

A SHORT-CUT METHOD FOR PREDICTING THE TOTAL
REFLUX PERFORMANCE OF DISTILLATION
COLUMNS HANDLING THREE PHASE
SYSTEMS

By

YUSUF HEKIM
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Bachelor of Science

Middle East Technical University

Ankara, Turkey

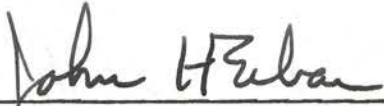
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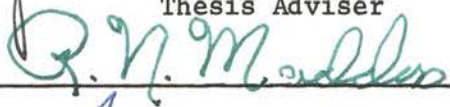
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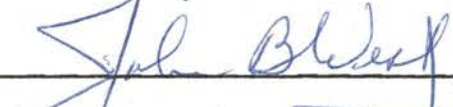
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Thesis Approved:



Thesis Adviser






Dean of the Graduate College

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PREFACE

This study was carried out to develop a short-cut method of predicting the minimum number of theoretical trays in distillation columns operating on feeds which can exhibit partial miscibility. These systems are usually encountered in the organic chemical industry. The method was applied to one binary and two ternary systems which exhibit heterogeneous azeotropic behavior. The method was developed specifically for single feed, two product distillation columns; but it can be easily extended to describe the behavior of various complex column configurations as multiple feeds and more than two products. This will lead to an increase in the computational time requirements.

Description of the thermodynamic behavior of the systems handled was critical to the solution of this problem. The Renon Non Random Two Liquid method of predicting liquid phase activity coefficients coupled with the Prausnitz model for the vapor phase fugacity was found to be the most successful method for predicting the vapor-liquid-liquid equilibria constants.

I would like to give my sincere appreciation to Prof. J. H. Erbar for his encouragement and valuable advice during this work. The financial assistance provided by the School of Chemical Engineering and Institute of International Education to carry out my studies are gratefully acknowledged. I would like to express my deepest appreciation to my parents for their support and enthusiasm.

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LIST OF SYMBOLS

Major Symbols

English Letters

a	-nonrandomness parameter in the NRTL approach
b	-moles of any component in the bottom product/unit time
B	-total moles of bottom product/unit time, second virial coefficient if subscripted
d	-moles of any component in the distillate/unit time
D	-total moles of distillate/unit time
f	-moles of any component in the feed/unit time, fugacity if superscripted
F	-total moles of feed/unit time
g	-Gibbs free energy in calories/gram mole
H	-enthalpy in calories/gram mole
K	-vapor-liquid distribution coefficient of any component
l	-moles of any component in liquid leaving any tray/unit time
L	-total moles of liquid leaving any tray/unit time
N	-minimum theoretical trays
P	-absolute pressure

English Letters (Continued)

r	-damping factor
R	-universal gas constant
T	-temperature
v	-moles of any component in vapor leaving any tray/ unit time
V	-total moles of vapor leaving any tray/unit time
x	-mole fraction of any component in liquid phase
y	-mole fraction of any component in the vapor phase
Z	-compressibility factor

Greek Letters

α	-relative volatility of any component based on heavy key
β	-Winn model parameter
ϵ	-Winn model parameter
γ	-liquid phase activity coefficient
ϕ	-vapor phase fugacity coefficient

Subscripts

A	-liquid phase A
B	-liquid phase B
b	-bottom product
d	-distillate
i	-component index
j	-component index
n	-tray index

Subscripts (Continued)

HK	-heavy key component
LK	-light key component
NK	-non-key component

Superscripts

L	-liquid phase
S	-saturation state
V	-vapor phase
o	-reference state
'	-effective value
-	-partial value

CHAPTER I

INTRODUCTION

Short-cut methods of predicting the performance of distillation columns have played an important role in the hydrocarbon processing industry. Using these calculations, the designer can quickly and easily evaluate the feasibility of a proposed separation. Because the thermodynamic behavior of typical hydrocarbon systems is more or less ideal, the short-cut methods yield excellent results.

In the organic chemical industry, systems which exhibit very highly nonideal behavior are encountered. These systems show azeotropic behavior, and heterogeneous azeotropic behavior is not uncommon. Heterogeneous azeotropic behavior is the condition when one vapor and two liquid phases exist simultaneously and the volatility of one of the components shifts from being more volatile to less volatile than some other component in the system. Because of the extremely complex thermodynamics involved in these systems and the computational difficulty of applying these thermodynamic methods in the usual design procedures, few calculational tools are available to predict the performance of systems which exhibit heterogeneous azeotropic behavior. As a result of the lack of these computational tools, even the simplest distillation system is completely and thoroughly evaluated in a laboratory column to determine the operational characteristics of a column performing a given separation. These experiments are tedious to perform, time consuming, and

as a result extremely expensive. The development of reliable methods for performing screening calculations on such systems could eliminate a significant amount of the laboratory experimentation required to assess the feasibility of a given separation.

The objective of this study was to develop a short-cut method which would reliably predict the separation that can be achieved for a highly nonideal system in a distillation column operating at total reflux. In addition, the method should reliably predict impossible separations, i.e. those separations in which azeotropic behavior is found, the minimum number of trays, and the product distributions resulting from the specified key component splits. While the short-cut methods are not widely used by the practicing engineer at this time, they serve a valuable purpose in that they allow the design engineer to quickly and easily evaluate the feasibility of a given separation. Further, the results of the short-cut calculations can provide valuable information about the parameters for tray-by-tray calculations of columns operating at finite reflux rates.

CHAPTER II

LITERATURE SURVEY

There are two distinct areas that must be considered in the development of a method for predicting the minimum number of theoretical trays in highly nonideal systems. First, one must consider the computational methods currently available. Secondly, the methods of predicting the thermodynamic behavior of these highly nonideal systems must be considered. This latter category involves both the equations to be used in the description of thermodynamic behavior of these systems and the availability of data which can be used to evaluate the necessary constants for the various models. In the following sections each of these areas is discussed.

Prediction of the Minimum Number of Trays

The minimum number of theoretical trays is that number of trays required to accomplish a given separation at total reflux. The condition of total reflux can be visualized in one of two ways: (1) No feed is introduced to the column and no products are withdrawn. The vapor leaving the top tray is totally condensed and returned to the column. The liquid leaving the bottom tray is completely vaporized and returned to the column. Under adiabatic conditions, the heat supplied to the reboiler is equal to the heat removed in the condenser. (2) The column has both finite feed and product rates. The liquid and vapor

flow rates inside the column are infinitely large compared to the entering feed or leaving product rates, so that the total reflux condition is practically satisfied. Under these circumstances, the condenser and reboiler duties are infinitely large.

The first case is the theoretical definition of the total reflux condition encountered in standard chemical engineering textbooks. This case is also represented in industrial practice as the start-up procedure for a distillation column. In this procedure, a small amount of feed is charged to the column. The reboiler heat supply is started and the overhead vapors are totally condensed and returned to the column. No products are withdrawn from the column. The second case is a convenient mathematical simulation of the theoretical condition. Certain advantages are derived from this description: (1) Standard tray-by-tray calculations can be adapted to total reflux calculations using this approach. (2) The designer can determine the product rates and compositions for a specified key component separation with a minimum of computational difficulty. (3) Visualization of the total reflux condition is somewhat easier.

Computational Methods

Two methods are currently available for predicting the minimum number of stages required to accomplish a given separation for systems with nonideal behavior. These procedures, graphical in nature, were reported by Ellis and Pearce (1), and Tanaka and Yamada (2). The Ellis and Pearce procedure relies on the use of a modified McCabe-Thiele diagram. In this approach, McCabe-Thiele diagrams are plotted for each of the binary pairs with equilibrium lines corresponding to

various compositions of the third component. A complex procedure of stepping off the stages using both binary x-y diagrams is required. Further, the method requires two different plots and interpolation between these plots. It is limited to systems containing a maximum of three components. The Tanaka and Yamada procedure uses a triangular diagram which relates the vapor and liquid compositions of the ternary system. Although it requires the use of only one diagram, it is limited to ternary systems as well. Most of the separations in the chemical processing industry involve more than three components. Thus, improved computational tools are required if the designer is to be able to predict the performance of distillation columns using the short-cut procedures.

Two computational methods have been developed for predicting the minimum number of theoretical trays for multicomponent systems which exhibit more or less ideal thermodynamic behavior. These are reported by Fenske (3) and Winn (4). Both methods were developed from an analysis of the behavior of distillation columns operating at total reflux. Their methods of development are similar; the models of describing the behavior of the equilibrium constants over the range of concentrations encountered in the column represent the major difference between the two.

The Fenske representation of the variation of the vapor-liquid equilibrium constants from the condenser to the reboiler is:

$$K_i = \alpha_i K_{HK} \quad (1)$$

In the application of Equation (1), the relative volatility α_i of the individual components is assumed to be constant over the range of

temperatures and compositions encountered in a distillation column. But, this assumption is not valid unless very narrow boiling range feeds are encountered, i.e. those feeds in which the difference between the boiling points of the lightest and heaviest components is quite small. Therefore the assumption is not applicable to wide boiling range feeds.

Recognizing the problems encountered with the Fenske equation, Winn developed an alternate expression to predict the minimum number of theoretical trays. The only difference between the Winn equation and the Fenske equation is the representation of the behavior of the equilibrium K values. The Winn equation is expressed as:

$$K_i = \beta_i (K_{HK})^{\theta_i} \quad (2)$$

In this approach, the variation of the logarithm of the equilibrium K values as a function of the logarithm of the K value of the heavy key is presumed to be linear over the entire column. This type of behavior has been demonstrated to be reasonably acceptable for hydrocarbon systems. This form of representing the relationship between equilibrium constants is more general and should be capable for further generalization than the Fenske model.

Thermodynamic Behavior

In the usual design procedure, the thermodynamic properties of the components in the mixture must be predicted by some form of a correlation. The properties that are of most interest in distillation calculations are the vapor-liquid equilibrium constants and enthalpies of the vapor and liquid phases. The latter are important when

considering standard tray-by-tray calculations for columns at operational reflux rates and when using these calculational procedures to predict the minimum number of trays. However, other tray-by-tray procedures can be developed to predict the minimum number of theoretical trays without using enthalpy data. For this reason, only vapor-liquid equilibrium K value prediction methods will be discussed.

There are many methods for predicting vapor-liquid equilibrium constants available in the literature. Three of the most recent methods were considered for use in the proposed distillation calculations. Two of them are based on the following expression as proposed by Prausnitz (5):

$$K = \frac{f^o \gamma}{\phi P} \quad (3)$$

Two different methods for predicting the liquid phase activity coefficient γ , were chosen. For multicomponent mixtures this coefficient is determined by the Two Liquid Theory as follows:

$$\ln \gamma_i = \frac{\sum_{j=1}^m t_{ji} G_{ji} x_j}{\sum_{\ell=1}^m G_{\ell i} x_{\ell}} + \sum_{j=1}^m \frac{G_{ij} x_j}{G_{1j} x_1} \left(t_{ij} - \frac{\sum_{r=1}^m t_{rj} G_{rj} x_r}{\sum_{\ell=1}^m G_{\ell j} x_{\ell}} \right) \quad (4)$$

In the Renon Non Random Two Liquid Theory (6):

$$t_{ji} = \frac{(g_{ji} - g_{ii})}{R T} \quad (5)$$

and

$$G_{ji} = \exp(-a_{ji} t_{ji}) \quad (6)$$

However, in the Smith-Palmer Theory (7):

$$t_{ji} = \ln \left(\frac{P_{ji}^s}{P_{ii}^s} \right) \quad (7)$$

and

$$G_{ji} = \exp \left(\frac{\Delta H_{ji} - \Delta H_{ii}}{R T} + t_{ji} \right) \quad (8)$$

Both theories were reported of being able to predict liquid phase separation by proper adjustment of the empirical parameters involved in Equations 5, 6, 7 and 8. The Smith-Palmer equation appears to have an advantage over the Renon equation since the parameters may be predicted from generalized correlations.

The remaining terms in Equation 3 can be evaluated using the approach of Prausnitz for the vapor phase fugacity coefficients.

Assuming that the virial equation of state is valid for the vapor phase, the vapor phase fugacity coefficient ϕ , can be expressed as (5):

$$\ln \phi = \frac{P}{R T} \left(B_{ii} + y_j^2 (2B_{ij} - B_{jj} - B_{ii}) \right) \quad (9)$$

The standard liquid phase fugacity f^0 is evaluated using the Poynting correction for the liquid phase and the virial equation of state for the vapor phase as follows (5):

$$\ln f^0 = \frac{P_{ii}^s B_{ii}}{R T} + \frac{-L_i}{R T} \left(P - P_{ii}^s \right) + \ln P_{ii}^s \quad (10)$$

An alternate approach was developed by Wellendorf (8). This approach is based mainly on the modification of Redlich-Kwong equation of state approach for the liquid and vapor phases by Soave (9).

The modified equation of state is given as follows:

$$P = \frac{R T}{v-b} - \frac{a(T)}{v(v+b)} \quad (11)$$

where a and b are expressed in terms of critical properties and the proposed mixing rules for mixtures. Letting $A = \frac{a P}{R^2 T^2}$ and $B = \frac{b P}{R T}$ Equation 11 can be rewritten as:

$$Z^3 - Z^2 + Z (A - B - B^2) - AB = 0.0 \quad (12)$$

If Equation 12 is solved for the liquid and vapor phase compressibility factors using the respective A and B values for each phase, and the following definitions of fugacity coefficients

$$\ln \frac{\bar{f}_i}{P x_i} = \int_{\infty}^v \left(\frac{1}{v} - \frac{1}{R T} \left(\frac{dP}{dn_i} \right)_{T, P, n_j} \right) dv - \ln Z \quad (13)$$

and vapor-liquid equilibrium constant

$$K_i = \frac{(\bar{f}_i / P x_i)^L}{(\bar{f}_i / P x_i)^V} \quad (14)$$

are used, the thermodynamic behavior of highly nonideal systems can be evaluated. The approach seems particularly attractive, since it requires fewer parameters to be evaluated from experimental data than the preceding two methods by Renon and Smith-Palmer.

CHAPTER III

THEORY AND BACKGROUND

The development of a short-cut method for predicting the minimum number of theoretical trays required to accomplish a specified separation for multicomponent mixtures which exhibit nonideal behavior such as phase-splitting and/or azeotrope formation will be outlined in this chapter. The development of the equations follows the development presented earlier by Fenske and Winn. However, their procedures must be modified to define the phase behavior and compositions of the liquid and vapor phases on a given tray in the column. A suggested method for applying the final equations developed in this section is also presented.

Method of Development

From the sketch of a distillation column shown in Figure 1, the pertinent material balance relationships are given as follows:

Overall material balance

$$F = D + B \quad (15)$$

Overall component material balance

$$f_i = d_i + b_i \quad (16)$$

These material balances are standard and apply to any distillation

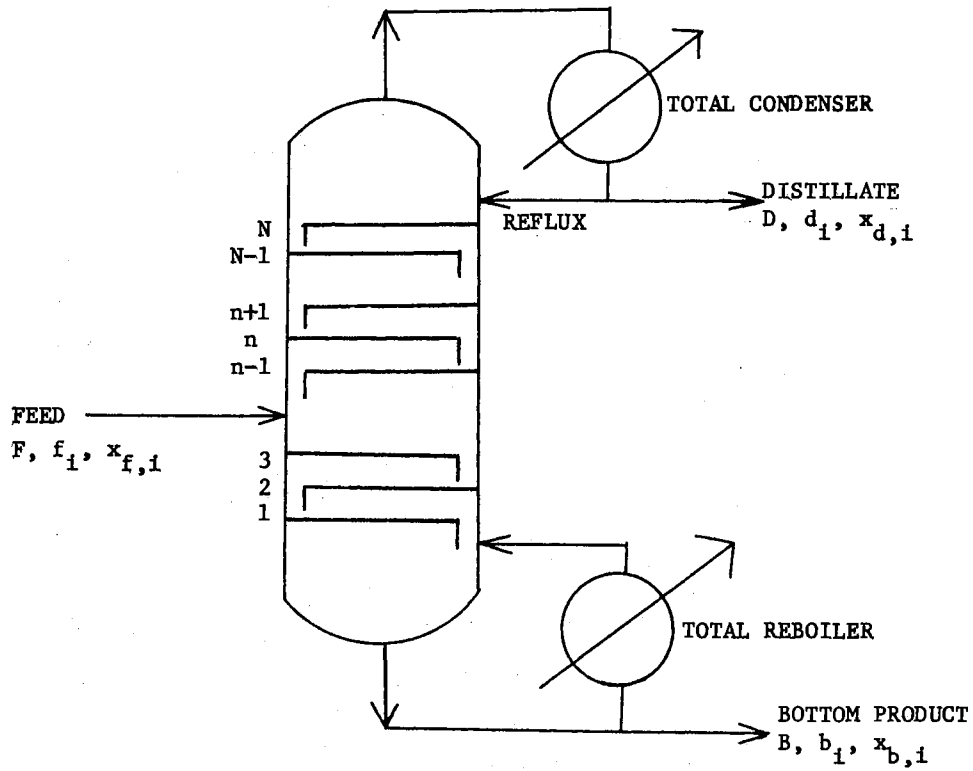


Figure 1. Schematic Diagram of a Simple Distillation Column

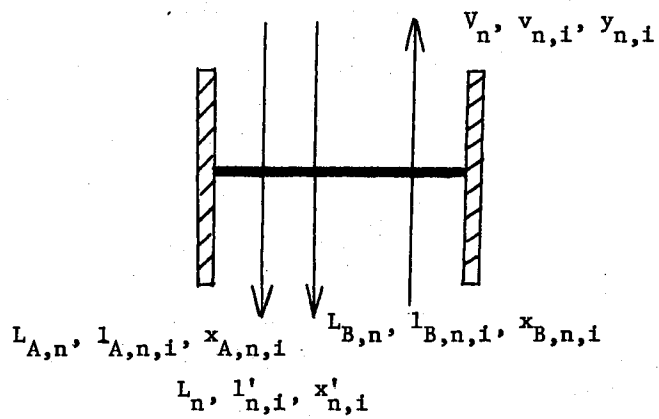


Figure 2. A Typical Tray which Exhibit Three Phase Behavior

column. The total material balance around a given tray and the condenser of the column is:

$$V_{n-1} = L_n + D \quad (17)$$

and a component material balance around the condenser and any tray in the column is:

$$v_{n-1,i} = l_{n,i} + d_i \quad (18)$$

or

$$V_{n-1} y_{n-1,i} = L_n x_{n,i} + D x_{d,i} \quad (19)$$

Under total reflux conditions, Equations 17 and 19 can be modified as follows:

$$V_{n-1} = L_n \quad (20)$$

$$V_{n-1} y_{n-1,i} = L_n x_{n,i} \quad (21)$$

From Equations 20 and 21 a significant result can be obtained

$$y_{n-1,i} = x_{n,i} \quad (22)$$

The vapor and liquid leaving any tray in the column are assumed to be in equilibrium with each other. This assumption allows the use of the following identity

$$y_{n,i} = K_{n,i} x_{n,i} \quad (23)$$

which relates the composition of the vapor to the composition of the

liquid leaving the tray. Using this definition and the total reflux condition (Equations 22 and 23), the composition of the distillate leaving the top tray can be related to the product leaving the bottom tray in the column, by the following equation:

$$x_{d,i} = K_N K_{N-1} \dots K_{n+1} K_n K_{n-1} \dots K_2 K_1 x_{b,i} \quad (24)$$

Designating the component whose concentration in the bottom product is to be controlled as the light key and the component whose concentration in the distillate is to be controlled as the heavy key, Equation 24 can be rewritten as follows:

$$\left(\frac{x_d}{x_b}\right)_{LK} \left(\frac{x_b}{x_d}\right)_{HK} = \left(\frac{K_{LK}}{K_{HK}}\right)_N \dots \left(\frac{K_{LK}}{K_{HK}}\right)_{n+1} \left(\frac{K_{LK}}{K_{HK}}\right)_n \left(\frac{K_{LK}}{K_{HK}}\right)_{n-1} \dots \left(\frac{K_{LK}}{K_{HK}}\right)_1 \quad (25)$$

To this point in the derivation, no assumptions have been made except the one regarding an equilibrium tray. The assumption of constant molal overflow or constant volatility has not been made at all.

At this stage, Fenske assumed that the ratio of the K values is constant over the entire column which leads to applying the constant relative volatility concept.

$$\left(\frac{x_d}{x_b}\right)_{LK} \left(\frac{x_b}{x_d}\right)_{HK} = \alpha_{LK}^N \quad (26)$$

However, using the Winn approach for describing the behavior of equilibrium K values over the column, Equation 25 can be rewritten as:

$$\left(\frac{x_d}{x_b}\right)_{LK} \left(\frac{x_b}{x_d}\right)_{HK}^{\theta_{LK}} = \beta_{LK}^N \quad (27)$$

or it can be simplified using the light and heavy key splits as:

$$\left(\frac{d}{b}\right)_{LK} \left(\frac{b}{d}\right)_{HK} e_{LK} \left(\frac{B}{D}\right)^{1-e_{LK}} = \beta_{LK}^N \quad (28)$$

At this point in the derivation, several decisions must be made. The material balance equations require that the liquid streams leaving a given tray be treated as a single stream, not as several liquid streams each having a different composition. If there are two liquid phases leaving a tray, the total liquid stream composition must be used under total reflux conditions. However, the thermodynamic calculation procedures, to function satisfactorily, require consideration of the possibility of the existence of two liquid phases with different compositions. This means that the two procedures are not compatible unless an artificial method of determining the total composition of the two liquid streams leaving the tray is developed, or a complex set of equations applicable to three phase systems under total reflux is developed. The former approach of computing the total stream composition of the two streams leaving the tray was chosen. This approach also requires that an effective equilibrium K value between the vapor and the combined liquid streams be calculated.

From material balance definitions, the composition of a single stream which is equivalent to the two real streams leaving the tray can be developed as follows:

$$x'_{n,i} = \frac{L_{A,n}}{L_n} x_{A,n,i} + \left(1 - \frac{L_{A,n}}{L_n}\right) x_{B,n,i} \quad (29)$$

Recognizing the fact that the vapor must be in equilibrium with both liquid phases leaving a given tray, a pseudo-equilibrium K value

can be defined as follows:

$$y_{n,i} = K'_{n,i} x'_{n,i} \quad (30)$$

Using Equations 29 and 30 a system which exhibits three phase behavior can be translated into a pseudo system which exhibits two phase behavior with a pseudo-equilibrium K value evaluated from the combination of Equations 29 and 30.

$$K'_{n,i} = \frac{K_{A,n,i} K_{B,n,i}}{\left(\frac{L_{A,n}}{L_n}\right) K_{B,n,i} + \left(1 - \frac{L_{A,n}}{L_n}\right) K_{A,n,i}} \quad (31)$$

The equations developed for total reflux can be applied to any mixture which exhibits three phase behavior. However, the necessity of describing the variation of the K values of the individual components over the column still remains. A reasonable assumption would be that Winn model will apply to the description of these pseudo K values. Thus, the modified Winn equation would take the following form:

$$K'_i = \beta'_i (K'_{HK})^{\epsilon'_i} \quad (32)$$

Certainly, the validity of this assumption should be questioned since azeotropic behavior is encountered in the majority of the three phase systems. If it is practically satisfied over the entire column, the minimum number of theoretical trays can be calculated from the specified feed composition and the two key component splits by the following equation:

$$\left(\frac{d}{b}\right)_{LK} \left(\frac{b}{d}\right)_{HK} \left(\frac{B}{D}\right)^{1-e'_{LK}} = \beta'_{LK} \quad (33)$$

Procedure of Application of Proposed Method

The equations developed in the preceding section can be applied to distillation calculations at total reflux as follows:

(1) Specify the feed composition, expected column pressure, and the desired light and heavy key component splits.

(2) Perform the appropriate equilibrium calculation on the feed such as bubble point, dew point, or flash.

(3) Based on the K values calculated for the feed, estimate the relative volatilities α'_i of individual components from the K'_i values.

(4) Predict the minimum number of theoretical trays for the specified key component separations.

(5) Predict the non-key component product distributions based on the preceding calculated information, replacing a non-key for the light key component in Equation 26.

(6) Perform bubble point calculations on both the distillate and bottom product streams.

(7) Compute the pseudo vapor-liquid equilibrium constants both at the top and at the bottom trays of the column using the individual equilibrium K values calculated during the bubble point calculations.

(8) Apply Equation 2 both to the top and the bottom trays of the column to estimate the β' and e' values for every component based on the heavy key.

(9) Perform the minimum number of stages calculation using Equation 33 with the total product rates computed in step 5.

(10) Recompute the product distributions and compare them with the assumed rates of every component present. If there is no significant difference between the assumed and calculated product rates, the calculations are terminated. If the agreement is not satisfactory, return to step 3.

This procedure is an application of both Fenske and Winn models to predict the minimum number of theoretical trays for a column handling systems which may exhibit heterogeneous azeotropic behavior. This combined application is necessary because the vapor-liquid equilibrium constants are highly composition dependent. The approximate composition of the terminal streams must be known before the equilibrium K values can be predicted for these terminal streams. Thus, the Fenske equation is used to obtain an initial estimate of these product compositions. Then, the Winn equation is employed to refine these estimates and ultimately, through a trial and error procedure, arrive at a final solution to the problem.

In theory, the top tray temperature should be predicted by a dew point calculation on the distillate composition, since the top tray in the distillation column is the last tray that performs a separation on the distillate. However, when considering dew point calculations in mixtures which may form two liquid phases, they will not properly determine the presence of these two distinct phases except in unusual circumstances. Furthermore, the dew point calculation will not predict the relative quantities of each phase that should appear at an equilibrium tray. If Equation 31 is to be used, the relative quantities of

each phase present must be known to predict the pseudo-equilibrium K values. Thus, the bubble point calculation was selected as the proper calculation to be performed at the top tray of the column, since it will predict the relative amounts of the phases present and allow estimation of the pseudo-equilibrium values. If the Winn model is able to predict correctly the variation of the K' values over the column, no significant differences should be noted between using the dew point or the bubble point calculation at the top tray.

In dealing with highly nonideal systems which can exhibit heterogeneous azeotropic behavior, several allowances must be made for the variation of the K' values. Some typical behavior is shown in Figure 3 where the hypothetical K' value behavior for components A, B, C, D, and E are plotted as a function of the heavy key component K' value. Components D and E azeotrope with each other, but they do not azeotrope with the heavy key. Components B and C also azeotrope with each other, but not with the heavy key. The behavior of component A is unusual. It azeotropes with components B, E, and the heavy key.

A plot similar to Figure 3 can be helpful in choosing components to be used as the light and the heavy keys. For example, if component A was selected as the light key component and the specified light and heavy key splits were such that the azeotropic point would be crossed, an impossible computational situation would result. This would be observed by the short-cut method predicting a negative number of minimum theoretical trays, or the distillate temperature being higher than the temperature of bottom product. However, components D or E could be selected as the light key component without any computational difficulty. The effect of the azeotropes between components D and E and between B and C is not known.

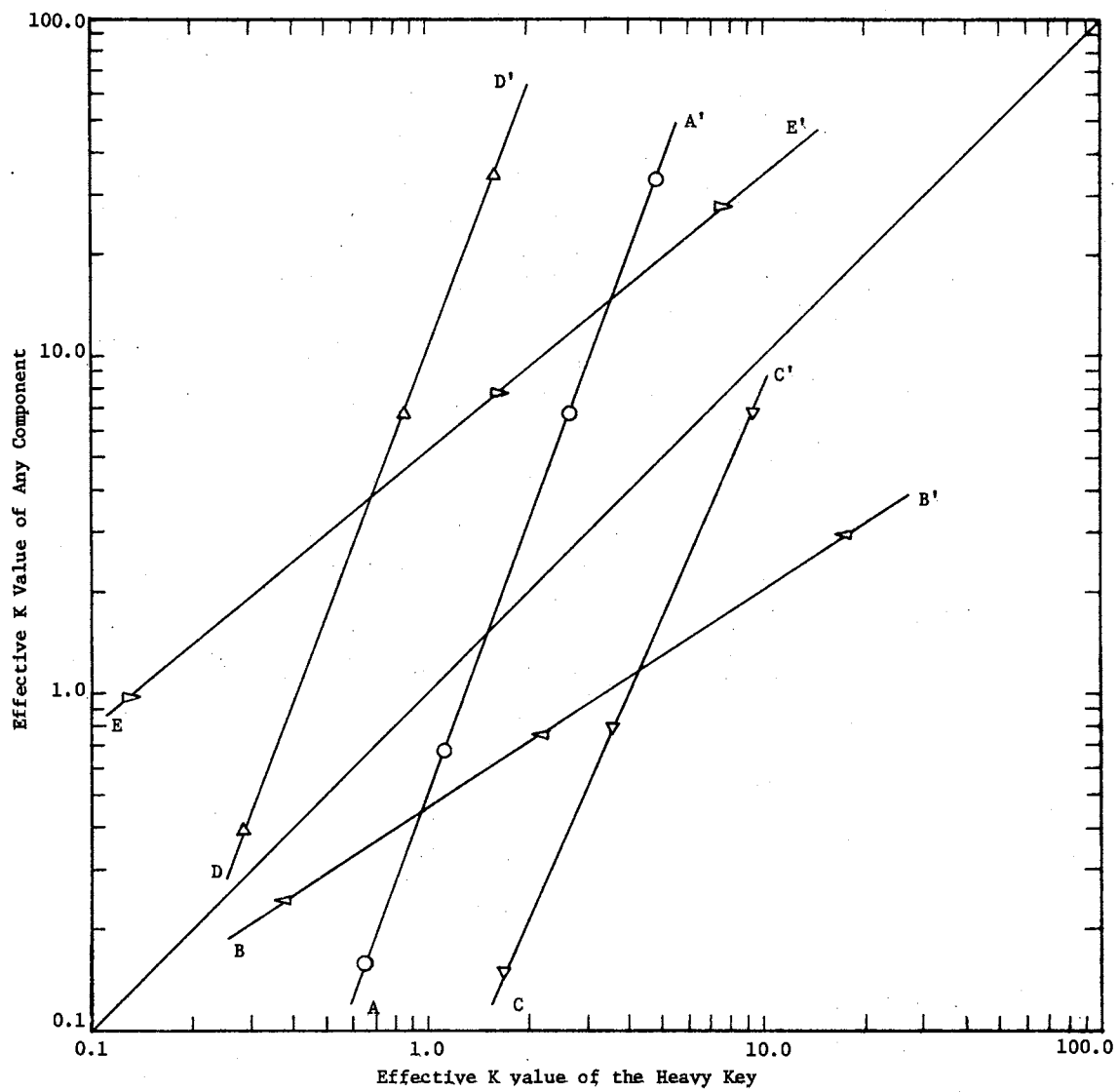


Figure 3. Typical Effective K Value Behavior Encountered in Multicomponent Organic Mixtures

Model Validation

There are two major ways of evaluating a given theoretical method:

(1) Substantiate the model by experimentation or (2) Compare the model with the results of other investigators and with sound theoretical predictions. In this study, the second approach was chosen. There are few results of minimum theoretical stage predictions available in the literature. The alternate method of evaluating the proposed procedure required the development of a tray-by-tray calculation for total reflux conditions. The procedure uses the bottom product composition predicted by the short-cut method as a starting point. From the earlier development, the vapor leaving a given tray is in equilibrium with the liquid or liquids leaving that tray. Likewise, the liquid entering the tray is equal in composition to the vapor leaving that tray. Then, by performing successive bubble point calculations on the liquid or liquids leaving any given tray in the column, the total reflux condition can be simulated mathematically. This procedure can be extended for any number of trays, however, it will not guarantee that the distillate composition predicted by the short-cut method will be calculated exactly.

The estimated composition of the vapor leaving two successive trays using the tray-by-tray procedure will usually cross the distillate composition predicted by the short-cut method. An interpolation scheme can be used to determine exactly the minimum theoretical trays required to accomplish the specified separation. Note that the short-cut procedure plays an important role in this calculation since the terminal stream compositions are used as the starting point for the tray-by-tray procedure.

CHAPTER IV

RESULTS AND DISCUSSION

Thermodynamic Property Predictions

Two ternary systems which are known to exhibit three phase behavior were chosen for the evaluation of the short-cut method. These systems were selected due to the availability of adequate binary and ternary vapor-liquid equilibrium data in the literature which would allow the evaluation of the various methods for predicting the equilibrium K values. As mentioned earlier, at least three methods of predicting the phase behavior of highly nonideal systems are available. These methods were all evaluated. The best method was found to be the Renon-Non Random Two Liquid approach combined with the Prausnitz et al. (10) procedure for predicting the vapor phase fugacity coefficients. The problems with the Smith-Palmer and Soave modified Redlich-Kwong methods were: (1) Binary interaction parameters evaluated for the Smith-Palmer method, when applied to the ternary systems, yielded values that were far beyond reality. These unreasonable values led to impossible computational situations within the program and completely unrealistic results for the ternary systems studied. (2) The Soave modified Redlich-Kwong approach would not adequately predict the observed presence of the two liquid phases. This problem may have been due to errors involved in the liquid phase compressibility factors predicted

by this approach. Because of these problems, neither the Soave approach, nor the Smith-Palmer approach were considered further.

Renon and Prausnitz (6) have presented binary interaction parameters for the various binary systems used in this study. Poor performance of the thermodynamic prediction procedures in the form of unrealistic results in bubble point temperatures and phase compositions in the short-cut method led to the revision of these parameters. The procedure applied was a scanning operation in which the values of the empirical parameters were varied over specific ranges and the absolute and percentage errors in the predicted K values with total system pressure were compared visually. The predicted K values and total system pressure based on the revised parameters were in better agreement with the experimental data than the ones based on the original parameters for three binaries. An error analysis of these new parameters is summarized in Table I. Two binaries which show azeotropic behavior, one binary with heterogeneous azeotropic behavior, and two other binaries were tested using the new parameters for prediction of azeotropes and phase-split behavior. The results were found satisfactory.

Short-Cut Method

After the thermodynamic prediction problems had been solved, the proposed short-cut method was evaluated from several different aspects. Three factors were considered in this evaluation: (1) Ease and reliability of convergence to a solution. (2) Ability to predict the feasibility of a proposed separation in a multicomponent mixture with

TABLE I
NRTL LIQUID PHASE ACTIVITY COEFFICIENT PARAMETERS WITH
THEIR ASSOCIATED PERCENT ERRORS

Binary system studied	$g_{12}-g_{22}$	$g_{21}-g_{11}$	a_{12}	Error% in K_1	Error% in K_2	Error% in P	Ref. No.
Water-Ethyl alcohol	1075.0 (976.0)	100.0 (88.0)	0.40 (0.30)	1.3 (2.2)	2.9 (6.5)	1.1 (2.3)	12
Water-Ethyl acetate	2415.0 (2510.0)	790.0 (1335.0)	0.35 (0.40)	3.5 (43.6)	3.4 (2.3)	2.3 (4.4)	14
Ethyl alcohol-Ethyl acetate	250.0 (301.0)	310.0 (322.0)	0.30 (0.30)	9.9 (11.3)	4.3 (2.0)	1.2 (1.1)	11
Acetic acid-Ethyl acetate	-35.0	55.0	0.30	15.5	4.8	3.4	13
Acetic acid-Water	20.0	175.0	0.30	1.1	3.5	1.3	15

() Original Prausnitz-Renon parameters and errors in K values and total pressure.

nonideal thermodynamic behavior. (3) The differences between the results obtained from the short-cut method and the tray-by-tray calculations.

During the early stages of evaluating the proposed method, oscillatory behavior of the terminal stream compositions for the non-key components was observed. In some cases, this oscillatory behavior was so pronounced that the calculations would never converge to a final solution or led to extended solution time requirements. To circumvent these convergence problems, a linear combination of the predicted and originally assumed distillate rates was used. The rule developed in this study is given by Equation 34:

$$d_{i,new} = r d_{i,predicted} + (1-r) d_{i,assumed} \quad (34)$$

The value of r can be varied between zero and unity. The selection of this factor was critical in that it would strongly effect the rate of the solution and whether or not a solution can be obtained. Several different values of r were used in a single problem. For damping factors of 0.2 and 0.6 no solution was obtained to the problem. Figure 4 shows this oscillatory behavior without a convergence possibility. Cases using factors 0.3, 0.4, 0.5 converged rapidly to a solution and gave essentially the same number of minimum theoretical stages.

From studies like the one summarized in Table II, the optimum value for the damping factor appeared to be about 0.5. This value was used in all further studies without any computational difficulty with respect to the convergence of the problem. It should be noted that using this factor would slow down the solution where values close to unity should have been used. However, a factor of 0.5 will probably

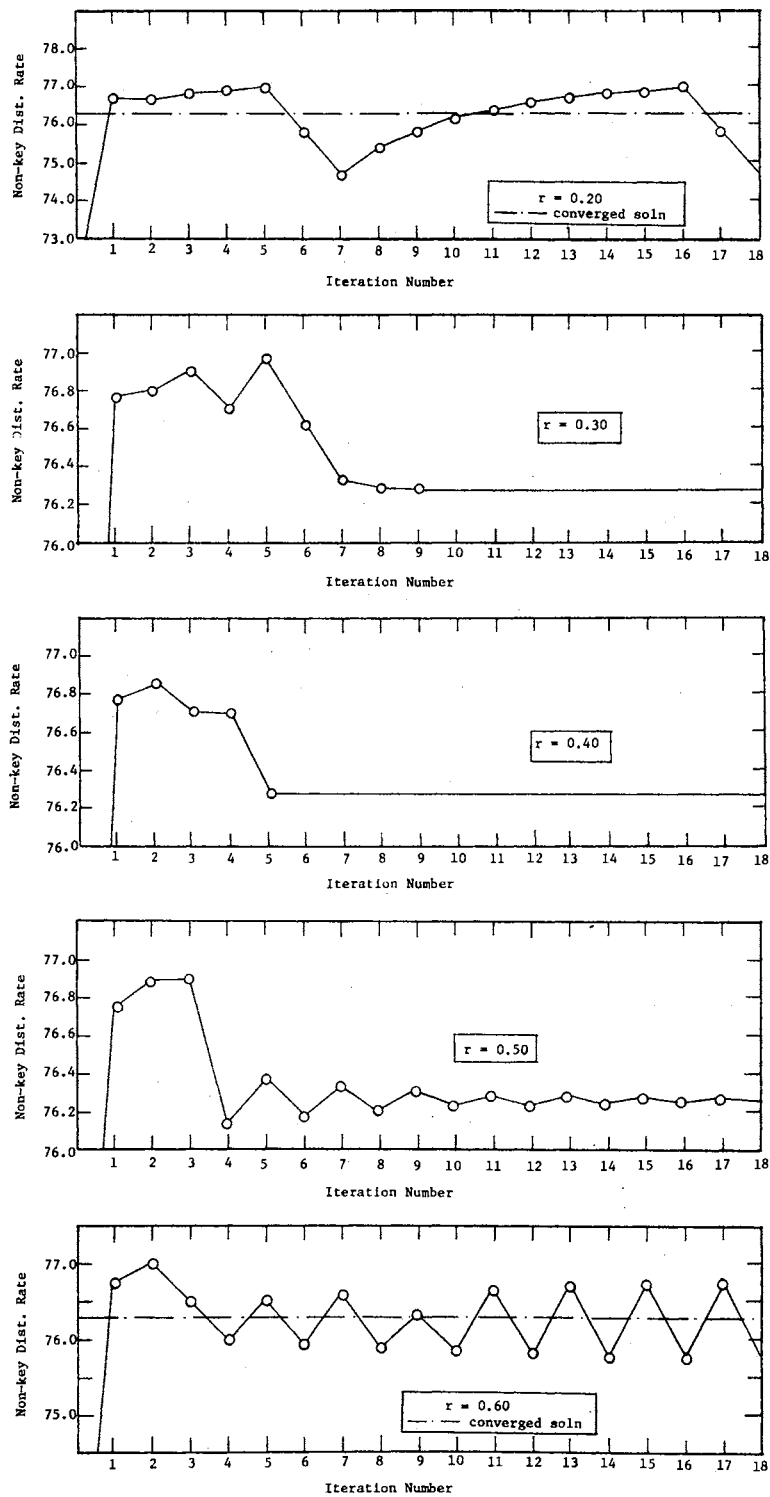


Figure 4. The Effect of Various Damping Factors on the Rate of Convergence of the Solution

preclude the possibility of extreme oscillatory behavior in the difficult problems where the problem could be expected to diverge and never reach a final answer.

TABLE II
THE EFFECT OF DAMPING FACTOR ON THE SOLUTION
TIME REQUIRED IN A 360/65 IBM COMPUTER

Damping factor used	Execution time required	Theoretical stages predicted
0.50	38.7 sec	20.4
0.40	15.4 sec	20.6
0.30	23.1 sec	20.1

Some other convergence problems were encountered in the bubble point calculations performed (16). These usually came from inconsistency problems in the thermodynamic prediction procedures. Using the values for the binary interaction parameters evaluated in this study eliminated most of these convergence problems. The revised values of these parameters gave excellent representation of the binary data including the points at which liquid phase separation and azeotrope formation would occur.

The determination of the feasibility of a given separation appears to be quite satisfactory. A number of cases were run which yielded

either a negative minimum number of theoretical trays or a separation in which the distillate temperature was greater than the bottom product temperature. Neither of these results is technically feasible. This condition would clearly indicate that the program is able to predict the infeasible separations correctly.

For those cases where feasible splits were specified, a positive number of theoretical trays was predicted and the distillate temperature was less than the bottom product temperature. These results are in accord with the observed behavior of real columns, the theory, and most calculational procedures. Further, the problem investigated by Ellis and Pearce with the dehydration of acetic acid was applied to the short-cut method developed in this study. The result obtained is in excellent agreement with the one reported by Ellis and Pearce.

The results of the short-cut method were compared with the tray-by-tray calculation results in Table III. There exists quite a good agreement between the results of the short-cut method and the tray-by-tray calculations performed. However, a certain amount of error is inherent in determining the exact number of theoretical trays required to accomplish a specified separation based on the tray-by-tray results. In a theoretical sense, there cannot be less than one theoretical stage. Therefore, a linear interpolation scheme was devised to determine the approximate number of fractional trays required to accomplish a given separation. When the short-cut distillate composition was bracketed between two successive theoretical trays, the vapor composition leaving the tray was assumed to be a linear function of the tray number.

The short-cut procedure predicts a minimum number of trays which is generally higher than the rigorous tray-by-tray computations.

TABLE III

SUMMARY OUTPUT OF CASES STUDIED WITH THE SHORT-CUT METHOD
IN COMPARISON WITH THE TRAY-BY-TRAY CALCULATIONS

System studied	W-HAc-EtAc	W-HAc-EtAc	W-HAc-EtAc	W-EtOh-EtAc	W-EtOh-EtAc	W-EtOh-EtAc
Light key	W	W	W	EtAc	EtAc	EtOh
Heavy key	HAc	HAc	HAc	EtOh	EtOh	W
$(d/b)_{LK}$	34.8	99.0	3.0	1215.0	94330.0	10.0
$(b/d)_{HK}$	2.8×10^{10}	99.0	9.0	10.0	12.0	1.33
N_{sh}	15.2	9.6	3.5	5.8	16.0	2.0
N_{tt}	16-17	7-8	2-3	4-5	9-10	1-2
$(d/b)_{NK}$	65.5	27300.0	77.0	0.667	0.335	104.4
$T_{top}^{\circ K}$	343.9	344.1	345.5	344.4	344.1	343.6
$(L_A/L)_{top}$	0.93	0.50	0.66	1.00	1.00	0.92
$T_{bot}^{\circ K}$	390.2	390.8	382.4	358.9	364.2	351.2
$(L_B/L)_{bot}$	1.00	1.00	1.00	1.00	1.00	1.00

W: water, HAc: Acetic acid, EtAc: Ethyl acetate, EtOh: Ethanol
sh: short-cut method, tt: tray-by-tray calculations

Thus, the short-cut procedure results are generally conservative and will lead the design engineer to reduce the contingency factors that are applicable.

The difference in the results between short-cut method and tray-by-tray calculations can be explained by referring to Figures 5 and 6. These figures represent the typical variation between effective equilibrium K values as evaluated using the modified Winn model for the short-cut method and the tray-by-tray computation results. The values predicted by use of the Winn model fell within the expected range of the tray-by-tray results with some discrepancy as summarized in Table III. Except at the points approaching azeotropic points, the effective K values predicted by the tray-by-tray procedure are higher than those predicted by the short-cut method in general. Because of this difference, the minimum number of theoretical trays predicted by the tray-by-tray procedure should be expected to be smaller than that predicted by the short-cut method. However, from an analysis of Figures 5 and 6, the conclusion can be reached that the modified Winn model will satisfactorily represent the behavior of the effective equilibrium constants over the entire column under total reflux conditions. This result is particularly useful in view of the fact that the systems handled exhibit highly nonideal thermodynamic behavior.

The recommended procedure for predicting the exact number of minimum theoretical stages is:

- (1) Predict the minimum theoretical trays using the proposed short-cut method and estimate the terminal stream compositions.
- (2) Use the tray-by-tray calculations with a linear interpolation to determine the desired distillate composition for the final

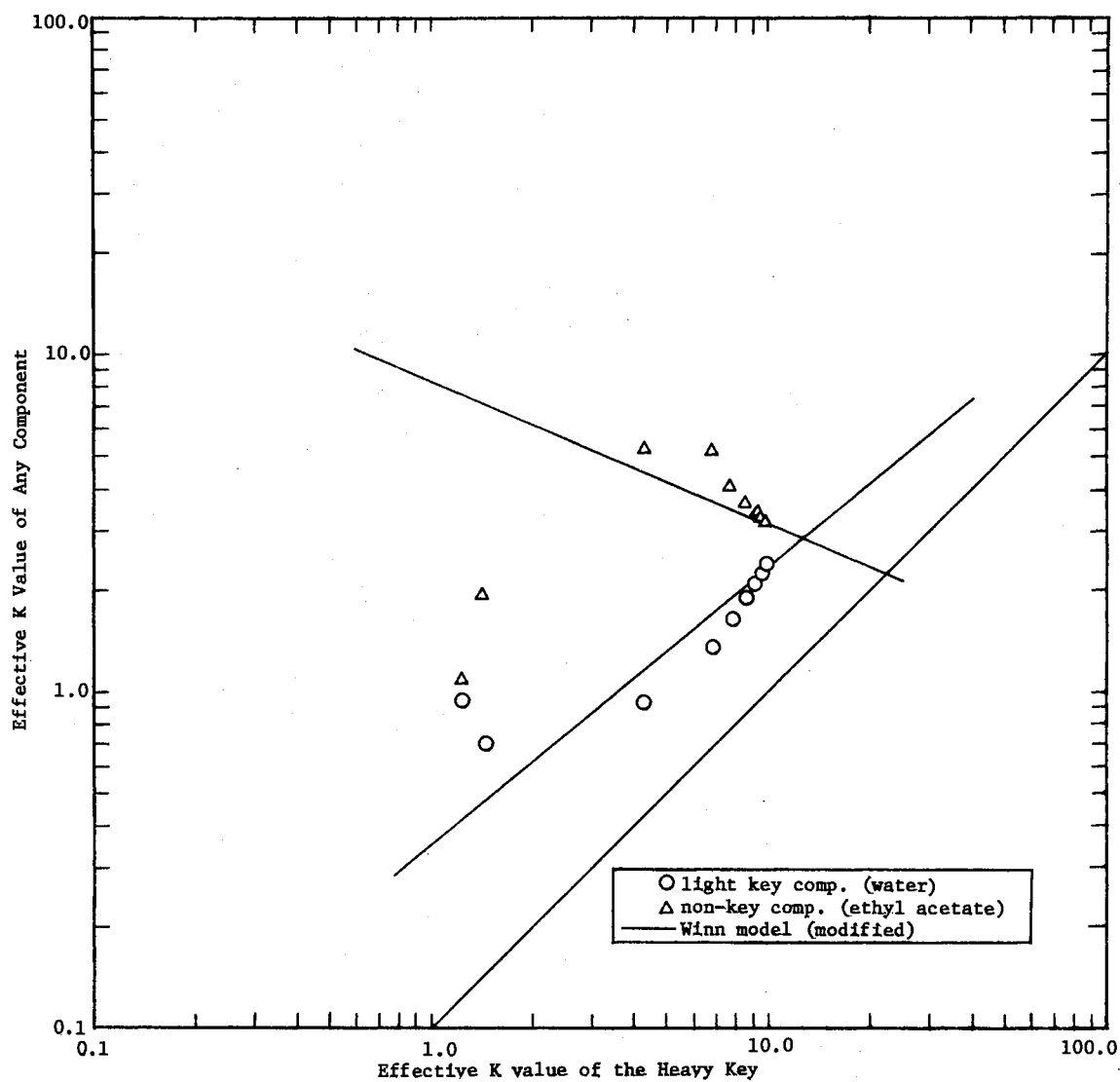


Figure 5. K Values from Short-Cut and Tray-by-Tray Results for the Water-Acetic Acid-Ethyl Acetate Ternary System

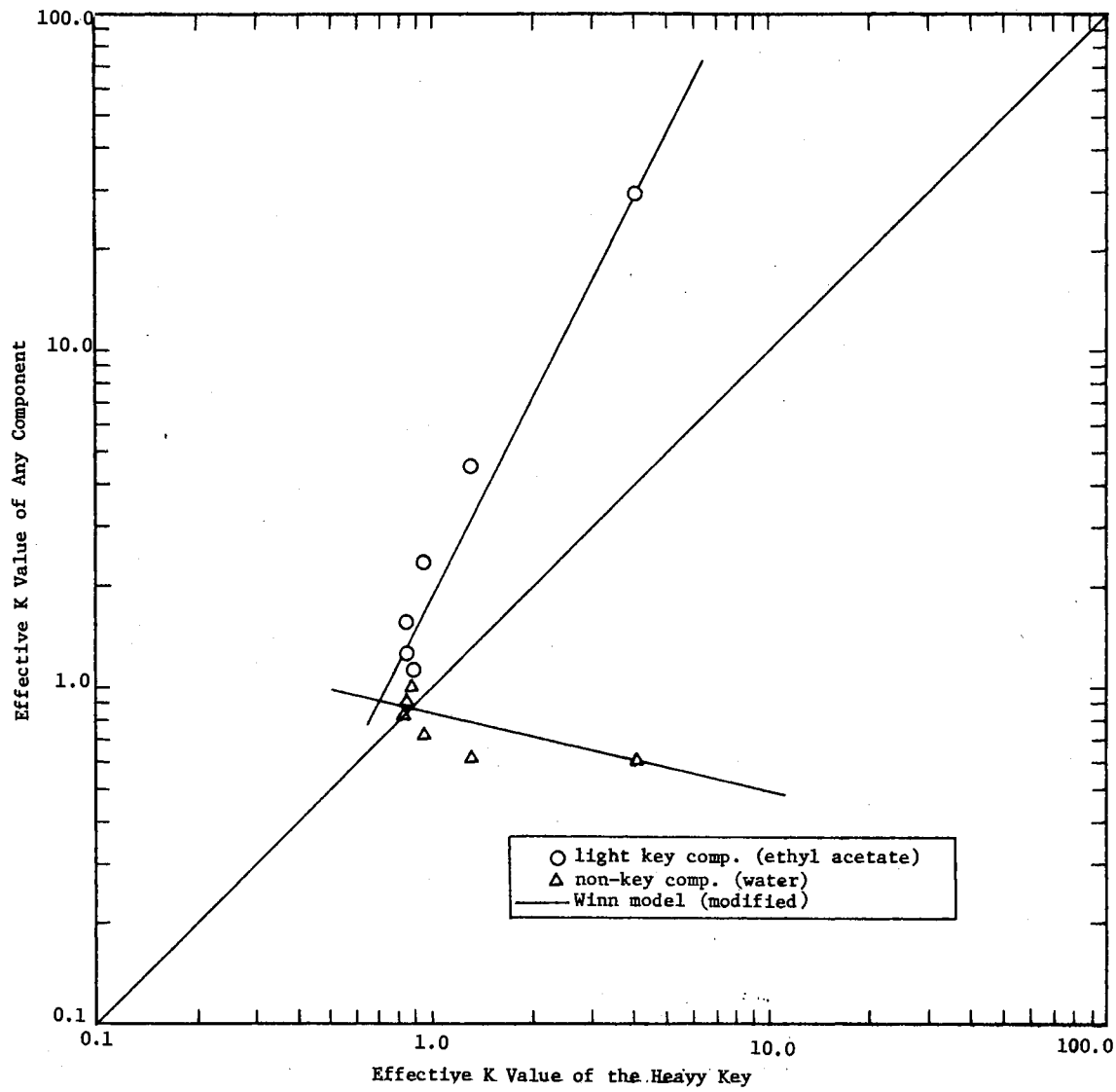


Figure 6. K Values from Short-Cut and Tray-by-Tray Results for the Water-Ethanol-Ethyl Acetate Ternary System

estimation of minimum theoretical trays to accomplish the given separation.

In this approach the modified Winn model furnishes the starting point for the tray-by-tray computations. This is essential since the terminal stream compositions are unknown due to the uncertainty in the distributions of all the non-key components between product streams. Therefore, all the non-key component distributions should be known as a rough estimate at the time the calculations are initiated for the tray-by-tray procedure. Time can be saved by investigating the feasibility of a given separation in a multicomponent mixture by the short-cut method before undertaking more rigorous computations.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

A short-cut method has been developed that describes the performance of distillation columns operating at total reflux on mixtures containing components which exhibit highly nonideal thermodynamic behavior. The procedure is an adaptation of the Winn method to systems which may form homogeneous and heterogeneous azeotropes.

The method of solution used in this study will reliably predict the minimum number of theoretical trays required to accomplish a given separation, the non-key component distributions between product streams, and the number of phases present; or it will indicate that an impossible separation between the key components has been specified. The results of the short-cut method are in good agreement with the tray-by-tray calculations and results reported by other investigators which employed more elegant procedures.

The recommended procedure for the design engineer in the evaluation of minimum theoretical trays for nonideal mixtures will be to use initially the short-cut method to determine the feasibility of the specified separation, and to estimate the minimum number of theoretical trays required with the resulting terminal stream compositions satisfactorily. Tray-by-tray calculations at total reflux can then be used to further refine the estimate of the minimum number of theoretical

trays and the related product distributions for individual components present.

The procedure developed can be easily extended to multiple feed, multiple product columns using the techniques reported by Joyner et al. (17). This extension would only involve additional programming effort; no computational difficulty should be anticipated due to this extension.

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VITA ✓

Yusuf Hekim

Candidate for the Degree of

Master of Science

Thesis: A SHORT-CUT METHOD FOR PREDICTING THE TOTAL REFLUX PERFORMANCE OF DISTILLATION COLUMNS HANDLING THREE PHASE SYSTEMS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Ankara, Turkey, October 17, 1949, the son of Mr. and Mrs. Kemal Hekim.

Education: Graduated from Middle East Technical University, Ankara, Turkey in Spring, 1971 with a Bachelor of Science in Chemical Engineering; attended Graduate School in Middle East Technical University, Ankara, Turkey; came to the U.S.A. as an exchange student in August, 1972; completed requirements for the Master of Science degree in Chemical Engineering at Oklahoma State University in December, 1973.

Membership in Professional Societies: Member of Turkish Institute of Chemical Engineers.

Professional Experience: Graduate research assistant in the Polymer Research Inc., Middle East Technical University, 1971-1972; graduate research student and graduate teaching assistant in the Chemical Engineering curriculum, Oklahoma State University, 1972-1973.