitious vapor composition was calculated at the actual plate temperature ($\Sigma Y_{ji} \neq 1$) and used in place of that calculated at the bubble point of the liquid. ($\Sigma Y_{ji} = 1$)

$$E^{M}_{ji} = \frac{y_{ji} - y_{j+1,i}}{Y_{ji} - y_{j+1,i}}$$

where

$Y_{ji} = K_{ji} x_{ji}$

x_{ji} = Liquid composition

K_{ji} = Evaluated at the actual temperature and pressure at which liquid leaves plate j.

Kastanek and Standart(11) suggested three different definitions of plate efficiency which consider the possible effects of entrainment or weeping during operation. The non-uniformities in tray hydraulics in a large experimental column usually lead to significant liquid weeping (carryover). Direct and accurate hydraulic measurements of entrainment and weeping should be made in order to obtain actual or reduced stream rates and phase compositions. Three different definitions were made.

(1) The reduced efficiency

$$\bar{E}_y' = \frac{\bar{y}_n' - \bar{y}'_{n+1}}{\bar{y}_n'^* - \bar{y}'_{n+1}}$$

(2) The apparent efficiency

$$\bar{E}_y = \frac{\bar{y}_n - \bar{y}_{n+1}}{\bar{y}_n^* - \bar{y}_{n+1}}$$

(3) The conventional efficiency

$$E_y = \frac{(\bar{y}_n) - (\bar{y}_{n+1})}{(\bar{y}_n^*) - (\bar{y}_{n+1})}$$

It was found the values of the conventional and reduced Murphree plate efficiencies are about the same, except at very high vapor velocity on certain plates. The apparent efficiency is greater than the reduced efficiency since for the former the denominator is smaller ($\bar{y}_n'^* > \bar{y}_n^*$, since $\bar{x}_n' > \bar{x}_n$), while the numerator is the same as in the latter case.

Davis, Taylor, and Holland(2) have studied experimental plate efficiency in the distillation of multicomponent hydrocarbon mixtures. To interpret the results obtained for commercial columns in various types of services, plate efficiency was considered to be the combined effects of component efficiency and a plate factor. The θ method and Newton-Raphson techniques were employed to obtain accurate sets of plate and component efficiencies. Normalization was required for both component efficiency and the plate factor. It was found that when the modified Murphree plate efficiency is less than unity, vaporization efficiency for the relatively light components is greater than unity. A component efficiency can be expected to be a decreasing function of volatility.

Diener and Gerster(4) have used an experimental column with two rectangular split-flow sieve trays for point efficiency studies in the distillation of the acetone-methanol-water system. Emphasis was placed on the approach to an efficiency evaluated from the fundamental mechanisms of mass and heat transfer. A prediction method for the ternary system based on binary data has been established.

A.I.Ch.E.(1) proposed empirical dimensional relations which relate point efficiency to the number of transfer units on the basis of operating conditions, design, and system variables. The number of transfer units is expressed as a function of diffusivity, gas viscosity, gas density, liquid and vapor flow rates, and outlet weir height. This correlation did not involve the analysis of stream composition or calculation of enthalpy and material balances. It was intended to be easily applicable in practical calculations.

Nord(15) reported the effects of concentration gradient, diffusion efficiency, and entrainment on plate efficiency for a benzene-toluene-xylene system. If diffusivities of each component in the mixture are not nearly the same, concentration will have an appreciable effect on the plate efficiency. Entrainment may be one of the factors reducing plate efficiency, but this effect can not account for a reduction at both high and low concentrations.

O'Connell(17) has found that viscosity and relative volatility were the most important physical properties affecting overall plate efficiency in the distillation of hydrocarbon mixtures, chlorinated hydrocarbons, alcohol-water, and in the trichloroethylene-toluene-water system. Overall plate efficiency was correlated as a decreasing function of the product of the relative volatility of the key components and the average molal liquid viscosity (in centipoises) of the column feed. Both properties were determined at the average tower temperature and pressure.

Drickamer and Bradford(5) showed that for commercial hydrocarbon fractionating columns, the overall plate efficiency was a decreasing function of the viscosity of the feed, if the relative volatility of the key components are low. For a plate absorber, it was correlated as an increasing function of the term, HP/u, which includes the effects of solubility and viscosity, where H is Henry's constant (lb moles/ft^3 atm), P is pressure (atm), u is viscosity of absorbent in centipoises.

Gerster et. al.(6) have used a 100-tray furfural extractive-distillation column to study experimental plate efficiency. For the purpose of making overall enthalpy balances, the flow rates obtained from operating data were slightly adjusted to give perfect material balance. The computed input and output enthalpies were not in rigorous agreement and hence were adjusted slightly to obtain perfect enthalpy balances before being used in the calculation of vapor and liquid flow rates within the column.

III. BASIC THEORIES AND ASSUMPTIONS FOR MULTICOMPONENT SYSTEM

A multicomponent distillation efficiency calculation must consider the following relations:

A. Relationship for Vapor-Liquid Equilibrium:

There are three requirements for vapor-liquid equilibrium in multicomponent system(25)

$$t^v = t^l,$$

$$p^v = p^l,$$

and $\bar{f}_i^v = \bar{f}_i^l$,

where superscripts refer to the phase.

The basic relationship between fugacity and pressure holds for component i existing either in vapor or liquid mixture.

$$RTd\ln\bar{f}_i = \bar{V}_i dp \qquad (3.1)$$

The choice of reference state was made so that at p = 0, $\bar{f}_i = p$, $\bar{v}_i = v^*$, that is

$$RTd\ln p = V^* dp \qquad (3.2)$$

When the liquid mixture is under a total pressure equal to its vapor pressure, subtract Equation (3.1) from Equation (3.2) and integrate from p = 0 to $p = p_i^*$, the following expression is obtained,

$$\ln\bar{f}_{i,pi^*} = \ln p_i^* + \int_0^{p_i^*} \frac{\bar{V}_i - V^*}{RT}\, dp \tag{3.3}$$

When the liquid mixture is under a pressure other than its vapor pressure, the correction for the effect of pressure on the fugacity is obtained by integrating Equation (3.1) from p_i^* to p and combining it with Equation (3.3):

$$\ln\bar{f}_{i,p} = \ln p_i^* + \int_0^{p_i^*} \frac{\bar{V}_i - V^*}{RT}\, dp + \int_{p_i^*}^{p} \frac{V_i}{RT}\, dp \tag{3.4}$$

The effect of composition on fugacity is considered as follows

For the vapor mixture: $\ln\bar{f}^v_{i,p} = \ln y_i f_{i,p} + \int_0^p \frac{\bar{V}_i - V_i}{RT}\, dp$

For the liquid mixture: $\bar{f}^L_{i,p} = \gamma_i x_i f_i^o$

When the equilibrium state is reached, fugacities of the vapor and the liquid should be the same, $\bar{f}_i^l = \bar{f}_i^v$.

$$y_i f_{i,p} \exp\left(\int_0^p \frac{\bar{V}_i - V_i}{RT}\, dp\right) = \gamma_i x_i f_i^o$$

f_i^o can be replaced by Equation (3.4),

$$\therefore \ln y_i + \ln f_{i,p} + \int_0^p \frac{\bar{V}_i - V_i}{RT}\,dp = \ln\gamma_i + \ln x_i + \ln p_i^* + \int_0^{p_i^*} \frac{V_i - V^*}{RT}\,dp + \int_{p_i^*}^{p} \frac{V_i^L}{RT}\,dp.$$

By arrangement and substitution of fugacities terms for pressure terms,

$$\ln\gamma_i = \ln\frac{y_i p}{x_i p_i^*} + \int_{p_i^*}^{p} \frac{V_i - V^*}{RT}\,dp + \int_0^p \frac{\bar{V}_i - V_i}{RT}\,dp - \int_{p_i^*}^{p} \frac{V_i^L}{RT}\,dp. \qquad (3.5)$$

Equation (3.5) should be employed along with suitable equation of state for the evaluation of activity coefficients, whence equilibrium data are derived.

B. Assumption for Calculation of Equilibrium Data:

Due to chemical dissimilarity, the system under investigation forms non-ideal solutions in which the activity coefficient may not be unity. Some experimental data which are under higher temperatures and pressures may not be applied to this equilibrium conditions. Therefore rough estimates of equilibrium data have to be made based upon the assumption of ideal liquid solution.

By assuming γ_i to be unity, partial molar volume to be equal to molar volume of the pure component of ideal gas, and the pressure effect on liquid volume being neglected, Equation (3.5) reduces to a combination of Dalton's and Raoult's law,

$$y_i p = x_i p_i^*, \quad \text{and} \quad K_i \equiv \frac{y_i}{x_i} = \frac{p_i^*}{p}$$

Prausnitz, Eckert, Orye(23) et. al. have proposed an empirical equation relating vapor pressure of the pure component to a function of absolute temperature:

$$\ln p_i^* = C_{1i} + \frac{C_{2i}}{T} + C_{4i}\, T + C_{6i} \ln T$$

These constants were shown in Table 3.1.

This research was conducted under total pressure of one atmosphere,

$$\therefore\ K_i = p_i^*,\ \ln K_i = \ln p_i^*, \ln K_i = C_{1i} + \frac{C_{2i}}{T} + C_{4i}\, T + C_{6i} \ln T \tag{3.6}$$

Equilibrium data were expressed as a function of temperature alone. Equation (3.6) was employed to calculate equilibrium data of each component under specified temperatures. These values, as listed in Table 3.2, were used to make a curve-fit with Holland's type constants(9):

$$K_i = (a_{1i} + a_{2i}\, T + a_{3i}\, T^2 + a_{4i}\, T^3)^3\, T \tag{3.7}$$

The equilibrium constants as a function of temperature were as follows:

Water:

$$\left(\frac{K_i}{T}\right)^{1/3} = -0.02569219+0.1773240\text{x}10^{-4}T-0.1780874\text{x}10^{-6}T^2 +0.6871899\text{x}10^{-9}T^3$$

Methanol:

$$\left(\frac{K_i}{T}\right)^{1/3} = -0.1228759+0.7404905\text{x}10^{-4}T+0.3787396\text{x}10^{-6}T^2 +0.2463494\text{x}10^{-9}T^3$$

Acetone:

$$\left(\frac{K}{T}\right)^{1/3} = -0.2439641+0.1627855\text{x}10^{-3}T+0.1255913\text{x}10^{-5}T^2 -0.8441363\text{x}10^{-9}T^3$$

C. Rigorous Enthalpy Relationships:

Like equilibrium data, enthalpy data should be theoretically a function of both temperature and composition due to chemical dissimilarity(25).

$$H_j = f_1(T_j, y_{ji}), \text{ for vapor mixture}$$

$$h_j = f_2(T_j, x_{ji}), \text{ for liquid mixture}$$

or

$$H_j = \sum_{i=1}^{C} \bar{H}_{ji} y_{ji}$$

$$h_j = \sum_{i=1}^{C} \bar{h}_{ji} x_{ji}$$

D. Assumption for Calculation of Enthalpy Data:

The composition effect is nearly negligible in the calculation of vapor enthalpies. Thus these may be considered functions of temperature alone for the calculations made in this work.

The composition effect is generally not negligible for the liquid phase, and values of $\bar{h}_{ji}$ are required. These would have been easily calculated if experimental partial molar heats of solution (defined as $L_{ji} = \bar{h}_{ji} - h_{ji}$) over the entire range of composition had been available(25). Since these data were not available, the ideal solution approximation is made for calculations of vapor and liquid enthalpies.

$$H_j = \sum_{i=1}^{C} H_{ji} y_{ji} \tag{3.8}$$

$$h_j = \sum_{i=1}^{C} h_{ji} x_{ji} \tag{3.9}$$

E. Source of Enthalpy Data:

Vapor enthalpy data for these components at zero pressure are available from literature as shown in Table 3-3. This research, however, was conducted under one atmosphere, and it is necessary to make a correction for pressure change.

The variation of enthalpy with pressure in a system at constant temperature is given by

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{3.10}$$

By integration at constant temperature,

$$H = H_o + \int_1^2 \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dp \tag{3.11}$$

The Berthelot Equation(19) is an accurate equation of state and may be differentiated to give the derivative of volume with respect to temperature at constant pressure.

$$PV = RT\left[1 + \frac{9}{128}\frac{P_r}{T_r}\left(1 - \frac{6}{T_r^{\,2}}\right)\right] \tag{3.12}$$

This derivative was substituted in Equation (3.11) to give

$$H_P = H_o + \frac{9RT_CP_r}{128}\left(1 - \frac{18}{T_r^{\,2}}\right)$$

where

$$P_r = \frac{P}{P_C},\ T_r = \frac{T}{T_C},\ R = 1.987$$

Since relative enthalpies with the base value at 492°R liquid were used, vapor enthalpy should be elevated to a base value at 492°R liquid equals zero. The heat of vaporization at 492°R (Table 3.4) was added to this base value to obtain the values shown in Table 3.6.

No liquid enthalpy data except for water in the desired range are available from the literature. However, they could be calculated by subtraction of latent heat of vaporization from corresponding vapor enthalpy. The latent heats of vaporization and liquid enthalpies were shown in Table 3.7, and Table 3.8 respectively.

The vapor enthalpy equations obtained by least squares technique were:

Water:

$$H_i^{\frac{1}{2}} = 0.12375660\text{x}10^{3}+0.32756421\text{x}10^{-1}T-0.31256958\text{x}10^{-5}T^{2}$$

Methanol:

$$H_i^{\frac{1}{2}} = 0.10984052\text{x}10^{3}+0.31790598\text{x}10^{-1}T+0.10287539\text{x}10^{-4}T^{2}$$

Acetone:

$$H_i^{\frac{1}{2}} = 0.85837260\text{x}10^{2}+0.57459815\text{x}10^{-1}T+0.18562340\text{x}10^{-4}T^{2}$$

The liquid enthalpy equations obtained by least squares technique were:

Water:

$$h_i^{\frac{1}{2}} = -0.55510291\text{x}10^{3}+0.17535334\text{x}10T-0.12486742\text{x}10^{-2}T^{2}$$

Methanol:

$$h_i^{\frac{1}{2}} = -0.53609748\text{x}10^{3}+0.16521577\text{x}10T-0.11176039\text{x}10^{-2}T^{2}$$

Acetone:

$$h_i^{\frac{1}{2}} = -0.63942181\text{x}10^{3}+0.19733626\text{x}10T-0.13442990\text{x}10^{-2}T^{2}$$

Table 3.1

Constants for the Vapor Pressure Equation

$$\ln P(\text{atm}) = C_1 + \frac{C_2}{T} + C_4 T + C_6 \ln T$$

Constant	Water	Methanol	Acetone
C_1	75.7356943	53.3628096	2.0377274
C_2	-13252.85658	-10747.48122	-7144.59924
C_4	0.0038625784	0.0023612572	-0.0046496708
C_6	-9.00000	-5.79200	2.00000

Taken from "Computer Calculations for Multicomponent Vapor-Liquid Equilibria" by Prausnitz et. al. PP218-219, with conversion of temperature unit from ^{o}K to ^{o}R.

Table 3.2

Equilibrium Data at One Atmosphere

Point No.	T °R	Water	Methanol	Acetone
1	590.399900	0.154216	0.662616	0.956418
2	594.000000	0.169627	0.720416	1.024495
3	597.599800	0.186333	0.782362	1.096370
4	601.199900	0.204422	0.848728	1.172181
5	604.800000	0.223983	0.919698	1.252083
6	608.399900	0.245109	0.995585	1.336214
7	612.000000	0.267917	1.076598	1.424725
8	615.599800	0.292486	1.163051	1.517770
9	619.199900	0.318942	1.255180	1.615496
10	622.800000	0.347394	1.353265	1.718058
11	626.399900	0.377950	1.457635	1.825610
12	630.000000	0.410762	1.568570	1.938304
13	633.599800	0.445933	1.686378	2.056292
14	637.199900	0.483590	1.811457	2.179739
15	640.800000	0.523892	1.944002	2.308798
16	644.399900	0.566973	2.084433	2.443622
17	648.000000	0.612978	2.233099	2.584370
18	651.599800	0.662070	2.390325	2.731194
19	655.199900	0.714395	2.556474	2.884255
20	658.800000	0.770139	2.732045	3.043698
21	662.399900	0.829447	2.917225	3.209688
22	666.000000	0.892491	3.112580	3.382379
23	669.599800	0.959477	3.318384	3.561916
24	673.199900	1.030562	3.535098	3.748453
25	676.800000	1.106004	3.763206	3.942134
26	680.399900	1.185917	4.003102	4.143122
27	684.000000	1.270518	4.255173	4.351551
28	687.599800	1.360055	4.519873	4.567564
29	691.199900	1.454747	4.797816	4.791301
30	694.800000	1.554773	5.089201	5.022926

Table 3.3

Vapor Enthalpy at Zero Pressure, BTU/LB. Mole

T °R	Water	Methanol	Acetone
492	0	0	0
500	64.02	88.8	138.5
520	224.2	291.8	491.5
537	360.5	473.4	799.8
600	867.5	1180.0	2006.0
700	1679.0	2377.0	4113.0

Taken from "Petroleum Refiner", p. 127, November, 1949 (water), p. 136, September, 1950 (methanol), p. 120, August, 1951 (acetone). Base value was set at 492°R equal zero.

Table 3.4

Heat of Vaporization at 492°R, BTU/Lb. Mole

Water	19352.88
Methanol	16375.68
Acetone	14066.85

Taken from Perry's Chemical Engineers Handbook.

Table 3.5

Critical Properties for Water, Methanol, Acetone

Vapor	Water	Methanol	Acetone
T_C °R	1165	924	916
P_C atm	218.3	78.5	46.6

Taken from Perry's Chemical Engineers Handbook

Table 3.6

Vapor Enthalpy at One Atmosphere, BTU/Lb. Mole

T °R	Water	Methanol	Acetone
492	0	0	0
500	66.39	91.31	143.94
520	232.08	302.74	509.46
537	372.58	490.16	827.31
600	891.65	1214.20	2062.13
700	1717.07	2429.83	4199.70

Calculated by Computer Program using the Berthelot Equation. Base value was set at 492°R equal zero.

Table 3.7

Latent Heats of Vaporization at One Atmosphere, BTU/Lb. Mole

T °R	Methanol	Acetone
492	1.6375104×10^4	1.4066856×10^4
500	1.6280000×10^4	1.4014000×10^4
520	1.6071000×10^4	1.3840000×10^4
537	1.5900000×10^4	1.3678000×10^4
600	1.5180000×10^4	1.2894444×10^4
700	1.3385000×10^4	1.1200000×10^4

Taken from J. M. Smith's "Introduction to Chemical Engineering Thermodynamics", p. 134, Second Edition (1959).

Table 3.8

Liquid Enthalpy at One Atmosphere, BTU/Lb. Mole

T °R	Water	Methanol	Acetone
492	0	0	0
500	145.0	186.99	196.79
520	505.80	607.42	736.31
537	812.48	965.84	1216.16
600	1949.0	2409.88	3234.540
700	3753.0	5420.51	7066.55

Obtained by subtraction of latent heat of vaporization from vapor enthalpy. Base value was set at 492°R equal zero.

IV. CALCULATIONAL PROCEDURE TO DETERMINE PLATE EFFICIENCY FROM EXPERIMENTAL DATA

Determination of experimental efficiency was based upon the operating data of an existing distillation unit, the liquid-vapor equilibrium relationship of mixture, and the material and the energy balance around each plate. Plate-to-plate calculation could proceed either from the top down to the reboiler or vice versa.

A. Degrees of Freedom in Multicomponent Distillation Column(7):

The independent variables describing the operation of a multicomponent distillation unit are of two types: the thermodynamic intensive variables and the relative quantities of the various streams of matter and energy. The "Phase Rule" enunciates the degrees of freedom of a system as the number of independent intensive thermodynamic properties present. It states

$$F = C - P + 2$$

A distillation unit may be considered as j contacting stages in series (Figure 4.1); each stage functions as a mixer and adiabatic separator (Figure 4.2). The inlet stream(s) enters the mixer while two equilibrium outlet streams leave the separator. A detailed analysis of the whole distillation unit is divided into four parts:

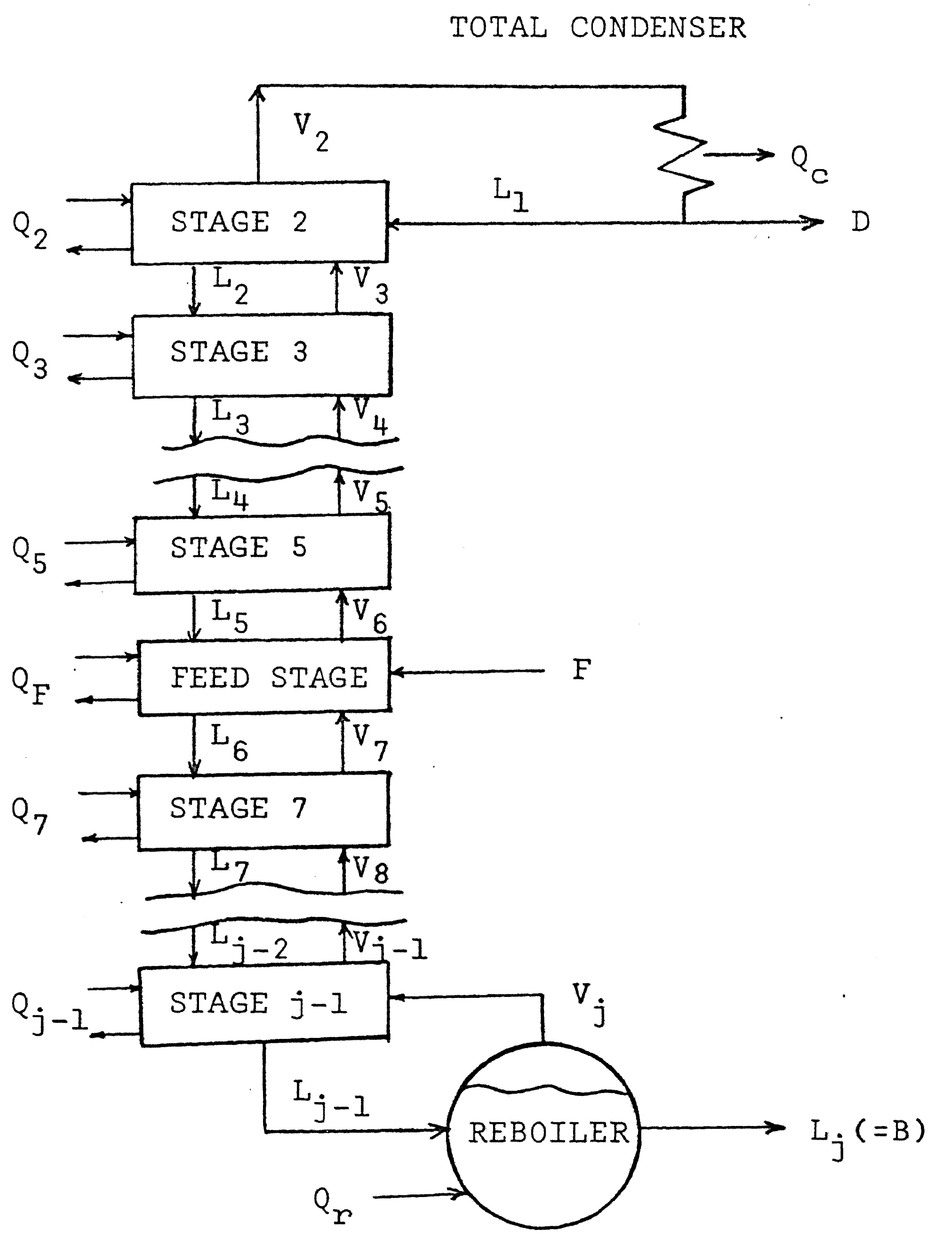


Figure 4.1 Distillation Column Containing J Equilibrium Stages

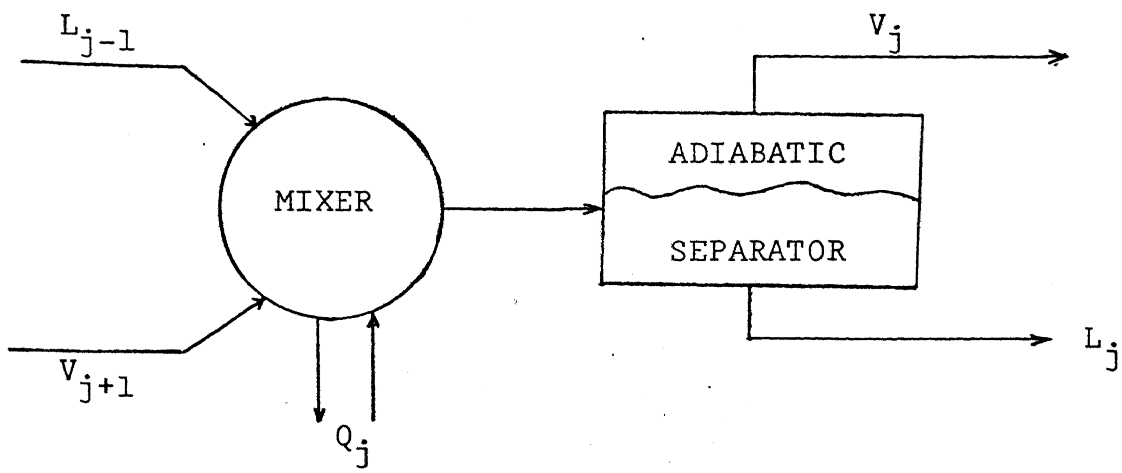


Figure 4.2 Operational Representation of a Single Contacting Stage j

A1. Condenser

There is one inlet stream and two outlet streams around the total condenser (Figure 4.5). The feed to the condenser is a one-phase system possessing (C + 1) degrees of freedom. Since the reflux and distillate are each one-phase systems of identical composition and condition, they account together for a total of (C + 1) degrees of freedom. There are two quantity ratios and one heat ratio (with one quantity ratio fixed at unity) corresponding to the three streams. Therefore the total number of variables associated with the condenser is 2C + 5. There are C component material balances and one enthalpy balance; thus the number of independent variables is C + 4.

A2. Single Stage (Excluding Feed Stage)

It is assumed that the two streams leaving any plate are in equilibrium and therefore constitute a two-phase, thermodynamic equilibrium system (Figure 4.3). This two-phase system and the two one-phase streams entering each plate possess a total of (3 C + 2) degrees of freedom. Associated with each plate are four quantity ratio variables and one heat ratio variable. The total number of independent intensive variables, quantity ratios, and heat ratio then becomes:

(3 C + 2) independent thermodynamic intensive variables + 4 quantity ratios + 1 heat ratio.

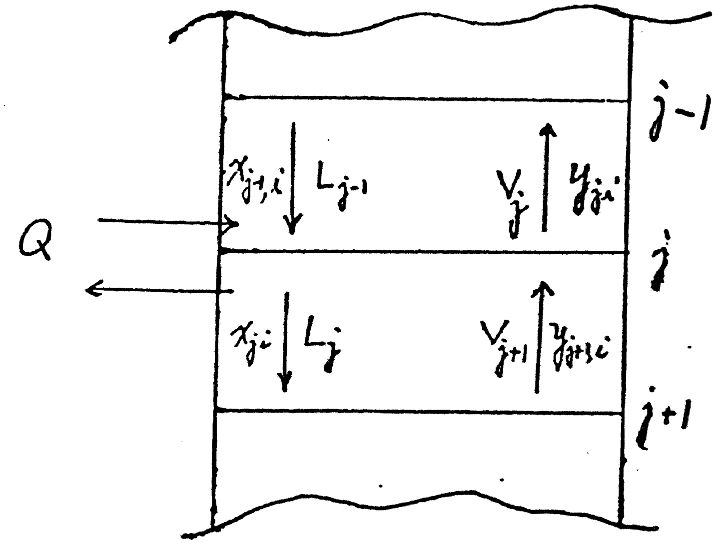


Figure 4.3 Operational Representation of Single Stage j in a Distillation Column with T_j, and x_{ji} Fixed by Experiment

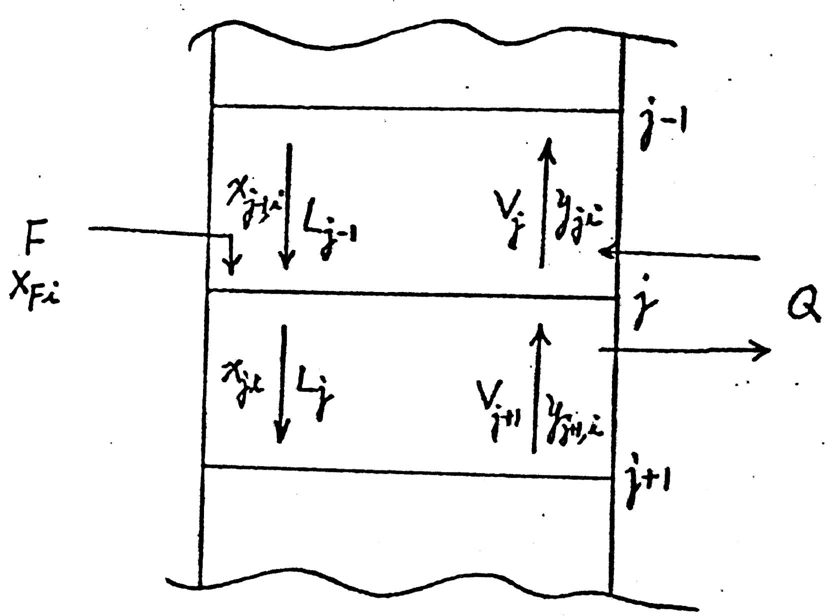


Figure 4.4 Operational Representation of Feed Stage in a Distillation Column with T_j, x_{ji} F, and x_{Fi} Fixed by Experiment

Relating these variables are a total of C independent material balances and one independent enthalpy balance. Besides, one quantity ratio is fixed at unity. Therefore the total number of degrees of freedom is 2 C + 5.

A3. Feed Stage

Since there are three one-phase streams entering the feed stage, and one two-phase stream leaving in equilibrium (Figure 4.4), with one quantity ratio fixed at unity, the number of independent intensive variables and quantity ratios associated with this plate is:

3(C + 1) independent intensive variables in feed streams + C independent intensive variables in equilibrium exit streams + 5 quantity ratios + 1 heat ratio -1 quantity ratio fixed at unity.

There are C independent material balances and one enthalpy balance, therefore the total number of independent variables is 3 C + 7.

A4. Reboiler

A single one-phase stream is entering the reboiler, and two streams in equilibrium with each other are leaving the reboiler (Figure 4.6). By the "Phase Rule", these streams together possess (2 C + 1) independent intensive variables. Also associated with the reboiler are three quantity ratios and one heat ratio, making a total of 2 C + 5.

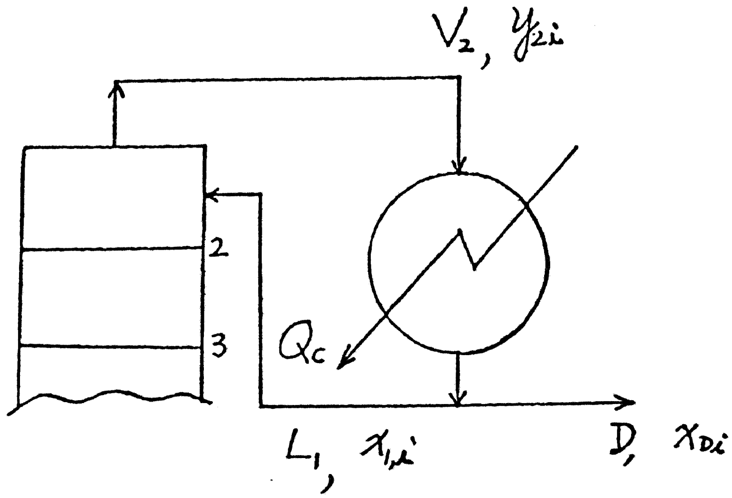


Figure 4.5 Operational Representation of Total Condenser in a Distillation Column with T_D, x_{Di}, D, L_1, and x_{1i} Fixed by Experiment

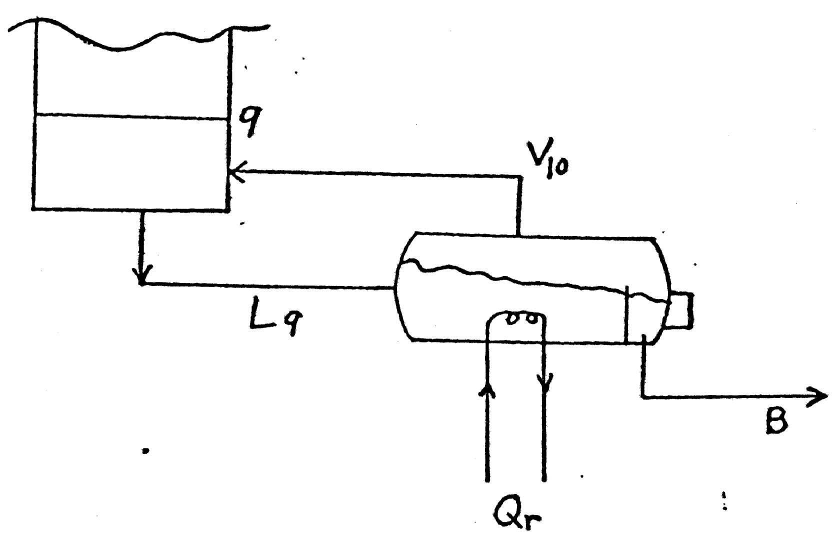


Figure 4.6 Operational Representation of Partial Reboiler in a Distillation Column with B, T_B, x_{Bi} and Q_r Fixed by Experiment

Relating these variables are C independent material balances and one independent enthalpy balance. Therefore the total number of independent variables is C + 1.

B. Vapor Composition and Internal Flow Rates

For an experimental run on the distillation tower (described in Appendix C) the reboiler duty, the reflux rate, and the bottoms product rate are controllable and are maintained at specified values. The feed composition is determined by the make-up of the particular mixture chosen for a run and placed in the feed tank. The feed temperature is specified and is controlled by adjusting a feed preheater. During the run the tray temperatures may be recorded from the column instruments (with the exception of the second stage or top tray) and samples may be withdrawn from each internal overflow stream. The composition of the internal overflow streams is determined from the analysis of these samples.

For a complete column description each variable which may be specified or determined from operational data reduces the required number of equations by one. The remaining equations for this column may be developed from heat and/or material balances written around the condenser, the reboiler, and around each tray of the column. Modifications of the general tray balances are required for the feed tray and for the first tray. The special approach to the first tray is necessary to determine its operating temperature which is not available from recorded data.

B1. Total Condenser

As analyzed in Section A1, the number of independent variables for the total condenser is C + 4. The experimental data specify (C - 1) compositions, the distillate rate, the reflux rate, the stage temperature, and the stage pressure. Therefore only one equation is left to determine the condenser duty. It is readily solved, because an enthalpy balance around the whole distillation tower states:

$$Q_C = F\ h_F + Q_R - B\ h_B - D\ h_D \tag{B.1}$$

This condenser duty is calculated by the programs referred to in block 3 of Figure 4.7, the flow chart for the computer program.

B2. Calculation of Second Stage Temperature

Because there is no thermocouple on the second stage of the experimental column used, a special calculation must be made to determine its operating temperature before an efficiency calculation is made. There are (C + 4) independent variables around the total condenser. The experimental data specify (C + 3) variables, such as (C - 1) compositions, the distillate rate, the reflux rate, the stage temperature, and the stage pressure. An enthalpy balance equation around the total condenser can be used to solve for the enthalpy of the vapor stream leaving the second stage. It states

$$H_2 = \frac{L_1 h_1 + D\, h_D + Q_C}{L_1 + D}$$

or

$$H_2 = \frac{(R \cdot D) h_1 + D\, h_D + Q_C}{(R \cdot D) + D} \tag{B2.1}$$

These enthalpies, calculated from tower composition data, are determined by the programs shown in block 4 of Figure 4.7, the flow chart for the computer program.

The enthalpies of the reflux and of the distillate are equal to each other. The reflux was neither heated nor cooled before it entered the second stage. If the enthalpy is a function of temperature alone, a fourth order algebraic equation must be solved to determine the stage temperature. This equation could be solved by using either the Newton or the False Position Method(9) to obtain accurate temperature. This equation states

$$H_2 = \sum_{i=1}^{C} H_{2i} y_{2i}, \quad \text{where } H_{2i}^{\frac{1}{2}} = l_{1i} + l_{2i} T_2 + l_{3i} T_2^{\,2}$$

$$\therefore H_2 = \Sigma l_{1i}^{\,2} y_{2i} + \Sigma (2 l_{1i} l_{2i}) y_{2i} T_2 + \Sigma (2 l_{1i} l_{3i} + l_{2i}^{\,2}) y_{2i} T_2^{\,2}$$

$$+ \Sigma (2 l_{2i} l_{3i}) y_{2i} - T_2^{\,3} + l_{3i}^{\,2} y_{2i} T_2^{\,4}$$

$$= A + B\, T_2 + C\, T_2^{\,2} + D\, T_2^{\,3} + F\, T_2^{\,4} \tag{B2.2}$$

The vapor composition of the second stage is the same as that of the first stage, and is also identical with the liquid composition on the first stage. The total condenser causes only a phase change in the stream. A, B, C, D, and F are all calculated constants, which stand for the product of enthalpy coefficients and vapor composition of the second stage. These are all known values as shown in Equation (B2.2).

The iterative procedure required to determine the temperature of the second stage is referred to in block 5 of Figure 4.7. It includes the following steps:

1. The estimated second stage temperature is first calculated from experimental first and third stage temperature.
2. The second stage temperature estimated in Step 1 is used to calculate the estimated enthalpy.
3. The estimated enthalpy value is compared with the correct enthalpy value calculated in Step (b). If $\left|(H_2)_{estimated} - (H_2)_{correct}\right| < \varepsilon$, the second stage temperature has been determined.
4. If the test condition is not met, return to Step 2, using the revised value for the stage temperature.

B3. Single Stage Equations

As analyzed in Section A2, the total number of independent variables for each stage is 2 C + 5. The experimental data determine (C - 1) liquid compositions, $x_{j-1,i}$, the stage temperature, T_{j-1}, and the stage pressure, P_{j-1}. The liquid overflow from the tray above, L_{j-1}, is determined prior to solving the balances for tray j. Similarly, for the liquid stream leaving the stage j, the experimental data determine (C - 1) liquid compositions, x_{ji}, the stage temperature, T_j, and the stage pressure, p_j. Therefore C variables remain to be solved by two equations around stage j. There are C component material balances around stage j and one enthalpy balance around stage j.

The component material balance equation is used to solve for the composition of the entering vapor stream, $y_{j+1,i}$. The enthalpy balance equation is used to solve for the flow rate of leaving liquid stream, L_j. These equations are stated as follows:

(1) A component material balance equation around stage j states

$$y_{j+1,i} = \frac{L_j x_{ji} - L_{j-1} x_{j-1,i} + (L_{j-1} + D - F) y_{ji}}{L_j + D - F} \quad \text{(B3.1)}$$

(2) An enthalpy balance equation around stage j states

$$L_j = \frac{L_{j-1}(H_j - h_{j-1}) + D(H_j - H_{j+1}) + F(H_{j+1} - H_j)}{H_{j+1} - h_j} \quad \text{(B3.2)}$$

(3) An overall material balance equation around the section which encompasses the stage j and the total condenser states

$$V_j = L_{j-1} + D - F \quad \text{(B3.3)}$$

For the rectifying section, F should be zero in Equation (B3.3). By stage-to-stage calculation from the top of the distillation tower down to the reboiler, Equation (B3.1) determines the vapor composition of the entering stream, $y_{j+1,i}$, while Equation (B3.2) is used to calculate the flow rate of leaving liquid stream, L_j. These C + 1 independent equations may be solved simultaneously to determine the values of the C + 1 unknown variables. The nature of these equations is such that an iterative procedure must be used to solve them.

An iterative procedure for each stage is required to determine $y_{j+1,i}$, and L_j.

1. Beginning with stage 2, L_j is assumed to be equal to L_{j-1}, which may be obtained from experimental data. This step is taken in block 6 of Figure 4.7.
2. In block 10 it is shown that the initial value for each $y_{j+1,i}$, is set at the value determined for y_{ji}.
3. Equation (B3.1) is solved for $y_{j+1,i}$ as shown in block 11A of Figure 4.7.
4. Equation (B3.2) is solved for L_j, using the values of $y_{j+1,i}$ calculated in Step 3. This enthalpy balance is included in blocks 13A and 13B of Figure 4.7.
5. Equation (B3.3) is solved for V_j, using the value of L_{j-1}, calculated in Step 4. This overall material balance is shown in blocks 9A and 9B of Figure 4.7.

6. The values of the $y_{j+1,i}$ are compared with the previous (or estimated) values. This action is shown in blocks 14A and 14B of Figure

If $\left|(y_{j+1,i})_{revised} - (y_{j+1,i})_{estimated}\right| < \varepsilon$, the solutions for this stage have been determined. The calculations for the next stage should be initiated as shown in blocks 15 and 16 of Figure 4.7. If the test conditions are not met, control is returned to Step 2, (block 11A), and new trial values are calculated for L_j and the $y_{j+1,i}$'s.

B4. <u>The Feed Stage</u>

The feed stage has (3 C + 7) independent variables as analyzed in Section A3. The experimental data specify (C + 2) variables for the entering liquid stream, and the feed stream respectively. The leaving liquid stream is specified by (C + 1) known variables such as (C - 1) liquid compositions, the stage temperature, and the stage pressure. Therefore two unknown variables are left to be solved for by two equations around this stage. The component material balance equation is used to solve the composition of entering vapor stream, $y_{j+1,i}$. The enthalpy balance equation is used to solve for the flow rate of leaving liquid stream, L_j. These equations are mathematically expressed as follows:

(1) A component material balance equation around feed stage states

$$y_{j+1,i} = \frac{L_j x_{ji} - L_{j-1} x_{j-1,i} + (L_{j-1} + D - F) y_{ji} - FX_{Fi}}{L_j + D - F}$$

(B4.1)

(2) An enthalpy balance equation around feed stage states

$$L_j = \frac{L_{j-1}(H_j - h_{j-1}) + D(H_j - H_{j+1}) + F(H_{j+1} - H_j - h_F)}{H_{j+1} - h_j}$$

(B4.2)

(3) An overall material balance equation around the section which emcompasses the feed stage and the total condenser states

$$V_j = L_{j-1} + D \qquad \text{(B4.3)}$$

As explained in Section B3, the Equation (B4.1) expresses $y_{j+1,i}$ as a function of L_j, and the Equation (B4.2) expresses L_j as a function of $y_{j+1,i}$. An iterative procedure is required to solve for these three unknown variables.

The iterative procedure for the feed stage is outlined in the following steps:

1. L_j is equal to the sum of the feed rate and the liquid rate leaving the stage immediately above the feed. The latter value is available from earlier calculations in the rectifying section.
2. Equation (B4.1) is solved for $y_{j+1,i}$.
3. Equation (B4.2) is solved for L_j, using the values of $y_{j+1,i}$ calculated in Step 2.
4. Equation (B4.3) is solved for V_j, using the value of L_{j-1} calculated in Step 3.

5. The values of the $y_{j+1,i}$ are compared with the previous (or estimated) values. If $\left|(y_{j+1,i})_{revised} - (y_{j+1,i})_{estimated}\right| < \varepsilon$, this stage is solved.

If the test conditions are not met, return to Step 2, using the revised value for the L_j.

B5. <u>The Reboiler</u>

The reboiler possesses (C + 1) independent variables as analyzed in Section A4. The experimental data specify (C - 1) bottoms compositions, x_{Bi}, the bottoms rate, and the bottoms temperature. Therefore the reboiler is fixed by experimental data. Solution of the heat and material balances written around the reboiler would therefore yield no new information.

C. Efficiency Calculations

As described in Section B3 and B4, the vapor compositions and stream flow rates can be calculated from experimental data by iterative procedures. Once all of the vapor compositions have been determined the plate efficiency may be calculated. They are mathematically expressed as follows:

Modified Murphree Plate Efficiency(9)

$$E_{ji}^{M} = \frac{y_{ji} - y_{j+1,i}}{Y_{ji} - y_{j+1,i}} \tag{C.1}$$

Vapc ·ization Efficiency(9)

$$E_{ji}^{V} = \frac{y_{ji}}{Y_{ji}} \tag{C.2}$$

Where Y_{ji} is ideal vapor compositions which would be in ıuilibrium with liquid, and is mathematically expressed as ›llows:·

$$Y_{ji} = K_{ji} * x_{ji} (9)$$

D. Model Validation

The calculational model developed in Section B is tested .th hydrocarbon and non-hydrocarbon systems on a hypotheti- ıl simulated distillation tower with component efficiencies :t equal to unity. For a third trial system, the efficien- .es for the non-hydrocarbon case were given random values. .e hypothetical distillation towers have the same number of grees of freedom as the experimental tower, and the oper- ing conditions are arbitrarily specified. The calculated por compositions and the stream flow rates are both within e desired accuracy when compared to the known data taken om the hypothetical tower. Three test problems are shown Table 4.1, Table 4.2, and Table 4.3. The calculated sults are compared to the standard values in Table 4.4, ble 4.5, and Table 4.6.

The method used to simulate the above columns was the -method of convergence for a conventional column" proposed by Holland(9). The input known variables include feed rate, distillate rate, bottoms rate, external reflux ratio, feed compositions, feed temperature, assumed vaporization efficiencies, assumed temperature profile, assumed vapor and liquid stream flow rates. The outputs from the simulation program are correct temperature profile, vapor and liquid stream flow rates, vapor and liquid compositions, condenser duty, and reboiler duty when θ converge to unity.

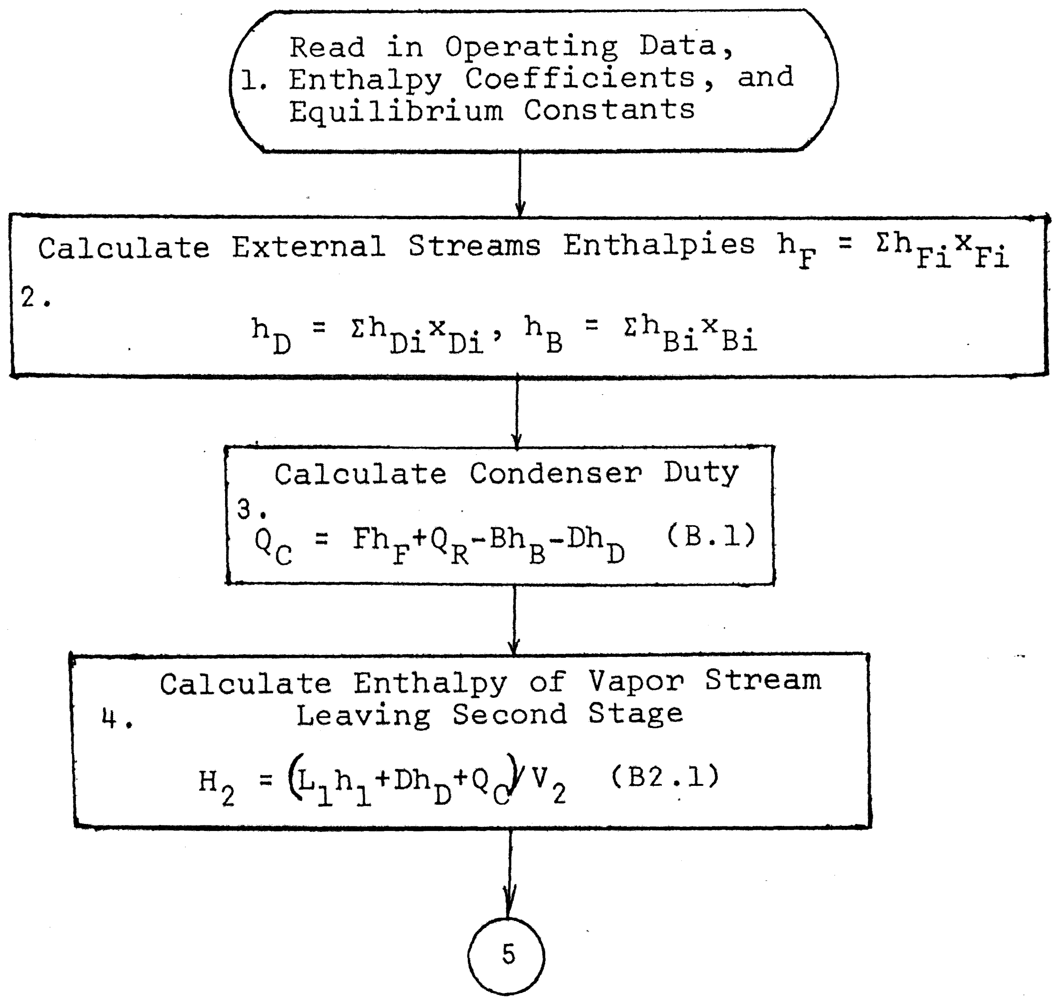
The simulation program as well as the program used for efficiency calculations is given in Appendix E.

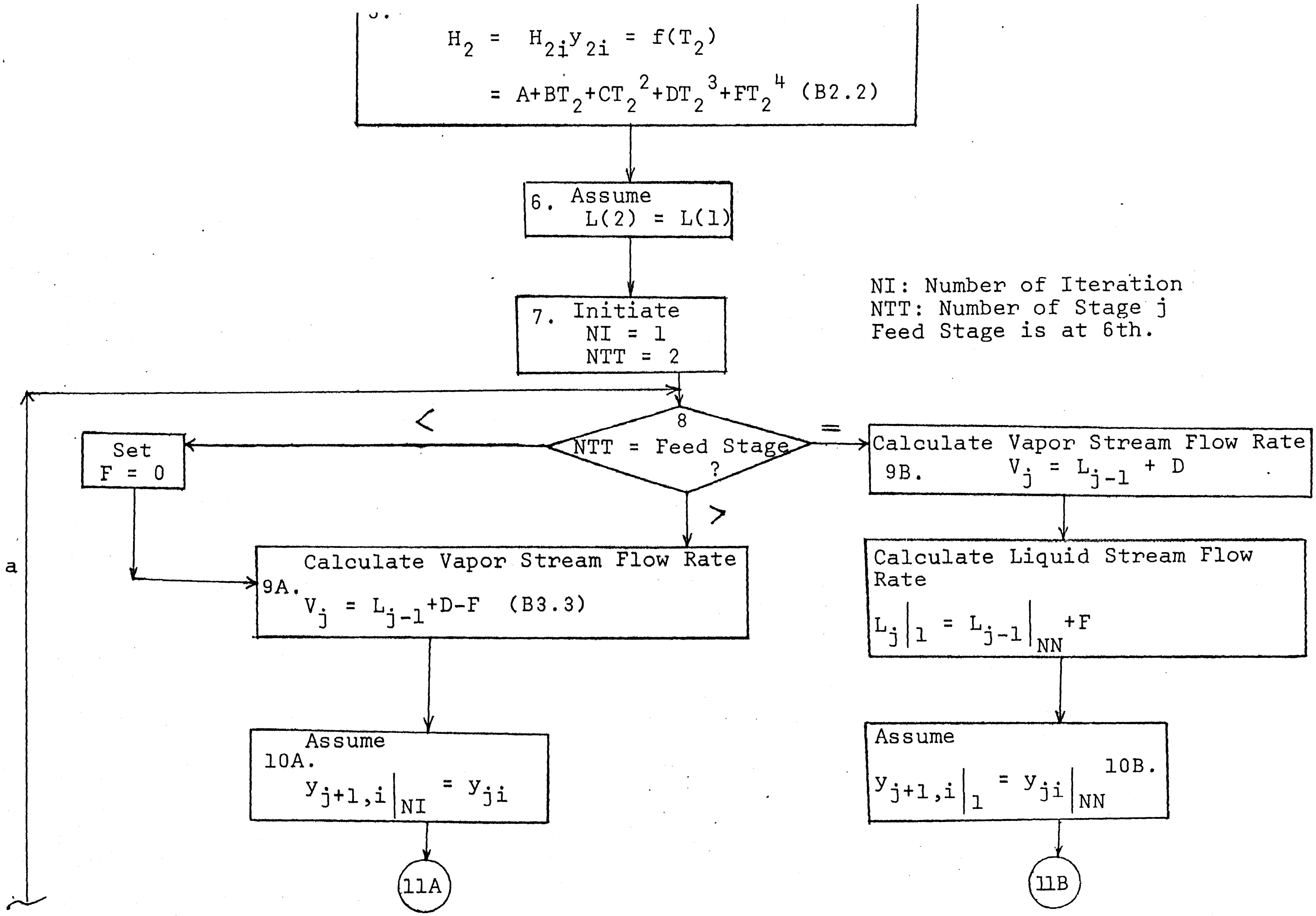
E. Application to Experimental Data

This method of calculating distillation efficiencies was also applied to experimental data obtained on a laboratory distillation column. The column characteristics and operating procedures used are given in Appendix C. Since there is no way of experimentally checking the efficiencies at various points in the column without measurement of vapor compositions, which was not feasible in the runs made, the application to experimental data does not verify the methods developed. However, it does provide an example of the potential use of the methods. This example can be partially verified by the use of the obtained efficiencies in a distillation simulation program, to see if calculated performance matches the experimental data used to determine efficiencies. The results of the efficiency calculations from experimental data are given in Tables 4.7 to 4.10. The simulation results using calculated efficiencies are in Table 4.11.

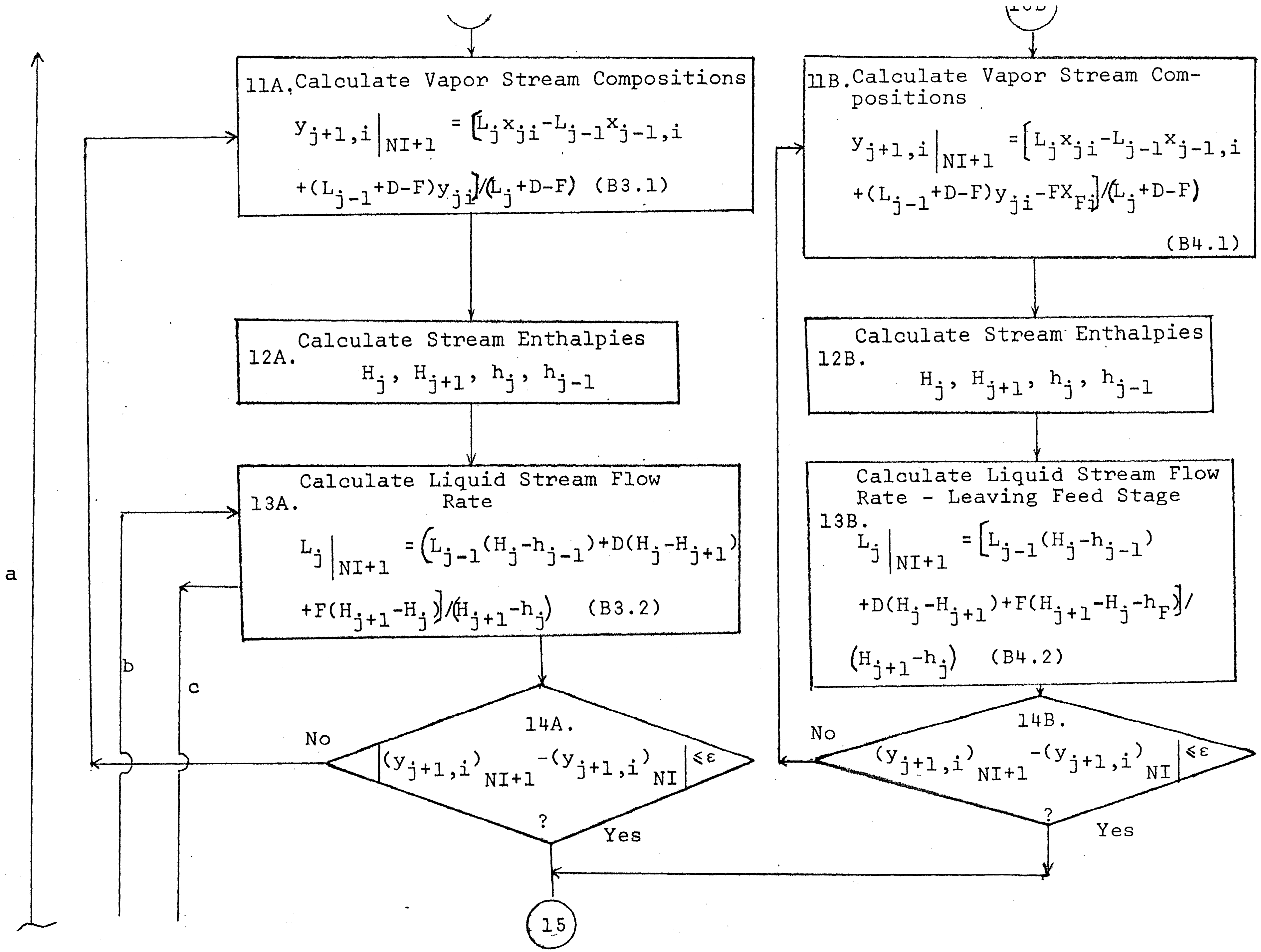
Figure 4.7

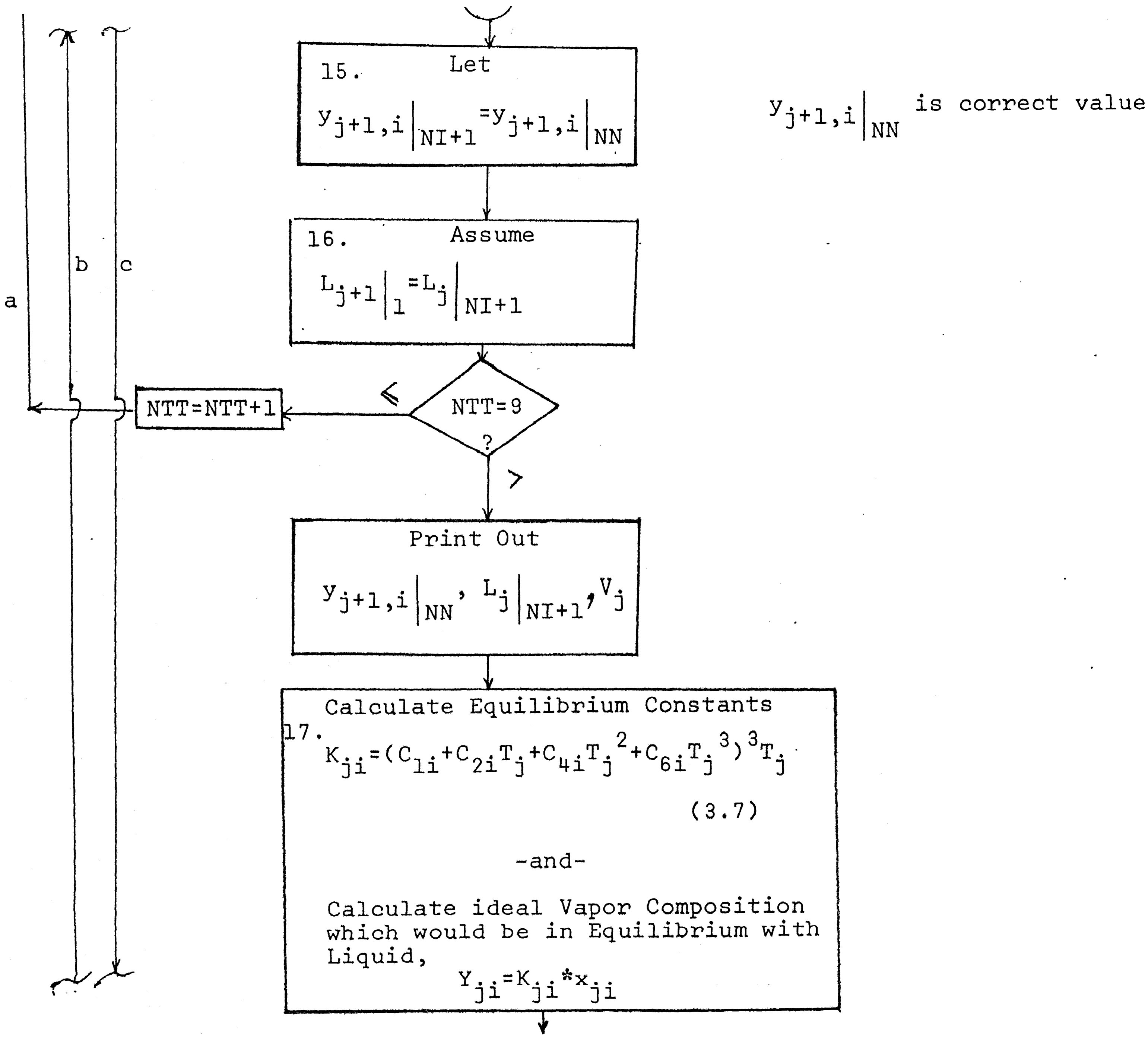
Flow Chart for the Efficiency Calculation





5.
$H_2 = H_{2i}y_{2i} = f(T_2)$
$= A+BT_2+CT_2^2+DT_2^3+FT_2^4$ (B2.2)
6. Assume
L(2) = L(1)
7. Initiate
NI = 1
NTT = 2
NI: Number of Iteration
NTT: Number of Stage j
Feed Stage is at 6th.
8
NTT = Feed Stage ?
<
=
>
Set
F = 0
Calculate Vapor Stream Flow Rate
9B. $V_j = L_{j-1} + D$
Calculate Vapor Stream Flow Rate
9A. $V_j = L_{j-1}+D-F$ (B3.3)
Calculate Liquid Stream Flow Rate
$L_j|_1 = L_{j-1}|_{NN} + F$
a
Assume
10A. $y_{j+1,i}|_{NI} = y_{ji}$
Assume
$y_{j+1,i}|_1 = y_{ji}|_{NN}$ 10B.
11A
11B


11A. Calculate Vapor Stream Compositions
$y_{j+1,i}\Big|_{NI+1} = \left[L_j x_{ji} - L_{j-1} x_{j-1,i} + (L_{j-1}+D-F) y_{ji}\right] / (L_j+D-F)$ (B3.1)
12A. Calculate Stream Enthalpies
$H_j,\ H_{j+1},\ h_j,\ h_{j-1}$
13A. Calculate Liquid Stream Flow Rate
$L_j\Big|_{NI+1} = \left[L_{j-1}(H_j - h_{j-1}) + D(H_j - H_{j+1}) + F(H_{j+1} - H_j)\right] / (H_{j+1} - h_j)$ (B3.2)
14A.
$\left|(y_{j+1,i})_{NI+1} - (y_{j+1,i})_{NI}\right| \leq \varepsilon$
?
No
Yes
a
b
c
11B. Calculate Vapor Stream Compositions
$y_{j+1,i}\Big|_{NI+1} = \left[L_j x_{ji} - L_{j-1} x_{j-1,i} + (L_{j-1}+D-F) y_{ji} - FX_{Fj}\right] / (L_j+D-F)$
(B4.1)
12B. Calculate Stream Enthalpies
$H_j,\ H_{j+1},\ h_j,\ h_{j-1}$
13B. Calculate Liquid Stream Flow Rate - Leaving Feed Stage
$L_j\Big|_{NI+1} = \left[L_{j-1}(H_j - h_{j-1}) + D(H_j - H_{j+1}) + F(H_{j+1} - H_j - h_F)\right] / (H_{j+1} - h_j)$ (B4.2)
14B.
$\left|(y_{j+1,i})_{NI+1} - (y_{j+1,i})_{NI}\right| \leq \varepsilon$
?
No
Yes
15


15. Let
$y_{j+1,i}\big|_{NI+1} = y_{j+1,i}\big|_{NN}$
$y_{j+1,i}\big|_{NN}$ is correct value
16. Assume
$L_{j+1}\big|_{1} = L_j\big|_{NI+1}$
a
b
c
NTT=NTT+1
NTT=9 ?
≤
>
Print Out
$y_{j+1,i}\big|_{NN},\ L_j\big|_{NI+1}, V_j$
Calculate Equilibrium Constants
17. $K_{ji} = (C_{1i} + C_{2i}T_j + C_{4i}T_j^2 + C_{6i}T_j^3)^3 T_j$
(3.7)
-and-
Calculate ideal Vapor Composition which would be in Equilibrium with Liquid,
$Y_{ji} = K_{ji} * x_{ji}$

17

18. Calculate Vaporization Efficiency (VE)

$$E_{ji}^{O} = y_{ji}/Y_{ji} \qquad (C.2)$$

-and-

Murphree Plate Efficiency (PE)

$$E_{ji}^{M} = (y_{ji}-y_{j+1,i})/(Y_{ji}-y_{j+1,i}) \qquad (C.1)$$

STOP

b

c

Function Subprogram Calculate Stream Enthalpies

$H_j = \Sigma H_{ji} y_{ji}$, $h_j = \Sigma h_{ji} x_{ji}$ etc.

Table 4.1

Statement of Numerical Test for Calculational Procedure on Hydrocarbon System with Efficiency Equals to Unity

Specifications

Component	Component Feed Rate Lb.Mole/Hr.	Feed Comp. Mole Frac.
Propane	33	0.33
N-Butane	33	0.33
N-Pentane	34	0.34

Feed Rate = 100 Lb.Mole/Hr.

Distillate Rate = 50 Lb.Mole/Hr.

Bottoms Rate = 50 Lb.Mole/Hr.

Reflux Rate = 100 Lb.Mole/Hr.

Boiling Point Liquid Feed,

Total Condenser, Ten Stages

Including the Reboiler,

Distillation Column Pressure = 300 psia

The Equilibrium Data and Enthalpy

Data are Given in Table A-4 and Table A-8 of Ref. (9)

Data for Distillation Plate Efficiencies Calculations

Stage Number	T °R	Liquid Comp. Mole Frac.		
		$N-C_3$	$N-C_4$	$N-C_5$
1.(Condenser)	625.3027	0.6418696	0.3517753	0.0063547
2.	648.7966*	0.4191279	0.5567314	0.0241408
3.	665.8925	0.2875983	0.6564091	0.0559927
4.	677.3037	0.2211437	0.6727295	0.1061264
5.	686.2082	0.1880474	0.6348891	0.1770635
6.	694.6486	0.1698862	0.5650709	0.2650431
7.(Feed)	703.0651	0.1581966	0.4831434	0.3586599
8.	721.0854	0.0872821	0.4741603	0.4385577
9.	738.7072	0.0427546	0.4104019	0.5468435
10.(Reboiler)	756.0747	0.0181301	0.3082241	0.6736456

Miscellaneous Data:

Condenser Duty = 1039340 BTU/Lb.Mole

Feed Temperature = 676.4080°R

*Calculated

Specifications		
Component	Component Feed Rate Lb.Mole/Hr.	Feed Comp. Mole Frac.
Water	1.91983	0.5625
Methanol	1.27193	0.3725
Acetone	0.22301	0.0650

Feed Rate = 3.41 Lb.Mole/Hr.

Distillate Rate = 1.12 Lb. Mole/Hr.

Bottoms Rate = 2.29 Lb.Mole/ Hr.

Reflux Rate = 1.570 Lb.Mole/ Hr.

Boiling Point Liquid Feed

Total Condenser, Eight Trays

Reboiler, Distillation

Column Pressure Maintained at

One Atmosphere.

Data for Distillation Plate Efficiencies Calculations				
		Liquid Comp. Mole Frac.		
Stage Number	T °R	Water	Methanol	Acetone
1.(Condenser)	599.65280	0.0104540	0.8189646	0.1705809
2.	601.91650*	0.0424265	0.8285156	0.1290581
3.	603.76870	0.1098638	0.7847897	0.1053467
4.	608.20230	0.2275898	0.6847721	0.0876387
5.	614.63350	0.3805187	0.5477149	0.0717667
6.(Feed)	621.45190	0.5200827	0.4210669	0.0588508
7.	622.97260	0.5463138	0.4040496	0.0496366
8.	626.26070	0.6028088	0.3585168	0.0386741
9.	632.60740	0.7032492	0.2708313	0.0259201
10.(Reboiler)	642.15470	0.8324966	0.1541414	0.0133622

Enthalpy Equations:

Water

$$h^{\frac{1}{2}} = -0.55510291\times10^{3}+0.17535334\times10T-0.12486742\times10^{-2}T^{2}$$

$$H^{\frac{1}{2}} = 0.12375660\times10^{3}+0.32756421\times10^{-1}T-0.31256958\times10^{-5}T^{2}$$

Methanol

$$h^{\frac{1}{2}} = -0.53609748\times10^{3}+0.16521566\times10T-0.11176039\times10^{-2}T^{2}$$

$$H^{\frac{1}{2}} = 0.10984052\times10^{3}+0.31790598\times10^{-1}T+0.10287539\times10^{-4}T^{2}$$

Acetone

$$h^{\frac{1}{2}} = -0.63942181\times10^{3}+0.19733626\times10T-0.13442990\times10^{-2}T^{2}$$

$$H^{\frac{1}{2}} = 0.85837260\times10^{2}+0.57459815\times10^{-1}T+0.18562340\times10^{-4}T^{2}$$

Miscellaneous Data: Condenser Duty = 38855.80 BTU/Lb.Mole -- Feed Temp. = 623.5840°R

*Calculated

Table 4.3

Statement of Numerical Test for Calculational Procedure on Non-Hydrocarbon System with Made-up Random Efficiency

Specifications			Data for Distillation Plate Efficiencies Calculations				
					Liquid Compositions Mole Frac.		
Component	Component Feed Rate Lb.Mole/Hr.	Feed Comp. Mole Frac.	Stage Number	T ^{o}R	Water	Methanol	Acetone
Water	1.9198	0.5625	1.(Condenser)	599.0292	0.0002508	0.8067961	0.1929532
Methanol	1.2719	0.3725	2.	615.7465*	0.0021573	0.8867980	0.1110455
Acetone	0.2230	0.0650	3.	601.3769	0.0153424	0.8944494	0.0902090
			4.	623.8000	0.401418	0.9171325	0.0427262
			5.	605.0327	0.1389493	0.8169599	0.0440916
			6.(Feed)	621.8903	0.4470339	0.5226896	0.0302764
			7.	625.9306	0.4785022	0.5086399	0.0128580
			8.	631.5791	0.5541156	0.4361750	0.0097092
			9.	647.0654	0.7092515	0.2859765	0.0047718
			10.(Reboiler)	642.7292	0.8374869	0.1600931	0.0024204

Feed Rate = 3.41 Lb.Mole/Hr.

Distillate Rate = 1.12 Lb. Mole/Hr.

Bottoms Rate = 2.29 Lb.Mole/ Hr.

Reflux Rate = 1.57 Lb.Mole/Hr.

Boiling Point Liquid Feed, Total Condenser, Eight Trays, Reboiler, Distillation Column Pressure Maintained at One Atmosphere

*Calculated

Table 4.4

Calculated Values Compared to the Standard Values from Table 4.1

Basic Distillation Programs									
Stage	Temp.	Vapor Composition			Stream Flow Rates		E_{ji}^{o}		
		Propane	N-Butane	Pentane	V_j	L_j	Propane	N-Butane	Pentane
1	625.3027	0.6418698	0.3517755	0.0063547	50.0000	100.0000	1.000	1.000	1.000
2	648.7983	0.6418697	0.3517756	0.0063547	150.0000	95.96486	1.000	1.000	1.000
3	665.8925	0.4954266	0.4865251	0.0180483	145.9648	94.54015	1.000	1.000	1.000
4	677.3037	0.4101477	0.5510303	0.0388219	144.5401	92.71796	1.000	1.000	1.000
5	686.2082	0.3685405	0.5602869	0.0711726	142.7179	89.99084	1.000	1.000	1.000
6	694.6486	0.3501378	0.5337700	0.1160921	139.9908	86.85050	1.000	1.000	1.000
7	703.0651	0.3422057	0.4871968	0.1705974	136.9505	190.19420	1.000	1.000	1.000
8	721.0854	0.2081496	0.5455264	0.2463239	140.1940	183.8103	1.000	1.000	1.000
9	738.7072	0.1113243	0.5318516	0.3568240	143.8101	197.1968	1.000	1.000	1.000
10	756.0747	0.0511190	0.4451094	0.5037717	147.1967	50.0000	1.000	1.000	1.000

Efficiency Calculations Program								
Stage	Vapor Compositions			Stream Flow Rates		E_{ji}^{o}		
	Propane	N-Butane	Pentane	V_j	L_j	Propane	N-Butane	Pentane
1	0.6418696	0.3517753	0.00 3547	50.0000	100.0000	1.0000000	1.0000000	1.0000000
2	0.6418696	0.3517753	0.0063547	150.0000	95.96351	0.9998480	1.0000460	0.9999993
3	0.4954287	0.4865229	0.0180481	145.963500	94.53936	1.0001160	1.0000010	1.0000000
4	0.4101505	0.5510275	0.0388215	144.5398	92.71931	0.9999758	0.9999865	1.0000000
5	0.3685406	0.5602860	0.0711725	142.7173	89.98828	0.9999653	0.9999916	1.0000000
6	0.3501389	0.5337690	0.1160913	139.9900	86.94805	1.0000110	0.9999989	1.0000000
7	0.3422066	0.4871963	0.1705961	136.9491	190.19120	1.0002520	1.0000130	0.9999930
8	0.2081517	0.5455278	0.2463197	140.1930	193.81480	0.9999537	0.99991702	1.0000270
9	0.1113243	0.5318531	0.3568208	143.80890	197.1933	0.9999134	0.9999738	1.0000620
10	0.0511184	0.4451065	0.5037737	147.19330	50.0000	0.9999134	0.9999957	1.0000620

Table 4.5

Calculated Values Compared to the Standard Values from Table 4.2

Stage	Temp.	Basic Distillation Programs							
		Vapor Compositions			Stream Flow Rates		E_{ji}^{o}		
		Water	Methanol	Acetone	V_j	L_j	Water	Methanol	Acetone
1	599.6528	0.0104540	0.8189655	0.1705808	1.12000	1.56800	1.000	1.000	1.000
2	601.2329	0.0104540	0.8189653	0.1705809	2.68800	1.54645	1.000	1.000	1.000
3	603.7687	0.0289969	0.8245041	0.1464992	2.66645	1.51694	1.000	1.000	1.000
4	608.2023	0.0676403	0.7993056	0.1330544	2.63694	1.47540	1.000	1.000	1.000
5	614.6335	0.1338882	0.7426812	0.1234310	2.59540	1.42965	1.000	1.000	1.000
6	621.4519	0.2179581	0.6668689	0.1151734	2.54965	4.82549	1.000	1.000	1.000
7	622.9726	0.2379199	0.6621458	0.0999346	2.53549	4.79868	1.000	1.000	1.000
8	626.2607	0.2850776	0.6321739	0.0827488	2.50868	4.74909	1.000	1.000	1.000
9	632.6074	0.3889150	0.5488397	0.0622456	2.45909	4.67205	1.000	1.000	1.000
10	642.1547	0.5789950	0.3830125	0.0379926	2.38205	2.29000	1.000	1.000	1.000

Stage	Efficiency Calculations Programs							
	Vapor Compositions			Stream Flow Rates		E_{ji}^{o}		
	Water	Methanol	Acetone	V_j	L_j	Water	Methanol	Acetone
1	0.0104540	0.8189646	0.1705809	1.119999	1.567998	1.00000	1.00000	1.00000
2	0.0104540	0.8189646	0.1705809	2.6879980	1.5505620	0.9696383	0.9862729	0.9824863
3	0.0290176	0.8245099	0.1464722	2.6705620	1.5185660	0.9999918	0.9997904	0.9997186
4	0.0676670	0.7992957	0.1330367	2.6385660	1.4769850	0.9999804	0.9998898	0.9998467
5	0.1339458	0.7426450	0.1234090	2.5969850	1.4312020	0.9999147	0.9998083	0.9997249
6	0.2180570	0.6667953	0.1151468	2.5512030	4.8309860	0.9997369	0.9997764	0.9996689
7	0.2378564	0.6609544	0.0993092	2.5409820	4.8041310	0.9957421	0.9937279	0.9899784
8	0.2849659	0.6309986	0.0821343	2.5141420	4.7545360	0.9952991	0.9925786	0.9864598
9	0.3886942	0.5477256	0.0616398	2.4645260	4.6774120	0.9933385	0.9902653	0.9756176
10	0.5785592	0.3820444	0.0373941	2.3874130	2.2899990	0.9933385	0.98425 4	0.9756176

Table 4.6

Calculated Values Compared to the Standard Values from Table 4.3

Basic Distillation Programs										
Stage	Temp.	Vapor Compositions			Stream Flow Rates		E_{ji}^{o}			
		Water	Methanol	Acetone	V_j	L_j	Water	Methanol	Acetone	
1	599.0292	0.0002508	0.8067966	0.1929530	1.12000	1.56800	1.000	1.000	1.000	
2	615.7465	0.0002508	0.8067967	0.1929531	2.68800	1.64582	0.321	0.654	0.989	
3	601.3769	0.0013853	0.8544015	0.1442136	2.76582	1.52863	0.365	0.963	1.206	
4	623.8000	0.0089607	0.8573837	0.1336559	2.64863	1.63155	0.502	0.560	1.530	
5	605.0327	0.0239044	0.8722202	0.1038758	2.75155	1.49582	0.630	0.986	1.652	
6	621.8903	0.0795632	0.8126075	0.1078293	2.61582	4.90278	0.420	0.972	1.805	
7	625.9306	0.1048133	0.8404958	0.0546914	2.61278	4.87981	0.467	0.944	2.000	
8	631.5791	0.1610734	0.8168392	0.0220874	2.58981	4.81588	0.539	0.945	0.965	
9	647.0654	0.2972075	0.6864756	0.0163174	2.52588	4.76127	0.537	0.872	1.105	
10	642.7292	0.590422	0.4026274	0.0069508	2.47127	2.29000	1.000	1.000	1.000	

Stage	Efficiency Calculations Programs							
	Vapor Compositions			Stream Flow Rates		E_{ji}^{o}		
	Water	Methanol	Acetone	V_j	L_j	Water	Methanol	Acetone
1	0.0002508	0.8067961	0.1929532	1.119999	1.5679980	1.0000	1.0000	1.0000
2	0.0002508	0.8067961	0.1929532	2.6879980	1.6458220	0.3210242	0.6540031	0.9889998
3	0.0013853	0.8544018	0.1442134	2.7658220	1.5286230	0.3649967	0.9629986	1.2059880
4	0.0089608	0.8573840	0.1336555	2.6486230	1.6315450	0.5020087	0.5599968	1.5300120
5	0.0239043	0.8722205	0.1038751	2.7515460	1.4958200	0.6299961	0.9859940	1.6519960
6	0.0795634	0.8126079	0.1079286	2.6158200	4.9027860	0.4200025	0.9719953	1.8049830
7	0.1048178	0.8404901	0.0546910	2.6127880	4.8798110	0.4670250	0.9440005	2.0000500
8	0.1610752	0.8169366	0.0220872	2.5898070	4.8158840	0.5390093	0.9450021	0.9650069
9	0.2972086	0.6864722	0.0163162	2.5258840	4.7612750	0.5370036	0.8719929	1.1049990
10	0.5904236	0.4026235	0.0069506	2.4712750	2.2899990	1.0000	1.0000	1.0000

Table 4.7

Column Operating Specifications for the Experimental Run

Component	Feed Composition
Water	0.5625
Methanol	0.3725
Acetone	0.0650

Reboiler Duty: 38833.84 BTU/Hr.

Saturated Liquid, single feed at 6th stage

Total Condenser, partial reboiler, eight trays

Column Pressure maintained at one atmosphere

Feed Temperature =632.8 ^{o}R

Table 4.8

Recorded Data from the Experimental Run

Stage No.	State Temperature ^{o}R
1.	599.0
3.	607.5
4.	610.0
5.	613.5
6.	616.5
7.	617.5
8.	619.0
9.	620.5
10.	631.5

Table 4.9

Liquid Composition from the Experimental Run

Stage No. \ Component	Water	Methanol	Acetone
1. (Distillate)	0.08030	0.69830	0.22150
2.	0.13540	0.74790	0.11670
3.	0.23560	0.70060	0.06380
4.	0.26760	0.66290	0.06950
5.	0.43920	0.51270	0.04810
6.	0.47950	0.48620	0.03430
7.	0.49350	0.48290	0.02360
8.	0.48370	0.47700	0.03930
9.	0.52800	0.45100	0.02090
10. (Bottoms)	0.68170	0.31670	0.00160

Table 4.10

Calculated Plate Efficiency from the Experimental Run

A. Vaporization Efficiencies

Stage No. \ Component	Water	Methanol	Acetone
1. (Condenser)	1.000000	1.000000	1.000000
2.	2.689555	1.035124	1.551230
3.	1.979364	1.063257	1.926422
4.	2.471257	1.023089	1.376361
5.	1.530720	1.187591	1.912198
6.	1.964793	1.028444	2.337735
7.	1.275923	1.248234	2.029173
8.	1.418174	1.216088	0.870131
9.	1.166023	1.221924	2.437330
10. (Reboiler)	1.000000	1.000000	1.000000

B. Modified Murphree Efficiencies

Stage No. \ Component	Water	Methanol	Acetone
1. (Condenser)	1.0000000	1.0000000	1.0000000
2.	0.7984002	5.3236990	1.8542650
3.	0.7516394	3.9640850	3.3532810
4.	0.5244161	2.0740340	1.8020660
5.	0.5890076	-0.0916074	4.2391920
6.	-0.0121830	0.8202689	29.8126200
7.	0.6765847	-0.7543365	-1.8504300
8.	0.4929407	-0.8109535	0.3646300
9.	0.7294070	-0.5106649	-2.1478600
10. (Reboiler)	1.0000000	1.0000000	1.0000000

Table 4.11

Simulation Results Using Calculated Efficiencies

Stage No.	Liquid Phase Compositions			
	T ^{o}R	Water	Methanol	Acetone
1	608.75090	0.0898018	0.7195766	0.1906224
2	604.98260	0.1477591	0.7537201	0.0985212
3	608.60660	0.2515171	0.6949877	0.0534966
4	610.68840	0.2825325	0.6585318	0.0589362
5	614.63590	0.4540599	0.5053589	0.0405816
6	617.33340	0.4883227	0.4825480	0.0291295
7	619.32000	0.5161940	0.4679613	0.0158451
8	621.88810	0.5423563	0.4393568	0.0182870
9	629.89330	0.6503112	0.3429968	0.0066921
10	650.69160	0.7936891	0.2027507	0.0035603

V. DISCUSSION OF RESULTS

Both the theoretical and experimental results of distillation depend on a number of variables, and in some cases relatively small deviations from the desired conditions can cause appreciable changes in performance. This may be particularly true of variations in reflux rate, reboil rate, and feed enthalpy. Since either a reduction of reflux temperature from the bubble point or heat losses from a column will affect the liquid flows from essentially all stages of distillation, changes in these variables can also cause variations of performance throughout a column with appreciable overall effects.

The experimental Murphree efficiencies at some trays have negative values as shown in Table 4.10. This indicates that vapor composition has been changed in a direction opposite from that expected for some components along consecutive trays. Such a situation may exist due to certain operating factors, and they may be improved by better operating conditions, such as a relocated feed tray, or by utilizing a distillation tower more suitable for the specific separation desired.

In validating the proposed method of calculating efficiencies by comparing calculated efficiencies with efficiencies used in simulations, the agreement is very good as shown in Tables 4.4 through 4.6. This is true because both calculation and simulation were based on the same assumptions concerning column operating conditions.

In comparing experimental liquid compositions with the compositions obtained from the simulation using calculated efficiencies, Tables 4.9 and 4.11, the agreement is reasonable in the upper trays but there is considerable deviation in the lower part of the column. This can be partially explained by the fact that the data used to determine reboiler duty was not very accurate and could have introduced some deviation from the simulation. In general, the liquid flows throughout the column were undoubtedly different from those calculated in determining efficiencies and those in the simulation since there was ample opportunities for heat losses in the reflux line and the column of the experimental system. These errors might be expected to accumulate as the calculation proceeds from top to bottom of the column, and the deviations due to erroneous flows would result in erroneous efficiencies. Also, the feed enthalpy was probably less than that indicated by temperature and this would be expected to have a greater effect in the bottom of the column in both calculations. Due to complex interrelations among variables it is difficult to estimate where the errors originate, but considering all the results, the implication is that the experimental system is presently inadequate for reliable and accurate estimation of distillation efficiencies. Some changes which might improve the reliability would be insulation of feed, reflux and reboiler lines, better insulation of the column, and more adequate means to measure and control feed, distillate, and bottoms flows as well as reboiler duty.

VI. CONCLUSIONS

With a distillation column operated at steady state, quick, accurate calculations of stream flow rates, vapor compositions, and component efficiencies on each plate within the column were made from experimental data on liquid plate compositions, plate temperatures, the reflux rate, and the overall material balance. The digital computer is essential to these computations.

As is shown in Example 4.1 and 4.2, the calculational procedure developed in this investigation is applicable to both hydrocarbon systems and non-hydrocarbon systems. Therefore it should be useful for calculation of multicomponent distillation efficiencies in many types of distillation operations.

This study indicates that component efficiencies in the experimental distillation system studied varied appreciably from plate to plate. Plate efficiencies can be readily calculated from experimental measurements, and a logical extension of this method could be to use chromatographic data from a distillation unit as inputs to a digital computer to periodically monitor efficiencies and possibly adjust conditions for improved performance.

APPENDIX A

Analytical Procedure of Samples on Gas Chromatography

The optimum operating condition for this chromatograph was determined by considering the many factors which have advantageous and adverse effects on the degree of resolution and symmetry of peak area.(3)

1. Column Temperature: A higher temperature will reduce resolution, lower temperature has the reverse effect.
2. Sample Size: Small sample size will improve symmetry and resolution of peaks. But, large sample size will increase sensitivity of detector.
3. Column Length: Longer column has better resolution of peaks.
4. Carrier Gas Flow Rate: Faster carrier gas flow rate will decrease sample retention time to a great extent, but has adverse effect on detector sensitivity to a small effect.
5. Injector Temperature: Too high or too low will cause tailing peak and or leading peak.
6. Sample Injection Technique: The best technique insures the most accurate result of analysis. It is important that:

   a) The needle be quickly inserted its full length through the injection seal.

b) The plunger be depressed as quickly as possible.

c) The needle be quickly withdrawn from the seal as soon as the sample is expelled.

Injection seal should be prevented from leaks which may cause baseline drift on the chart and/or sample loss.

Based on above considerations, the optimum operation conditions are:

1. Turn on carrier gas. Adjust as 14.6 ml/min.
2. Turn on column and injector temperatures setting. Set column temperature at 62°c. injector temperature at 112°c.
3. Allow about three hours for column temperature to be stable.
4. Adjust baseline of recorder chart according to specific recorder manual.
5. Sample size ranged from 0.1 μl to 0.2 μl depending on sample compositions.

Qualitative analysis was carried out by measuring the retention time of each component under identical operation conditions. The retention time of each component using two feet, polypak #2 packing column under the above conditions are:

Water:	0.25 minute
Methanol:	0.50 minute
Acetone:	2.50 minutes

After qualitative analysis was completed, quantitative analysis can be done for known composition samples to calculate a correction factor from peak area converted to compositions.

Calculation of Correction Factors:

Standard samples of the water-methanol-acetone system were prepared by measuring the volume (buret) of each component in accordance with the following relationship and density data:

$$W_w = \rho_w . V_w; \quad W_m = \rho_m . V_m; \quad W_a = \rho_a . V_a .$$

$$\rho_w = 1.000 \text{ g/ml}$$

$$\rho_m = 0.7928 \text{ g/ml}$$

$$\rho_a = 0.7920 \text{ g/ml}$$

at 20^oc. (from "Handbook of Chemistry & Physics")

The result showed the peak area of each component did not exactly represent the weight per cent of each component, though closely related. The same conclusion has been drawn by several investigators on different columns analyzed different systems(8, 16, 24). Therefore correction factors for each component needed to be calculated in order to get correct compositions.

The following table shows the result from chromatogram.

Table A-1

Correction Factors for Compositions of Water-Methanol-Acetone System

Water			Methanol			Acetone		
True Comp.	Cal. Comp.	Correction Factor	True Comp.	Cal. Comp.	Correction Factor	True Comp.	Cal. Comp.	Correction Factor
25.0	27.27	0.9165	50.0	52.22	0.958	25.0	20.40	1.125
33.3	35.85	0.929	33.3	34.90	0.954	33.3	29.40	1.130
50.0	54.10	0.923	25.0	26.75	0.935	25.0	19.20	1.300
80.0	82.25	0.972	10.0	10.43	0.959	10.0	7.27	1.375
10.0	11.00	0.910	80.0	82.60	0.968	10.0	6.36	1.573
25.0	28.25	0.885	25.0	26.70	0.936	50.0	45.20	1.108
10.0	11.84	0.845	10.0	11.80	0.847	80.0	76.30	1.050

APPENDIX B

Explanation of Fortran Variables and Computer Program

Fortran Variables:

1. XY is used in the computer program to denote the composition of either liquid or vapor stream. The first parameter denotes the phase of the stream with one (1) representing the liquid phase, two (2) representing the vapor phase; the second parameter the stages; the third parameter the components; the fourth parameter the number of the iteration.

2. ENTH is used in the computer program to denote the stream enthalpy, the first parameter denotes the phase enthalpy with one (1) representing liquid phase enthalpy, two (2) representing vapor phase enthalpy; the second parameter denotes phase compositions; the third parameter the stage temperatures; the fourth parameter the stage compositions.

3. All other variables are explained in computer program.

Computer Program:

(a) The calculation of condenser duty

The condenser duty is first determined from tower operating data as shown in block 3 of the flow chart.

(b) The calculation of enthalpy of vapor stream leaving second stage

This is calculated from tower operating data and condenser duty determined in Step (a) as shown in block 4 of the flow chart.

(c) The calculation of second stage temperature

With the calculated enthalpy value from Step (b), the second stage temperature is solved from the fourth-order algebraic equation by False-Position Method(9). This is shown in block 5 of the flow chart.

The iterative procedure includes the following steps:

(1) The estimated second stage temperature is first calculated from experimental first and third stage temperatures.

(2) The second stage temperature estimated in Step (1) is used to calculate the estimated enthalpy.

(3) The estimated enthalpy value is compared with the correct enthalpy value calculated in Step (b), if the second stage temperature has been determined

(4) If the test condition is not met, return to Step (2), using the revised value for the stage temperature.

(d) Stage-to-stage calculation of vapor composition and internal flow rates

As described in Section B3 and B4 of Chapter IV, the vapor composition is simply a function of liquid stream flow rate. Alternately, the liquid stream flow rate is a function of vapor composition. These functions are both first-order equations, but the function form for the feed stage is different from that for the non-feed stage. Therefore, it is convenient to calculate these variables separately in the beginning of the iterative procedure as shown in block 11A, B, 13A, B of the flow chart.

(1) The liquid stream flow rate leaving the second stage is first assumed to be equal to that leaving first stage which is experimentally measured as shown in block 6 of the flow chart.

(2) Before the iterative procedure proceeds, the first iterated value of vapor composition leaving stage j+1 is assumed to be equal to the correct value leaving previous stage j in order for the comparisons of the two consecutive calculated values in the latter step as shown in block 10 of the flow chart. The vapor compositions are readily calculated based on the assumed liquid flow rate as shown in block 11A and 11B of the flow chart.

(3) The liquid stream flow rate is calculated based on the vapor compositions previously calculated by calling the enthalpy subprogram as shown in block 13A and 13B of the flow chart. Once the test condition is met at a specific stage for the specific component, the correct value of vapor composition is duplicated from the last iterated value to the 50th time.

Repeat the same procedure for all the other components before proceeding to the next stage. The correct value of liquid stream flow rate is also duplicated from the last iterated value to the 50th time before making calculations on the next stage.

(4) At the beginning of calculation on each stage, the vapor stream flow rate is calculated from the correct liquid stream flow rate as shown in blocks 9A and 9B of the flow chart.

```
C       CALCULATION OF PLATE EFFICIENCIES FROM OPERATIONAL DATA OF TEMP.
C       AND COMPOSITION AT STEADY STATE FOR CONVENTIONAL COLUMN
C       DISTILLING  WATER, METHANOL, ACETON5
C       LET FF BE FEED RATE,DD BE DISTILLATE RATE,BB BE BOTTOM RATE,QR BE
C       REBOILER DUTY,QC BE CONDENSER DUTY,HFF BE FEED ENTHALPY,HDD BE
C       DISTILLATE ENTHALPY,HBB BE BOTTOM ENTHALPY.
        DIMENSION XF(10),VL(10,55),VV(10),HV(20),HL(20),VE(10,3),
       1PE(10,3),XK(10,3),CY(10,3),C1(10),C2(10),C4(10),C6(10)
        COMMON T(20),XY(2,11,3,50),E(2,4,3),NI
C       BLOCK 1, READ IN OPERATING DATA, EQUILIBRIUM CONSTANT ,AND ENTHALPY
C       COEFFICIENT
        READ(1,11) (T(NTT),NTT=3,11)
        READ (1,12) ((XY(1,NTT,I,1),I=1,3),NTT=1,11)
        READ (1,13) ((E(KH,1,I),E(KH,2,I),E(KH,3,I),KH=1,2),I=1,3)
        READ (1,14) (XF(I),I=1,3)
        READ (1,15) (C1(I), C2(I),C4(I),C6(I),I=1,3)
        FF=3.41
        DD=1.12
        BB=2.29
        VV(1)=DD
        VL(10,1)=BB
        DO 16 NN=1,50
     16 VL(10,NN)=VL(10,1)
        QR=38840.93
C       BLOCK 2, CALCULATE EXTERNAL STREAMS ENTHALPIES
        NI=0
        KH=1
        KC=1
        NTF=11
        MF=11
        HFF= ENTH (KH,KC,NTF,MF)
        KH=1
        KC=1
        NTT=10
        NTX=10
        HBB=ENTH(KH,KC,NTT,NTX)
        KH=1
        KC=1
        T(1)=599.65280
        NTT=1
        NTX=1
        HDD=ENTH(KH,KC,NTT,NTX)
C       BLOCK 3,CALCULATE CONDENSER DUTY
```

```
      QC=FF*HFF+QR-BB*HBB-DD*HDD
C     CALCULATION OF SECOND STAGE TEMPERATURE
C     LET REFLUX RATIO AS RR,LIQUID STREAM FLOWRATE AS VL, VAPOR
C     STREAM FLOWRATE AS VV,SPECIES COMPOSITION ON EACH TRAY AS XY
C     LET ENTHALPY OF LIQUID AS HL, ENTHALPY OF VAPOR AS HV
C     BLOCK 4, CALCULATE ENTHALPY OF VAPOR STREAM LEAVING SECOND STAGE
      RR=1.4
      VL(1,1)=RR*DD
      VV(2)=VL(1,1)+DD
      HV(2)=(VV(2)*HDD+QC)/VV(2)
C     BLOCK 5, CALCULATE SECOND STAGE TEMPERATURE
      DO 101 NI=1,50
      DO 101 I=1,3
      XY(2,1,I,NI)=XY(1,1,I,1)
  101 XY(2,2,I,NI)=XY(2,1,I,NI)
      A=0.
      B=0.
      C=0.
      D=0.
      F=0.
      DO 102 I=1,3
      A=A+XY(2,2,I,1)*(E(2,1,I)**2)
      B=B+XY(2,2,I,1)*2.*E(2,1,I)*E(2,2,I)
      C=C+XY(2,2,I,1)*(E(2,2,I)**2+2.*E(2,1,I)*E(2,3,I))
      D=D+XY(2,2,I,1)*2.*E(2,2,I)*E(2,3,I)
  102 F=F+XY(2,2,I,1)*(E(2,3,I)**2)
      T1=T(1)+0.25*(T(3)-T(1))
      T2=T(1)+0.75*(T(3)-T(1))
    8 G1=A+B*T1+C*T1**2+D*T1**3+F*T1**4-HV(2)
      G2=A+B*T2+C*T2**2+D*T2**3+F*T2**4-HV(2)
      T(2)=(T1*G2-T2*G1)/(G2-G1)
      IF(T(2)-T(3)) 5,6,6
    5 IF(T(2)-T(1)) 4,4,9
    6 T(2)=(T2+T(3))/2.
      GO TO 9
    4 T(2)=(T2+T(1))/2.
    9 G=A+B*T(2)+C*T(2)**2+D*T(2)**3+F*T(2)**4-HV(2)
      H=0.000001*HV(2)
      IF(ABS(G)-H) 10,10,20
   20 T1=T2
      T2=T(2)
      GO TO 8
   10 WRITE(3,1001)
      WRITE(3,1003)
      WRITE(3,1005)
      DO 51 NTT=1,10
   51 WRITE (3,1006)  NTT,T(NTT),(XY(1,NTT,I,1),I=1,3)
C     BLOCK 8 CALCULATION OF VAPOR COMPOSITION AND LIQUID STREAM FLOWRATES
```

```
C         THROUGH WHOLE COLUMN WITH FEED PLATE FIXED AT 7TH
          DO 100 NTT=1,11
          DO 100 I=1,3
          DO 100 NI=1,50
      100 XY(1,NTT,I,NI)=XY(1,NTT,I,1)
          DO 200 NN=1,50
          VL(1,NN)=VL(1,1)
      200 VL(2,NN)=VL(1,NN)
          NTF=2
          NTL=9
          NN=1
          NP=3
          NM=1
          DO 104 NTT=NTF,NTL
          NP=NTT+1
          NM=NTT-1
          I=1
          FT=6
          IF(NTT-FT) 105,106,107
      105 FF=0.
      107 NI=1
          VV(NTT)=VL(NM,NN)+DD-FF
          DO 301 J=1,3
      301 XY(2,NP,J,NI)=XY(2,NTT,J,NN)
C         BLOCK 11A CALCULATE VAPOR STREAM COMPOSITIONS
      210 DO 401 J=1,3
      401 XY(2,NP,J,NI+1)=(VL(NTT,NI)*XY(1,NTT,J,1)-VL(NM,NN)*XY(1,NM,J,1)
         1+(VL(NM,NN)+DD-FF)*XY(2,NTT,J,NN))/(VL(NTT,NI)+DD-FF)
C         BLOCK 12A CALL FUNCTION SUBROUTINE TO CALCULATE STREAM ENTHALPIES
          KH=2
          KC=2
          HV(NTT)=ENTH(KH, KC,NTT,NTT)
          KH=2
          KC=2
          HV(NP)= ENTH(KH,KC,NP,NP)
          KH=1
          KC=1
          HL(NTT)=ENTH(KH, KC,NTT,NTT)
          KH=1
          KC=1
          HL(NM)= ENTH( KH,KC,NM,NM)
C         BLOCK 13A CALCULATE LIQUID STREAM FLOWRATES
          VL(NTT,NI+1)=(VL(NM,NN)*(HV(NTT)-HL(NM))+DD*(HV(NTT)-HV(NP))+FF*
         1(HV(NP)-HV(NTT)))/(HV(NP)-HL(NTT))
      603 IF (ABS(XY(2,NP,I,NI+1)-XY(2,NP,I,NI))-1.0E-5) 203,203,108
      108 NI=NI+1
          GO TO 210
```

```
  203 NN=NI+1
  303 XY(2,NP,I,NN)=XY(2,NP,I,NI+1)
      NN=NN+1
      IF (NN-50) 303,303,403
  403 NN=50
      I=I+1
      IF (I-3) 603,603,103
  103 CONTINUE
      NN=NI+1
  413 VL(NTT,NN)=VL(NTT,NI+1)
      NN=NN+1
      IF(NN-50) 413,423,423
  423 VL(NTT,50)=VL(NTT,49)
      VL(NP,1)=VL(NTT,NN)
      W=VL(NTT,NN)
      VL(NM,NN)=W
      GO TO 104
  106 VV(NTT)=VL(NM,NN)+DD
      FF=3.41
      NI=1
      VL(NTT,NI)=VL(NM,NN)+FF
      DO 501 J=1,3
  501 XY(2,NP,J,NI)=XY(2,NTT,J,NN)
C     BLOCK 11B CALCULATE COMPOSITION OF VAPOR STREAM LEAVING (F+1)TH PLATE
  220 DO 601 J=1,3
  601 XY(2,NP,J,NI+1)=(VL(NTT,NI)*XY(1,NTT,J,1)-VL(NM,NN)*XY(1,NM,J,1)
     1+(VL(NM,NN)+DD)*XY(2,NTT,J,NN)-FF*XF(J))/(VL(NTT,NI)+DD-FF)
C     BLOCK 12B CALL FUNCTION SUBROUTINE TO CALCULATE STREAM ENTHALPIES
C     LEAVING FTH, (F+1)TH,   (F-1)TH PLATES
      KH=2
      KC=2
      HV(NTT)=ENTH(KH,KC,NTT,NTT)
      KH=2
      KC=2
      HV(NP)=ENTH(KH,KC,NP,NP)
      KH=1
      KC=1
      HL(NM)=ENTH(KH,KC,NM,NM)
      KH=1
      KC=1
      HL(NTT)=ENTH(KH,KC,NTT,NTT)
C     BLOCK 13B CALCULATE FLOWRATE OF LIQUID STREAM LEAVING FEED STAGE
      VL(NTT,NI+1)=(VL(NM,NN)*(HV(NTT)-HL(NM))+DD*(HV(NTT)-HV(NP))+FF*
     1(HV(NP)-HFF))/(HV(NP)-HL(NTT))
  703 IF (ABS(XY(2,NP,I,NI+1)-XY(2,NP,I,NI))-1.0E-5) 211,211,208
  208 NI=NI+1
      GO TO 220
  211 NN=NI+1
```

```
  212 XY(2,NP,I,NN)=XY(2,NP,I,NI+1)
      NN=NN+1
      IF (NN-5C) 212,212,410
  410 NN=50
      I=I+1
      IF(I-3) 703,703,110
  110 CONTINUE
      NN=NI+1
  433 VL(NTT,NN)=VL(NTT,NI+1)
      NN=NN+1
      IF (NN-50) 433,443,443
  443 VL(NTT,5C)=VL(NTT,49)
      VL(NP,1)=VL(NTT,NN)
      V=VL(NTT,NN)
      VL(NM,NN)=V
  104 CONTINUE
      VV(10)=VL(9,50)-BB
      WRITE(3,1007)
      WRITE(3,1008)
      WRITE(3,1009)
      DO 61 NTT=1,10
   61 WRITE (3,1010)  NTT,(XY(2,NTT,I,50),I=1,3),VL(NTT,NI+1),VV(NTT)
      WRITE(3,1002) QC
      WRITE(3,1004) HV(2)
C     CALCULATION OF VAPORIZATION  EFFICIENCIES AND  MURPHREE
C     PLATE EFFICIENCIES
      DO 17 I=1,3
      VE(1,I)=1.00000
   17 PE(1,I)=1.00000
      DO  109  NTT=2,9
      DO 109 I=1,3
      NP=NTT+1
C     BLOCK I, CALCULATE EQUILIBRIUM CONSTANTS
      XK(NTT,I)=((((C6(I)*T(NTT)+C4(I))*T(NTT)+C2(I))*T(NTT)+C1(I))**3)
     1*T(NTT)
C     BLOCK J, CALCULATE IDEAL VAPOR COMPOSITIONS
  109 CY(NTT,I)=XK(NTT,I)*XY(1,NTT,I,1)
      DO 209 I=1,3
      XK(10,I)=((((C6(I)*T(10)+C4(I))*T(10)+C2(I))*T(10)+C1(I))**3)
     1*T(10)
  209 CY(10,I)=XK(10,I)*XY(1,10,I,1)
C     BLOCK K, CALCULATE VAPORIZATION $ MURPHREE PLATE EFFICIENCIES
      DO 309 NTT=2,9
      DO 309 I=1,3
      VE(NTT,I)=XY(2,NTT,I,NN)/CY(NTT,I)
  309 PE(NTT,I)=(XY(2,NTT,I,NN)-XY(2,NP,I,NN))/(CY(NTT,I)-XY(2,NP,I,NN))
      DO 72 I=1,3
```

```
      VE(10,I)=1.00000
   72 PE(10,I)=1.00000
      WRITE(3,1011)
      WRITE (3,1012)
      WRITE (3,1013)
      DO 71 NTT=1,10
   71 WRITE (3,1021) NTT,(VE(NTT,I),I=1,3),(PE(NTT,J),J=1,3)
   11 FORMAT (3F10.5)
   12 FORMAT (3F10.7)
   13 FORMAT(2X,6E13.7)
   14 FORMAT (3F10.7)
   15 FORMAT(6X,4F14.7)
 1001 FORMAT (1H1 ,20X,'*DISTILLATION COLUMN OPERATING CONDITIONS*')
 1002 FORMAT (/,20X,'CONDENSER DUTY=',5X,F12.4,5X,'BTU/MINUTE')
 1003 FORMAT (//,40X,'LIQUID PHASE COMPOSITIONS')
 1004 FORMAT (/,20X,'VAPOR ENTHALPY LEAVING SECOND STAGE=',F12.4,5X,
     1'BTU/MINUTE')
 1005 FORMAT (/,10X,'STAGE NO.',3X,'TEMPERATURE OR',5X,'WATER',5X,
     1'METHANOL',5X,'ACETONE')
 1006 FORMAT (15X,I2,5X,F10.5,5X,F10.7,2X,F10.7,2X,F10.7,/)
 1007 FORMAT (1H1 ,20X,'*CALCULATED OPERATING DATA FROM COLUMN OPERATING
     1 CONDITIONS*')
 1008 FORMAT (//,30X,'VAPOR PHASE COMPOSITIONS',10X,'STREAM FLOWRATES',
     15X,'MOLES/MINUTE')
 1009 FORMAT (/,10X,'STAGE NO.',10X,'WATER',5X,'M5CHINOL',5X,'ACETONE',
     110X,'LIQUID',5X,'VAPOR')
 1010 FORMAT (15X,I2,8X,F10.7,2X,F10.7,2X,F10.7,7X,F10.7,3X,F10.7,/)
 1011 FORMAT (1H1 ,25X,'CALCULATED PLATE EFFICIENCIES')
 1012 FORMAT (/,25X,'VAPORIZATION EFFICIENCIES',15X,
     1'MODIFIED MURPHREE EFFICIENCUES')
 1013 FORMAT (/,10X,'STAGE NO.',6X,'WATER',5X,'METHANOL',5X,'ACETONE',
     113X,'WATER',5X,'METHANOL',5X,'ACETONE')
 1021 FORMAT (15X,I2,5X,F10.7,2X,F10.7,2X,F10.7,10X,F10.7,2X,F10.7,
     12X,F13.7,/)
      STOP
      END

      FUNCTION ENTH(KH,KC,NTT,NTX)
      COMMON T(20),XY(2,11,3,50),E(2,4,3),NI
      ENTH=0.
      DO 112 I=1,3
  112 ENTH=ENTH+(((E(KH,3,I)*T(NTT)+E(KH,2,I))*T(NTT)+E(KH,1,I))**2)*
     1XY(KC,NTT,I,NI+1)
      RETURN
      END

/DATA
```

APPENDIX C

Experimental Equipment and Operating Procedure

1. Description of Pilot-Scale Distillation Column

The major piece of equipment used in this research was a pilot-scale distillation tower. Five components made up the experimental distillation unit:

(1) Bubble-cap distillation tower: It was constructed of brass, consisted of eight plates, 6 $\frac{5}{8}$ inch in outside diameter with six bubble-caps per plate, and was insulated to prevent heat loss. The column wall on the top plate was constructed of safety glass. Complete details are shown in Table C-1.

(2) Electrically-heated reboiler: High resistance coils were mounted on one end of the reboiler to supply the heat required by the distillation unit. It was adjustable.

(3) Overhead condenser:

Type - Total condenser, two-tube-pass, one-shell-pass, floating-head heat exchanger. Water was used as cooling medium.

shell diameter, inch 4.225

tube length, inch 23.5

(4) Automatic temperature recorder: Thermocouples on each plate except the top one were used to read temperatures. Additionally three thermocouples

Table C-1

Experimental Plates Characteristics

Tower Outside Diameter, inch	$6 \frac{5}{8}$
Tower Inside Diameter, inch	6
Plate Spacing, inch	6.11
Type of Plate	Crossflow plate, wherein the liquid flows directly across the plate.
The Bubble Caps	Round, bell-shaped cap with rectangle slots, shroud ring, and removable mounting. Six 1 inch O. D. bubble caps on each plate, with 11 straight slots, 0.12x0.5 inch. The total slot area is 4 inch^2 per plate. The caps are arranged in two rows of three caps each symmetric to the plate center and parallel to the weirs.
The Weirs	The top plate has a circular outlet weir 1.25 inches high and 3.55 inches in circumference. Plate 2 through 8 have inlet weirs 1.125 inches high and outlet weirs 1.25 inches high. Both weirs are straight, 4.2 inches long, and are located 7 inches from the center of the plate.
The Downcomers	Brass pipes, 0.68 inch internal diameter, which reach to within 0.5 inch of the surface of the plate below.

were used to measure the temperatures of feed, distillate, and bottoms. They were all electrically connected to a temperature recorder on the control panel.

(5) Automatic sampling device: Sampling probes were installed in the bottom of the downcomers from each plate to minimize the concentration non-uniformities in the liquid samples. The probes were all electrically connected to a switch on the control panel so that simultaneous sampling could be done.

Accessory equipment -

(6) Feed preheater: Feed temperature was manually adjusted. Steam was the heating medium.

(7) Feed pump: A 1/8 hp reciprocating pump was used to deliver the feed mixture to the distillation unit.

(8) Recovery pump: A 1/8 hp reciprocating pump was used to deliver the bottom product to a storage drum and to maintain constant level of reboiler.

(9) Rotameter: A float type rotameter was used to measure feed flow rate.

(10) Distillate divider: Three open-end glass cylinders with graduates were used to measure reflux ratio. It was calibrated with a curve showing relationship of height vs. flow rates.

(11) Piping system: 5/8" schedule 40 copper tube were used.

2. Description of Gas Chromatography

Gas Chromatograph consisted of four basic components(3):

(1) Carrier gas supply and flow control: Helium gas was used as carrier medium. The cylinder reducing valve and needle valve were used to control flow rate of helium gas, and soap-film flowmeter was used for measurement.

(2) Sample port: This consisted of a silicone rubber diaphragm, loosely packed with glass wool to provide a large surface over which the liquid samples were dispersed. A preheater consisting of a length of insulated resistance heating wire was wrapped about the port to insure rapid vaporization of liquid samples.

(3) Column: Dual 1/8" diameter, 2' long stainless steel columns were used. Polypak #2 (commercial name of chemical of polyethylene cross-linked polystyrene) with 60 mesh was used as packings. Thermostatted chamber was provided around the column to insure constant temperature in the column. Either column could be used for analysis.

(4) Detector: The thermoconductivity detector employed a dual, 100 µl volume thermistor as the resistance element. The detector had a fixed wattage heater that maintained the detector temperature above column temperature to prevent condensation.

Accessory Equipment -

(5) Strip-chart recorder: This recorded the response curve of components.

(6) Area integrator: Automatic evaluation of area under individual response curve.

(7) Thermometer: Measured chamber temperature.

3. Operating Procedure for the Pilot-Scale Distillation Column

This distillation column is operated primarily to produce engineering data such as plate temperatures, and sample compositions, to be used in the evaluation of plate efficiencies. Therefore steady state performance of the column is desirable.

The usual precautions regarding instrument calibration and careful measurements are made: The thermocouple on each tray should be checked with a potentiometer; the feed rotameter should be calibrated by weighing the feed for a certain period of time. Since no controller was installed, the manipulated variables are reduced as much as possible for steady state operation. In view of these considerations, the following procedures for this specific design column were followed:

(1) The continuous distillation runs begin by charging feed storage drum and calibrating the feed rotameter for the particular feed composition used. The feed then is directed into the column until the reboiler

is filled to a level slightly above the red line on the reboiler sight glass. This is necessary in order to keep the electric heater in reboiler from burning out.

(2) Feed is then stopped, the reboiler heater is turned on and the column is allowed to come to steady state at total reflux. When the plate temperatures cease changing this condition has been achieved. This closed loop operation without feed-charge for a pre-steady state period has several advantages:

a) The bubble point of the feed can be experimentally determined. It equals to the temperature of reboiler when bubbling vapor is first visible on the first plate.

b) The column can achieve steady state in a shorter time, because no outside stream could cause a disturbance.

c) The amount of hold up on each plate, usually difficult to measure accurately, need not to be known, because holdup has been established before feed enters column. Therefore the overall material balance, $F = B + D$, may be applied throughout the steady state period.

(3) After steady state is achieved under total reflux operation, the feed is started. The feed should be charged to the column gradually and slowly, because the small scale pilot plant distillation tower is

very sensitive to disturbances which may cause unstable operation. It is controlled at a specified flow rate and temperature by adjusting the steam rate through the feed preheater. The reboiler heater is charged with constant power (i.e. constant heat is supplied to the reboiler throughout the whole period of operation). Bottoms flow is adjusted to maintain a constant liquid level in the reboiler. The reflux heater and/or condenser water is adjusted to keep the reflux at the saturated liquid state. The reflux ratio is adjusted to ensure a constant reboiler level and steady column temperature. The reflux is the only manipulated variable. When the reflux is kept at the temperature of the saturated liquid, the internal liquid flow rate is constant. Neither condensation nor vaporization occurs when reflux contacts the top plate of the tower. Constant reboiler duty also facilitates keeping the internal vapor flow rate as constant as possible. Under these conditions plate temperatures readily approach steady state.

(4) After feed is charged the temperatures in the stripping section will be lower due to enrichment of the heavier component in this section. (All subcooled liquid comes down along this section.) After the reflux is decreased from total reflux, the temperature in the rectifying section will be higher due

to the decrement of the lighter components in this section. Column temperatures seemed to stabilize in two or three hours. After that, samples from each plate are taken. Samples are collected in tightly stoppered glass bottles to minimize evaporation prior to analysis.

(5) Finally, the molal flow rate of bottoms and distillate are calculated by weighing during the steady state operation period.

APPENDIX D

Nomenclature

a = a coefficient of the function of equilibrium constant

B = molar flow rate of bottoms product

C = number of independent components

c = a coefficient of the empirical equation proposed by Prausnitz, Eckert, Orye et. al.

D = molar flow rate of distillate

E_{ji}^{M} = modified Murphree plate efficiency

E_{ji}^{o} = modified vaporization efficiency

E^{V} = vaporization efficiency

$\bar{E}_{y}'$ = reduced efficiency

$\bar{E}_{y}$ = apparent efficiency

E_{y} = conventional efficiency

l = a coefficient of the function of enthalpy

F = degrees of freedom

= molar flow rate of feed

$\bar{f}_{i}$ = fugacity of component i in mixture. Superscripts L and V refer to liquid and vapor mixture respectively. Subscript p refers to the fugacity evaluated at total pressure p.

f_{i}^{o} = fugacity of component i in the standard state

H = enthalpy

H_{p} = enthalpy value evaluated at pressure p

H_o = enthalpy value evaluated at zero pressure

H_j = enthalpy of one mole of the vapor leaving stage j of a distillation column

h_j = enthalpy of one mole of the liquid leaving stage j of a distillation column

$\bar{H}_{ji}$ = partial molar enthalpy of component i in a vapor mixture leaving stage j of a distillation column

$\bar{h}_{ji}$ = partial molar enthalpy of component i in a liquid mixture leaving stage j of a distillation column

h_F = enthalpy of feed stream

h_B = enthalpy of bottoms product

h_D = enthalpy of distillate

K_{ji} = equilibrium constant for component i at the temperature of stage j

P = number of phases in a system

p = total pressure. Superscripts l and v refer to liquid and vapor respectively.

P_c = critical pressure

P_r = reduced pressure

p_i = partial pressure of component i in a mixture

p_i^* = vapor pressure of pure component i

Q_c = condenser duty

Q_r = reboiler duty

R = gas constant

= external reflux ratio at top of column

T = absolute temperature

t = temperature. Superscripts l and v refer to liquid and vapor respectively.

T_r = reduced temperature

T_c = critical temperature

V = molar volume of pure component

$\bar{V}_i$ = partial molar volume of component i in a mixture

V^* = molar volume of pure component if it were ideal gas

x_{ji} = mole fraction of component i in the liquid leaving stage j of a distillation column

$\bar{x}$ = actual liquid mole fraction

$\bar{x}'$ = reduced liquid mole fraction

x_{Fi} = mole fraction of component i in the saturated liquid feed

x_{Bi} = mole fraction of component i in the bottoms

x_{Di} = mole fraction of component i in the distillate

y_{ji} = mole fraction of component i in the vapor leaving stage j of a distillation column

y_{ji}^* = fictitious vapor composition which would be in equilibrium with the liquid leaving an equilibrium stage

Y_{ji} = product of K_{ji} and x_{ji}, where these quantities are evaluated at the actual conditions of the liquid leaving stage j of a distillation column

$\bar{y}$ = actual vapor mole fraction. Superscript * refers to equilibrium value.

$\bar{y}'$ = reduced vapor mole fraction. Superscript * refers to equilibrium value.

$(\bar{y})$ = conventional vapor mole fraction. Superscript * refer to equilibrium value.

Greek Letters

γ_i = liquid phase activity coefficient of component i

ρ_w = density of liquid water

ρ_m = density of liquid methanol

ρ_a = density of liquid acetone

Σ = denotes a sum

ε = error limit for two consecutive iterated values

Subscripts

j = stage number

i = component number

p = constant pressure

T = constant temperature

n = stage number

Appendix E. Simulation Program Used for Checking Efficiency Calculations

```
C        MAIN LINE PROGRAM---MULTICOMPONENT DISTILLATION
C
C        COMPONENTS ARE --WATER, METHANOL, AND ACETONE
C
         DIMENSION NAME(100)
C
         COMMON AAA,BBB,TLL,TUL,MC,A(15,4),N,NC,T(20),SKB(20),AK(20,15),SV(
        110),SL(20),W(20),D(20,15),ALP(20,15),AA(20,15),V(20,15),SUMV(20),T
        2HETN,      Y(20,15),X(20,15),TF(20),XX(20,15),YY(20,15),FV(20),FL
        3(20),E(15,3),C(15,3),XF(20,15),EF(20,20)
C
C        MC= MIDDLE COMPONENT AS BASE, N= NO. OF TRAYS,NC= NO. OF COMPONTS
         READ(1,1) TLL,TUL,MC,N,NC
         WRITE(3,1) TLL,TUL,MC,N,NC
       1 FORMAT(2F10.5,3I10)
         DO 19 I=1,NC
         READ(1,1000) A(I,1),A(I,2),A(I,3),A(I,4)
      19 WRITE(3,1000) A(I,1),A(I,2),A(I,3),A(I,4)
    1000 FORMAT(6X,4E14.7)
         DO 18 I=1,NC
         READ(1,1005) E(I,1),E(I,2),E(I,3),C(I,1),C(I,2),C(I,3)
      18 WRITE(3,1005) E(I,1),E(I,2),E(I,3),C(I,1),C(I,2),C(I,3)
    1005 FORMAT(2X,6E13.7)
         KK=1
     100 FORMAT(18A4)
         READ(1,14)(XF(I,3),I=1,NC)
         WRITE(3,14)(XF(I,3),I=1,NC)
      14 FORMAT(3F10.7)
         CALL AAABBB
         N=N+2
         READ(1,1007)((EF(J,I),I=1,NC),J=1,N)
         WRITE(3,1007)((EF(J,I),I=1,NC),J=1,N)
    1007 FORMAT(3F10.7)
         NUM=0
         READ(1,3)(T(J),J=1,N)
       3 FORMAT(F10.5)
         DO 4 J=1,N
         SKB(J)=EXP((AAA/T(J))+BBB)
       4 CONTINUE
         READ(1,5)B,DIST
       5 FORMAT(2F10.3)
         READ(1,6)(SV(I),SL(I),W(I),I=1,N)
       6 FORMAT(3F10.3)
```

```
      READ(1,101)(FV(J),J=1,N)
  101 FORMAT(5F10.5)
      READ(1,101)(FL(J),J=1,N)
      READ(1,102)((XX(J  ,I  ),I=1,NC),J=1,N)
      READ(1,102)((YY(J  ,I  ),I=1,NC),J=1,N)
  102 FORMAT(3F10.5)
      READ(1,103)(TF(J),J=1,N)
  103 FORMAT(5F10.5)
   13 CALL KCOMP
      CALL ALPHA
      CALL ABSFAC
      CALL MATBAL
      CALL THETA
      IF(ABS(THETN-1.0)-1.E-5) 9,9,10
    9 GO TO 11
   10 CONTINUE
   12 FORMAT(F30.6)
      CALL KBASE
      CALL TEMPJ
      KK=KK+1
      NUM=NUM+1
      IF(NUM-3) 13,13,33
   33 CALL ENTHAL
   87 FORMAT(5X,11F10.4)
      GO TO 13
   11 CONTINUE
      WRITE(3,38)
   38 FORMAT('1')
      DO 40 MM=1,10
      READ(1,100) (NAME(I),I=1,18)
   40 WRITE(3,100) (NAME(I),I=1,18)
      WRITE(3,41) KK,THETN
   41 FORMAT(////3X,'PROBLEM CONVERGED IN',I5,3X,'ITERATIONS TO A THETA
     1 OF',F10.6)
      WRITE(3,42)
   42 FORMAT(////7X,'TRAY TEMPERATURE  VAPOR RATES   LIQUID RATES
     2 --------EQUILIBRIUM CONSTANTS--------')
      WRITF(3,43)
   43 FORMAT(3X,/5X,'        T(J)              SV(J)             SL(J)
     1   WATER             METHANOL          ACETONE ')
      DO 44 J=1,N
   44 WRITE(3,45) J,T(J),SV(J),SL(J),AK(J,1),AK(J,2),AK(J,3)
   45 FORMAT(2X,I2,2X,6F15.5)
      WRITE(3,46)
   46 FORMAT(3X,////,45X,'TRAY COMPOSITIONS')
      WRITE(3,47)
   47 FORMAT(3X,/,16X,'--------LIQUID PHASE-----------          -------
     1---GAS PHASE--------------')
```

```
      WRITE(3,48)
   48 FORMAT(3X,/,'                              WATER          METHANOL            ACETONE
     1     WATER           METHANOL               ACETONE')
      DO 49 J=1,N
   49 WRITE(3,50)J,X(J,1),X(J,2),X(J,3),Y(J,1),Y(J,2),Y(J,3)
   50 FORMAT(/2X,I2,6F15.7)
      CALL EXIT
      END

      SUBROUTINE AAABBB
C
      COMMON AAA,BBB,TLL,TUL,MC,A(15,4),N,NC,T(20),SKB(20),AK(20,15),SV(
     110),SL(20),W(20),D(20,15),ALP(20,15),AA(20,15),V(20,15),SUMV(20),T
     2HETN,      Y(20,15),X(20,15),TF(20),XX(20,15),YY(20,15),FV(20),FL
     3(20),E(15,3),C(15,3),XF(20,15),EF(20,20)
      SKBU=((A(MC,1)+A(MC,2)*TUL+A(MC,3)*TUL**2+A(MC,4)*TUL**3)**3)*TUL
      SKBL=((A(MC,1)+A(MC,2)*TLL+A(MC,3)*TLL**2+A(MC,4)*TLL**3)**3)*TLL
      AAA=ALOG(SKBU/SKBL)/((1.0/TUL)-(1.0/TLL))
      BBB=-(1.0/TLL)*AAA+ALOG(SKBL)
      RETURN
      END
      SUBROUTINE KCOMP
C
      COMMON AAA,BBB,TLL,TUL,MC,A(15,4),N,NC,T(20),SKB(20),AK(20,15),SV(
     110),SL(20),W(20),D(20,15),ALP(20,15),AA(20,15),V(20,15),SUMV(20),T
     2HETN,      Y(20,15),X(20,15),TF(20),XX(20,15),YY(20,15),FV(20),FL
     3(20),E(15,3),C(15,3),XF(20,15),EF(20,20)
      DO 5 J=1,N
      DO 3 I=1,NC
    3 AK(J,I)=((A(I,1)+A(I,2)*T(J)+A(I,3)*T(J)**2+A(I,4)*T(J)**3)**3)*T(
     1J)
    5 CONTINUE
      RETURN
      END

      SUBROUTINE ALPHA
C
      COMMON AAA,BBB,TLL,TUL,MC,A(15,4),N,NC,T(20),SKB(20),AK(20,15),SV(
     110),SL(20),W(20),D(20,15),ALP(20,15),AA(20,15),V(20,15),SUMV(20),T
     2HETN,      Y(20,15),X(20,15),TF(20),XX(20,15),YY(20,15),FV(20),FL
     3(20),E(15,3),C(15,3),XF(20,15),EF(20,20)
      DO 5 J=1,N
      DO 3 I=1,NC
    3 ALP(J,I)=AK(J,I)/SKB(J)
    5 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE ABSFAC
C
      COMMON AAA,BBB,TLL,TUL,MC,A(15,4),N,NC,T(20),SKB(20),AK(20,15),SV(
     110),SL(20),W(20),D(20,15),ALP(20,15),AA(20,15),V(20,15),SUMV(20),T
     2HETN,      Y(20,15),X(20,15),TF(20),XX(20,15),YY(20,15),FV(20),FL
     3(20),E(15,3),C(15,3),XF(20,15),EF(20,20)
      DO 10 J=1,N
      DO 8 I=1,NC
C
C     TOTAL CONDENSER HAS A  K = 1.000
      AK(1,I)=1.0
    8 AA(J,I)=SL(J)/(AK(J,I)*SV(J)*EF(J,I))
   10 CONTINUE
      RETURN
      END

      SUBROUTINE MATBAL
C
      DIMENSION F(20),G(20)
      COMMON AAA,BBB,TLL,TUL,MC,A(15,4),N,NC,T(20),SKB(20),AK(20,15),SV(
     110),SL(20),W(20),D(20,15),ALP(20,15),AA(20,15),V(20,15),SUMV(20),T
     2HETN,      Y(20,15),X(20,15),TF(20),XX(20,15),YY(20,15),FV(20),FL
     3(20),E(15,3),C(15,3),XF(20,15),EF(20,20)
      N=N-1
      DO 100 J=1,N
      DO 100 I=1,NC
      D(J,I)=-XX(J,I)*FL(J)-FV(J+1)*YY(J+1,I)
      D(10,I)=0.0
  100 CONTINUE
      N=N+1
      DO 11 I=1,NC
      DO 8 J=1,N
      IF(J-1)1,1,3
    1 F(1)= -1./(1+AA(J,I))
      G(1)=F(1)*D(J,I)
      GO TO 8
    3 F(J)=1./(-(1.+AA(J,I))-AA(J-1,I)*(1.-W(J)/SL(J))*F(J-1))
      G(J)=(D(J,I)-AA(J-1,I)*(1.-W(J)/SL(J))*G(J-1))*F(J)
    8 CONTINUE
      DO 9 L=1,N
      IF(L-1)2,2,4
    2 V(N,I)=G(N)
      GO TO 9
    4 V(N-L+1,I)=G(N-L+1)-F(N-L+1)* V(N-L+2,I)
    9 CONTINUE
   11 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE THETA
C
      DIMENSION DCO(20),BCO(20)
      COMMON AAA,BBB,TLL,TUL,MC,A(15,4),N,NC,T(20),SKB(20),AK(20,15),SV(
     110),SL(20),W(20),D(20,15),ALP(20,15),AA(20,15),V(20,15),SUMV(20),T
     2HETN,       Y(20,15),X(20,15),TF(20),XX(20,15),YY(20,15),FV(20),FL
     3(20),E(15,3),C(15,3),XF(20,15),EF(20,20)
C
C     FOR THIS PROBLEM  F = 3.41
      FDT=3.41
      THET=0.0
    2 SUT=0.0
      DSUM=0.0
      DO 10 I=1,NC
      BDCA=V(N,I)*AA(N,I)/V(1,I)
      SUT=SUT+FDT*XF(I,3)/(1.0+THET*BDCA)
      DSUM=DSUM-BDCA*FDT*XF(I,3)/(1.0+THET*BDCA)**2
   10 CONTINUE
C
C     FOR THIS PROBLEM  D = 1.120
      THETN=THET-(SUT-1.120)/DSUM
      IF(ABS(THETN-THET)-2.E-5)15,15,20
   15 CONTINUE
      GO TO 40
   20 THET=THETN
      GO TO 2
   40 DO 50 I=1,NC
      DCO(I)=FDT*XF(I,3)/(1.+THETN*V(N,I)*AA(N,I)/V(1,I))
   50 BCO(I)=THETN*(V(N,I)*AA(N,I)/V(1,I))*DCO(I)
      DO 60 J=1,N
      SUMV(J)=0.0
      SLSUM=0.0
      SVSUM=0.0
      DO 55 I=1,NC
      SVSUM=SVSUM+(V(J,I)/V(1,I))*DCO(I)
      SLSUM=SLSUM+(AA(J,I)*V(J,I)/V(1,I))*DCO(I)
      GO TO 55
      WRITE(3,1112) I,SLSUM,SVSUM
 1112 FORMAT(6X,I4,'L=',F10.3,' V= ',F10.3)
   55 SUMV(J)=SUMV(J)+V(J,I)
      DO 56 I=1,NC
      X(J,I)=(AA(J,I)*V(J,I)*DCO(I)/V(1,I))/SLSUM
      Y(J,I)=((V(J,I)/V(1,I))*DCO(I))/SVSUM
   56 CONTINUE
   60 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE KBASE
C
      DIMENSION SUM(20)
      COMMON AAA,BBB,TLL,TUL,MC,A(15,4),N,NC,T(20),SKB(20),AK(20,15),SV(
     110),SL(20),W(20),D(20,15),ALP(20,15),AA(20,15),V(20,15),SUMV(20),T
     2HETN,       Y(20,15),X(20,15),TF(20),XX(20,15),YY(20,15),FV(20),FL
     3(20),E(15,3),C(15,3),XF(20,15),EF(20,20)
      DO 5 J=1,N
      SUM(J)=0.0
      DO 3 I=1,NC
    3 SUM(J)=SUM(J)+(X(J,I)*ALP(J,I)*EF(J,I))
      SKB(J)=1./SUM(J)
    5 CONTINUE
      RETURN
      END

      SUBROUTINE TEMPJ
C
      COMMON AAA,BBB,TLL,TUL,MC,A(15,4),N,NC,T(20),SKB(20),AK(20,15),SV(
     110),SL(20),W(20),D(20,15),ALP(20,15),AA(20,15),V(20,15),SUMV(20),T
     2HETN,       Y(20,15),X(20,15),TF(20),XX(20,15),YY(20,15),FV(20),FL
     3(20),E(15,3),C(15,3),XF(20,15),EF(20,20)
      DO 6 J=1,N
      T(J)=AAA/(ALOG(SKB(J))-BBB)
      WRITE(3,1111) J,T(J)
 1111 FORMAT(3X,I4,'TEMP= ',F10.3)
    6 CONTINUE
      RETURN
      END

      SUBROUTINE ENTHAL
C
      COMMON AAA,BBB,TLL,TUL,MC,A(15,4),N,NC,T(20),SKB(20),AK(20,15),SV(
     110),SL(20),W(20),D(20,15),ALP(20,15),AA(20,15),V(20,15),SUMV(20),T
     2HETN,       Y(20,15),X(20,15),TF(20),XX(20,15),YY(20,15),FV(20),FL
     3(20),E(15,3),C(15,3),XF(20,15),EF(20,20)
      DIMENSION H(20,15),HH(20,15),TOTH(20),HFL(20),HFV(20),ENTH1(20),EN
     1TH2(20),ENTH4(20),ENTH5(20),ENTH6(20),TOTHH(20)
      DO 26 J=1,N
      DO 24 I=1,NC
      H(J,I)=((C(I,1)+C(I,2)*T(J)+C(I,3)*T(J)**2)**2)
      HH(J,I)=((E(I,1)+E(I,2)*T(J)+E(I,3)*T(J)**2)**2)
   24 CONTINUE
   26 CONTINUE
      DO 1 J=1,N
      HFL(J)=0.0
```

```
      TOTHH(J)=0.0
      TOTH(J)=0.0
      HFV(J)=0.0
      DO 2 I=1,NC
      TOTH(J)=TOTH(J)+H(J,I)*X(J,I)
      TOTHH(J)=TOTHH(J)+HH(J,I)*Y(J,I)
      HFL(J)=HFL(J)+((C(I,1)+C(I,2)*TF(J)+C(I,3)*TF(J)**2)**2)*XX(J,I)
      HFV(J)=HFV(J)+((E(I,1)+E(I,2)*TF(J)+E(I,3)*TF(J)**2)**2)*YY(J,I)
    2 CONTINUE
    1 CONTINUE
      N=N-1
      DO 3 J=1,N
      ENTH1(J)=0.0
      ENTH5(J)=0.0
      ENTH6(J)=0.0
      DO 4 I=1,NC
      ENTH1(J)=ENTH1(J)+HH(J+1,I)*Y(J,I)
      ENTH5(J)=ENTH5(J)+HH(J+1,I)*XX(J,I)
      ENTH6(J)=ENTH6(J)+HH(J+1,I)*X(J,I)
    4 CONTINUE
    3 CONTINUE
      DO 5 J=2,N
      ENTH2(J)=0.0
      DO 6 I=1,NC
      ENTH2(J)=ENTH2(J)+HH(J+1,I)*X(J-1,I)
    6 CONTINUE
    5 CONTINUE
      DO 7 J=1,N
      ENTH4(J)=0.0
      DO 8 I=1,NC
      ENTH4(J)=ENTH4(J)+ HH(J+1,I)*YY(J+1,I)
    8 CONTINUE
    7 CONTINUE
      DO 9 J=2,N
C
C     FLOW RATES FOR THIS PROBLEM ONLY
      SV(1)=1.120
      SV(2)=2.688
      SL(1)=1.568
      SL(10)=2.290
      SL(J)=(SV(J)*(ENTH1(J)-TOTHH(J))+(W(J-1)-SL(J-1))*(ENTH2(J)-TOTH(J
     1-1))+FV(J+1)*(HFV(J+1)-ENTH4(J))+FL(J)*(HFL(J)-ENTH5(J)))/(TOTH(J)
     2-ENTH6(J))
      SV(J+1)=SV(J)+SL(J)-SL(J-1)+W(J-1)-FL(J)-FV(J+1)
    9 CONTINUE
   69 FORMAT(2X,'SL(J)=',F20.5,5X,'SV(J)=',F20.5)
```

```
      N=N+1
      DO 10 J=1,N
      WRITE(3,69)SL(J),SV(J)
   10 CONTINUE
      COND=(TOTHH(2)-TOTH(1))*SV(2)
      REBOIL=SL(N-1)*TOTH(N-1)-SV(N)*TOTHH(N)-SL(N)*TOTH(N)
      WRITE(3,52) TOTHH(2),TOTH(1)
   52 FORMAT(/2X,'VAP. ENTH. OFF 2 =',F12.3,2X,'LIQ. ENTH. OFF 1 =',F12.
     13)
      WRITE(3,51) COND,REBOIL
   51 FORMAT(//5X,'CONDENSER DUTY =',F12.2,' BTU/HR.',5X,'REBOILER DUTY

     1=',F12.2,' BTU/HR.'/)
      WRITE(3,11)THETN
   11 FORMAT(F10.7)
      RETURN
      END
```

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VITA

The author, Chorng Shyong Wang, was born on January 26, 1938 at Tainan, Taiwan, Republic of China. He attended elementary school and high school at Tainan. The author joined National Taiwan University in 1958 and obtained a B. S. Degree in Chemical Engineering in 1962. He then served in the Chinese Army Reserve for one year as a second lieutenant. He worked for Mobil China Allied Chemical Industries, Ltd at Miao-li, Taiwan from 1963 to 1965. He became a graduate student in the Chemical Engineering Department of the University of Missouri-Rolla in September, 1965.