TERNARY EFFICIENCIES IN A LABORATORY

DISTILLATION COLUMN

By

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PREFACE

The need for liquid-vapor contacting devices has increased significantly in recent years. The efficiency of liquid-vapor contacting is an important factor in the design of separation equipment, particularly fractionating columns. There is a lack of reliable efficiency data for multicomponent systems. Until such data are obtained, fractionating columns will continue to be uneconomically designed.

An Oldershaw laboratory distillation column was used in hopes of obtaining over-all column efficiency data for the ternary system of benzene, toluene, and p-xylene. The column was operated with the feed entering on the top tray. Over-all column efficiencies were not obtained. The difficulty encountered was believed to be due to fractionation occurring above the feed section. Equipment changes were recommended so that over-all column efficiencies might be obtained.

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CHAPTER I

INTRODUCTION

Stagewise contacting of vapor and liquid is a valuable tool of the chemical engineer. The stage efficiency is a measure of the degree of approach to vapor-liquid equilibrium. The efficiency is an important factor in the behavior of a contacting tower, and in many cases the efficiency varies significantly from the ideal performance.

The need for separation apparatus, particularly fractionating columns, has accelerated in recent years. Efficiency data is a valuable factor in the design of such apparatus. However, most of the efficiency data are unreliable, and efficiency data are difficult to generalize so as to predict column behavior. Accordingly, the cost of separation apparatus is higher than necessary, since equipment must be overdesigned to allow for the engineers' ignorance of column behavior.

Comprehensive investigations have been devoted to isolate the factors contributing to the performance of vapor-liquid contacting apparatus. These studies have been devoted primarily to binary systems. However, most industrial problems involve mixtures of several components. The lack of published information on multicomponent systems prompted the study of the efficiencies of the components in a ternary system.

The objective of this study was to determine experimentally the component efficiencies of a ternary system in a laboratory column. In particular, the following goals were set:

1. Construct an apparatus which may be used to obtain over-all column efficiency data.

2. Determine the efficiency for each component of a ternary system in a laboratory distillation column.

3. For each of the three binary systems associated with the three components, determine if the presence of the third component affects the binary efficiencies of the other two components.

CHAPTER II

LITERATURE SURVEY

Despite continued heavy investments in separation equipment, the
number of publications on tray and over-all column efficiencies is pro-
portionately small. One reason for this is that many design engineers
still rely on outdated methods and previous experience to predict ef-
ficiencies. Another reason is the research activity conducted by
Fractionation Research, Inc. (FRI), which receives co-operative support
from several industrial companies. The results from FRI are not made
public.

Efficiency research is usually classified according to binary or
multicomponent mixtures and experimental or correlation studies. Probably
the most important and encompassing work in recent years was carried out
under the sponsorship of the American Institute of Chemical Engineers'
Research Committee. The A. I. Ch. E. publications (39) provide a con-
venient dividing point for discussing efficiency research prior to the
publications and the most recent research efforts. Until very recently,
little research was conducted in the area of multicomponent distillation.

Lewis (21, 25) made one of the earliest attempts to define efficiency.
Lewis proposed the definition of over-all column efficiency as the number
of theoretical plates necessary for a given separation divided by the
number of actual plates required to perform the same separation, or

$$E^O = \frac{N_T}{N_A} \tag{1}$$

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Only terminal conditions are required for the Lewis efficiency. Thus over-all column efficiency is easily applied and is valuable as a design factor.

Murphree (21, 26) used a simplified expression for the instantaneous mass transfer to a vapor bubble rising through the liquid on a plate to define a vapor-phase plate efficiency. He expressed the approach to equilibrium on a tray as the ratio of actual change in vapor concentration through the tray to the change which would have occurred if the vapor had actually reached a state of equilibrium with the liquid leaving the tray, or

$$E_{MV}^{O} = \frac{y_i - y_{i-1}}{y_i - y^*} \tag{2}$$

Murphree assumed that the compositions were the same at all points on a plate. However, in many instances there are considerable differences in the compositions of the liquid at various points on a plate. Therefore, the conditions assumed are usually not satisfied for the whole plate. The Murphree derivation is based on fundamental mass-transfer concepts, but experimental data have indicated that the simple rate equation used is no more than a crude expression of the phenomena involved.

Murphree also developed a plate efficiency equation employing liquid-phase compositions. He expressed the efficiency as a mole fraction ratio,

$$E_{ML}^{O} = \frac{x_i - x_{i-1}}{x_i - x_i^*} \tag{3}$$

An assumption made in the derivation of equation (3) was that the vapor composition does not vary with liquid depth on a plate. Thus any mass-transfer process on a bubble-type plate corresponding to equation (3) is

difficult to picture.

A comparison of the efficiency definitions illustrates that the Lewis efficiency is easier to apply, since only terminal conditions are required for evaluation. In the calculation of the Murphree efficiency, plate-to-plate compositions are required. The Murphree equations have very little fundamental basis, and the Lewis efficiency has no fundamental basis.

The experimental determination of plate efficiency is the best means to obtain a plate efficiency. Early investigations provided an incoherent picture of the data. The major reason was the large number of unknown factors that were involved in the study of efficiencies.

A brief description, though not a comprehensive survey, of the experimental efficiencies found by early investigators follows. Gadwa (21) studied six binary systems on a small four-plate bubble-cap column. He concluded that the Murphree plate efficiency was substantially independent of the concentration of the mixture and of the vapor velocity. Brown (21) and Gunness (21) independently found a Murphree plate efficiency greater than 100% for large commercial gasoline stabilizers. Lewis and Smoley (21), using a ten-plate column with rectangular bubble caps, calculated plate efficiencies between 60% and 75% for the benzene-toluene and the benzene-toluene-xylene systems. Using the same column, Carey (21) reported an average Murphree efficiency of 70% for the benzene-toluene system.

Plate efficiency experiments have been conducted on small columns by several investigators. Collins and Lantz (9), in testing the suitability of the Oldershaw column as a research tool, found the fractionating efficiency nearly independent of throughput. The over-all column efficiency

was approximately 60% for the n-hexane-methylcyclohexane system. Berg and James (5) used a 60-plate Oldershaw column for a number of binary systems. They calculated an over-all column efficiency of about 60% for varying reflux ratios.

From their studies in transient distillation, Armstrong and Wilkinson (2) reported a constant Murphree efficiency of 72%. These efficiencies were determined on a four-inch 21-plate column for varying feed compositions of the benzene-carbon tetrachloride system.

As was implied earlier, the correlation of plate efficiency data is difficult because of the large number of unknown conditions. However, some correlations are helpful in the estimation of plate efficiency.

Walter and Sherwood (21) developed one of the most important of the early efficiency correlations. The correlation was based on the derivation of the Murphree equation and centered around the resistance to mass transfer. Walter and Sherwood separated the over-all mass transfer resistance into liquid and vapor film resistances. This correlation was developed only for bubble-cap plate columns.

Drickamer and Bradford (12) studied plant test data from refinery fractionating columns to arrive at a correlation. They expressed the over-all column efficiency as a function of the feedstock molal average viscosity. In their work Drickamer and Bradford found that the length of the liquid path across the tray was important.

O'Connell (27) was able to extend somewhat the Drickamer-Bradford correlation by the inclusion of the relative volatility. O'Connell related the over-all plate efficiency to feed viscosity and relative volatility. The use of relative volatility in the correlation implies that the plate efficiency of various components in a multicomponent

mixture is not the same.

A study of the Drickamer and the O'Connell methods indicates that neither method involves a basic mass transfer approach. The correlations are simple to use. Since only two of the many variables involved are considered, the result is necessarily an over-simplification of a complex problem.

In an effort to examine the effect of the many variables on efficiency, the A. I. Ch. E. Research Committee undertook a five-year study of bubble-tray efficiencies. A five-year experimental program at several universities and the evaluation of private commercial data were included in the study. As a result, the Bubble-Tray Design Manual (39), a method of prediction of fractionation efficiency, was published.

The A. I. Ch. E. method (39) postulated that there are four main factors affecting the magnitude of tray efficiency. These factors are listed as follows:

1. Rate of mass transfer in the vapor phase

2. Rate of mass transfer in the liquid phase

3. Degree of liquid mixing on the tray

4. Amount of liquid entrainment between trays.

The Research Committee developed separate correlations for each of these factors and showed how they can be used to predict the efficiency.

A brief summary of the A. I. Ch. E. method shows the advantages and limitations of this technique. The principal usefulness of the method is for systems for which no previous experience exists. However, in many instances physical properties cannot be predicted or measured conveniently to permit use of the A. I. Ch. E. method. Also, the correlation is limited to large diameter columns. Strictly speaking, the prediction

method applies only to binary systems, since no tests were made with multicomponent systems.

Efficiency research since the A. I. Ch. E. publication can be divided into the following classes:

1. Critical examination and extension of the A. I. Ch. E. method.

2. Correlations using the empirical approach.

3. Experimental study of selected effects.

4. Multicomponent efficiency research.

Swanson and Gerster (33) examined the A. I. Ch. E. correlation from the standpoint of column diameter. They found that an Oldershaw column gave a higher efficiency than large-diameter sieve-tray columns. Swanson and Gerster thus concluded that the A. I. Ch. E. method did not apply to sieve-tray columns having holes of small diameter.

Strand (31) attempted to explain why some experimental efficiencies were lower than the efficiencies predicted by the A. I. Ch. E. method. He suggested that the reason for poor agreement was that part of the vapor and liquid were by-passing each other. With the use of a liquid by-passing effect, Strand found reasonable agreement between the experimental and predicted efficiencies.

Eduljee (13) criticized the method of data analysis of the A. I. Ch. E. correlation. One aspect was that the predicted A. I. Ch. E. efficiency did not agree well with the A. I. Ch. E. data. Also, the A. I. Ch. E. data were based on air-water runs, which are not typical of distillation systems. Eduljee reported that the prediction method correlated only the Delaware data, and not that from the other universities.

Many attempts to derive correlations based solely on the so-called fundamental mass transfer models have been unsuccessful. The difficulty

lies in the visualization of a model that adequately describes the phenomena occurring on a plate. There is also the question as to the possibility of solving the equations derived from the model. For these reasons, recent correlations have been based on the empirical rather than the fundamental approach.

Chaiyavech and Van Winkle (8) developed an empirical correlation from system properties. System properties include relative volatility, surface tension, viscosity, density, and diffusivity. Chaiyavech studied the effects on a one-inch column with seven different binary systems. The resulting equation satisfactorily correlated the experimental data and selected sets of literature data.

Finch and Van Winkle (19) observed the effect of design and operating variables on the methanol-air-water system. They correlated plate efficiency as a function of gas and liquid mass velocity, hole diameter in the perforated plate, weir height, and tray length.

In yet another correlation study, English and Van Winkle (18) developed a correlation derived from experimental data in the literature. A multiple-regression analysis was used to express plate efficiency as a function of design, operating, and system variables for binary systems.

While the above correlations represent detailed investigations of plate efficiency, one must remember that the generalization of efficiency is a basic problem. Thus these correlations are not expected to reproduce all experimental data.

Several investigators have studied the effect of foaming in experimental determinations of plate efficiency. Work in this area was stimulated by the use of separate phase correlations in the A. I. Ch. E. method. Ellis and Rose (17) suggested that the limitations of the

A. I. Ch. E. method were due to different foam structures in various aqueous and organic mixtures. They showed that the addition of a small amount of methanol to an air-water system immediately changed the appearance of the froth. A large number of very small bubbles formed, and the plate efficiency showed a significant increase. In contrast, the addition of methanol to organic systems did not measurably affect the plate efficiency.

Other investigators observed the effect of the surface tension of components on efficiency. If the surface tension for the more volatile component is lower than the surface tension for the less volatile component, foaming will be present. For the reverse case, foaming will be absent. Ellis and Bennett (14) and Ellis and Contractor (15) found that efficiencies increased with foaming systems compared with non-foaming systems. For mixtures that do not foam, Ellis and Legg (16) found that the difference in surface tension of the components did not affect the efficiency obtained. Zuiderweg and Harmens (38) studied the affect of surface tension in the foaming range. In the spray regime, Bainbridge and Sawistowski (3) found results different from the data published by Zuiderweg.

The work described above indicates that efficiency prediction methods do have limitations, and that perhaps the best way to determine the efficiency is experimentally.

In another area Van Wijk and Thijssen (36) investigated the effect of composition on tray efficiency. They reported that the efficiency dropped off sharply at the extremes of the composition range. Their results compared favorably with those reported by Zuiderweg and Harmens. Danckwerts (20) suggested that this effect may have been caused by added

turbulence in the extreme composition range. Danckwerts assumed the absence of temperature gradients at the extremes, in contrast to the presence of temperature gradients over the remainder of the composition range. These studies indicate that more research should be conducted to develop means for handling cases in the extreme composition range.

Only very recently has efficiency research been extended to include multicomponent systems. Few generalizations have been made in this field, and yet fewer cases of experimental study have been undertaken.

Toor and Burchard (35) undertook a study of multicomponent efficiencies to explore conditions under which a simple extrapolation of binary data was possible. They combined equations for diffusion in a ternary gas mixture with a film model as a first approximation to the multicomponent problem. They were thus able to relate the multicomponent efficiency for each species in terms of the binary efficiency of a plate. They found the following results in considering a ternary mixture of components 'A,' 'B,' and 'C.' If species 'C' suffered no diffusional interactions in the presence of 'A' and 'B,' its efficiency was the same as the binary efficiency of the plate. If component 'A' showed minor interaction effects, its efficiency varied slightly from the binary efficiency. Strong interaction effects exhibited by component 'B' resulted in an efficiency that deviated significantly from the binary efficiency.

The limited results presented by Toor and Burchard indicate that there is a need for research in multicomponent systems, especially for those systems for which diffusion theory predicts strong interactions.

Walsh (37) added comments on multicomponent efficiencies. He proposed that when two components are similar and one is different, the

efficiencies of the similar components will be low. The efficiency of the dissimilar component will be close to that of the binary efficiency.

Gerster (20) reflected on the use of the A. I. Ch. E. tray efficiency methods for multicomponent mixtures. He reported that the A. I. Ch. E. method could be used in certain instances. If each of the binary pairs in a multicomponent mixture has about the same gas-phase diffusivity, then the multicomponent gas-phase efficiencies will equal the binary efficiencies. In another case, if two given components comprise nearly all of the mixture, then the two given components will also have an efficiency equal to their binary efficiencies. However, in the general case, each of the binary pairs have unequal gas-phase diffusivities. The computation of the efficiencies is then quite complex.

Holland and others (23, 34) developed a method for determining plate efficiencies from operating data. The objectives of their work were twofold. One objective involved the determination of sets of efficiencies from field tests for each of several operating conditions. From the efficiencies obtained, the efficiency at any intermediate set of operating conditions could be obtained by use of a correlation or by interpolation. The second objective was concerned with the design of new units utilizing the efficiencies obtained on similar units. The method supposes that the composition of the distillate, or bottoms, and the temperature on each plate are known. The usual specifications, such as feed condition and number of plates, are also assumed known.

The calculational procedure of Holland makes use of a modified vapor efficiency, defined as

$$E^o_{ji} = \frac{y_{ji}}{Y_{ji}} \tag{4}$$

where

$$Y_{ji} = K_{ji} x_{ji} \tag{5}$$

Subscript 'i' refers to the component and 'j' refers to the plate number. K_{ji} is evaluated at the temperature of the liquid, having composition x_{ji}, leaving the plate. A set of E^O_{ji} must be selected such that the sum of the y_{ji} is unity, or from (4) and (5),

$$\sum_{i=1}^{c} E^O_{ji} K_{ji} x_{ji} = 1 \tag{6}$$

Also, the E^O_{ji} must be chosen so that the calculated values of b_i/d_i from the Thiele-Geddes equations agree with the specified values. A measure of the accuracy of the assumed set of E^O_{ji} is given by the ratio

$$\theta = \frac{(b_i/d_i)_{specified}}{(b_i/d_i)_{calculated}} \tag{7}$$

The problem reduces to finding a set of E^O_{ji} such that simultaneously equation (6) is satisfied and that equation (7) reduces to θ equal to unity for each component.

The following equation is used in the selection of E^O_{ji} values to agree with the specifications:

$$E^O_{ji} = \beta_j \bar{E}^O_i \tag{8}$$

β is a plate factor and $\bar{E}^O_i$ is the component efficiency. The values of β and $\bar{E}^O_i$ are determined by a Newton-Raphson solution to equations (6) and (7).

Taylor (34) has observed that the vaporization efficiencies, and consequently the component efficiencies, for hydrocarbon systems are usually close to unity.

The literature review presented here describes most of the

previous work that is pertinent to this thesis. Only the method of Holland has been developed sufficiently to permit the calculation of multicomponent efficiencies. Unless one is intimately familiar with the detailed mechanics of Holland's method and the techniques used to program it, he will encounter several problems in trying to use the method. For this reason and since no other methods were immediately available, the present project utilizes a method developed in this thesis for obtaining efficiencies.

CHAPTER III

THE PROPOSED METHOD FOR DETERMINING EFFICIENCIES

Virtually all of the available studies on efficiency are based on
binary systems. For binary systems, the component efficiencies are
simply related. In particular, the Murphree equation can be used to
show that the plate efficiencies for both components in a binary system
are the same.

The problem of determining the efficiencies in a multicomponent
system has received little attention. There is no simple way to relate
plate efficiencies as there is in a binary system. Very little work has
been devoted to determine the effect that the presence of additional
components has on the efficiency of a given component or components.

The use of the concept of separation efficiency permits the calcu-
lation of distillation column behavior relatively easily. The over-all
column efficiency proposed by Lewis (25) and the plate-efficiency
concepts of Murphree (26) have very little mass-transfer basis. However,
the concept of efficiency serves as a measure of the transfer between
phases on plates in a column. Both the plate and over-all column ef-
ficiencies are useful in the respect that the efficiencies are independent
of the detailed mechanism of mass and heat transfer between phases.
These efficiencies apply to all types of plates, or separation stages,
and columns.

Distillation column behavior can be calculated from the efficiency

concept and a knowledge of the behavior of an ideal column. The ideal column is chosen so that the phases leaving the contacting stages are in physical and thermal equilibrium. Ideal column behavior is calculated solely from material balances, enthalpy balances, and phase equilibrium relationships.

For the general case, the ideal and the actual columns will not have the same separating ability. A basis is needed so that the two columns can be compared. One basis for comparison is the assumption of equal reflux rates and product concentrations for differing number of plates. This basis was used by Lewis in defining over-all column efficiency. However, this choice leads to difficulties for multicomponent systems. The ideal column cannot yield the same product compositions as those obtained from the actual column, unless the column efficiencies are the same for all components. However, this case is rather unlikely. Another possible basis is equal product rates and reflux rates for differing number of plates. Other combinations are also conceivable. Thus, picking a basis is difficult, expecially for generalization to multicomponent mixtures.

The proposed method utilizes the concept of an over-all column efficiency, similar to the definition by Lewis. The method is based on a separation efficiency concept. The separation efficiency for a column will be defined as the ratio of theoretical plates, N_T, to actual plates, N_A, that give the same split for a given component,

$$E = \frac{N_T}{N_A} \tag{9}$$

Here the split for a component is defined as the ratio of moles in the distillate product to moles in the bottoms product for that component,

d/b. For 'i' components in a multicomponent mixture, there will be 'i' efficiencies, one corresponding to each component.

The basis for comparison of the ideal and actual columns for the proposed method is the assumption of the same split for a given component for differing numbers of plates. The basis is described in the following manner. From experimental results the split for each component can be calculated. In the calculation of the theoretical separation of the ideal column, distillate and bottoms product rates identical to the experimental values will be assumed. The product rates and assumed number of theoretical plates will be applied to a tray-by-tray program to obtain the product compositions for the ideal column. The split for each component, for a given number of theoretical plates, can then be calculated from the product compositions and rates,

$$\frac{d}{b} = \frac{x_D D}{x_B B} \qquad\qquad (10)$$

In general, an assumption of 'N' theoretical plates will not yield the same split for a component as that separation obtained experimentally. This is usually the case since the number of plates must be an integer for a tray-by-tray program. For these cases, a graphical technique is useful for determining fractional values of plates. Different values for the calculated split for each component can be obtained by assuming different values of N_T. Figure 1, a plot of the calculated split versus the required number of theoretical plates, illustrates this technique. There will be a curve for each component in the mixture.

The efficiency for each component can be calculated using Figure 1. The assumption that provided the basis for determining the efficiency was the same split for the ideal and actual columns,
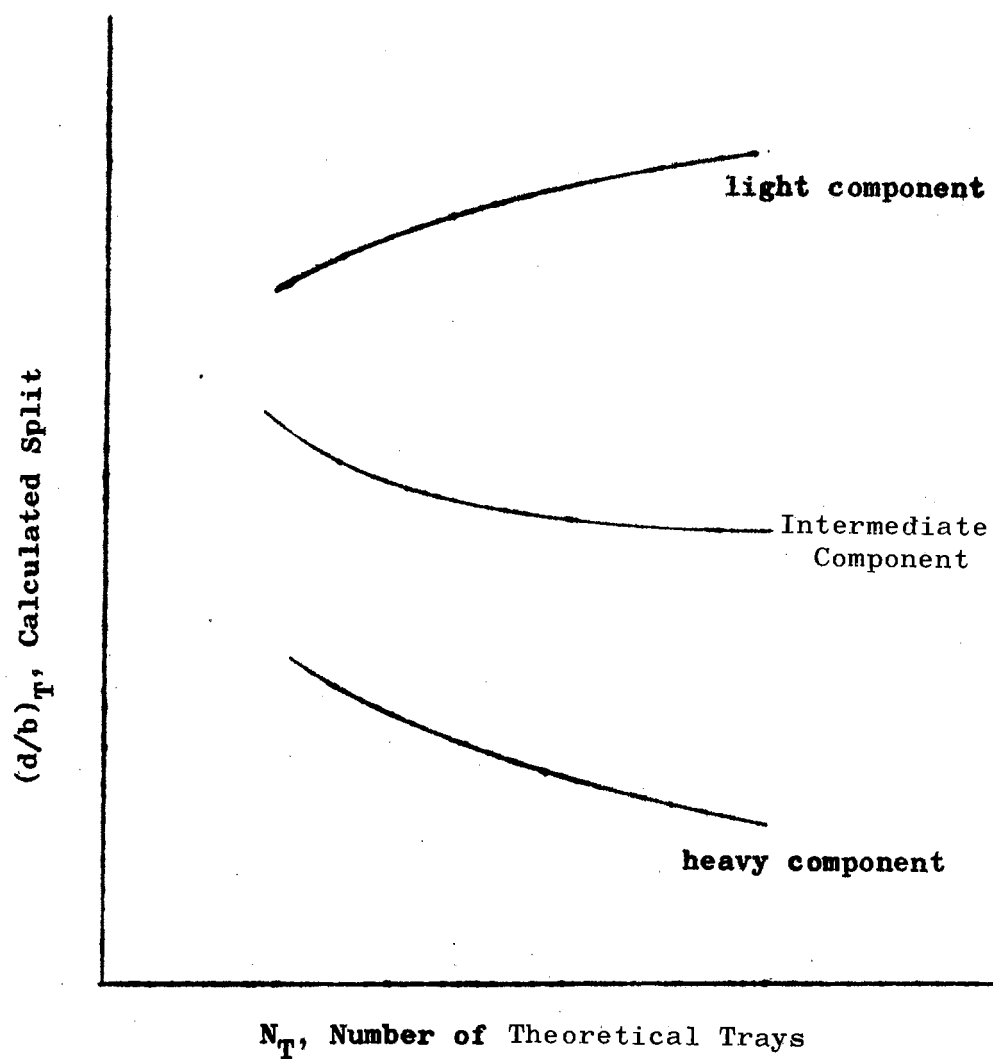
Figure 1. Calculated Splits from Tray-by-Tray Program

$$\left(\frac{d}{b}\right)_T = \left(\frac{d}{b}\right)_A \tag{11}$$

The value of N_T corresponding to the actual split can be determined from Figure 1. According to the definition of efficiency, the over-all column efficiency for a component is found using equation (9).

A tray-by-tray program written by Burman (7) was used to calculate the separations for the ideal column. The program was developed from Ball's modification (4) of Rose's relaxation technique (28). The tray-by-tray procedure uses the relaxation method, which starts with assumed initial tray compositions, tray temperatures, and vapor profiles. The column is traced through transient behavior to a steady-state solution.

Accurate efficiency data can be obtained only if accurate equilibrium and enthalpy data are available. The benzene-toluene-p-xylene system was chosen for this investigation, since these components are considered to form nearly ideal mixtures at low pressures. At these low pressures the nonidealities of the vapor and liquid phases can be neglected. For this reason, the use of the benzene-toluene-p-xylene system permits the application of ideal equilibrium and enthalpy values.

However, the data used for the tray-by-tray program should be as accurate as possible. The use of ideal data will introduce an error in the final plate compositions given by the program, since the system mixture is not really ideal, but only considered nearly ideal. An equation was sought by which the nonideality of the vapor and the liquid could be accounted. An equation that adequately accounts for departure from ideal solutions or mixtures in the liquid and vapor phases is presented by Stuckey (32),

$$K = \frac{1}{\Theta} \frac{P^O}{P} \frac{\gamma^L}{\gamma^V} \tag{12}$$

γ^L and γ^V are activity coefficients for the liquid and vapor phases, respectively. θ is an imperfection pressure correction term, a quantity used to factor out the pressure effects in the derivation of the activity coefficients. Equation (12) was used to calculate the equilibrium, or K, values for each component. As a check, these values were compared with ideal or Raoult Law equilibrium values. The results from both methods agreed closely. The K-values from equation (12) were regressed as a function of temperature for the tray-by-tray program,

$$K = A + BT + CT^2 + DT^3 \tag{13}$$

Saturated vapor enthalpy values were taken from A. P. I. Research Project 44 data (29). The vapor was considered as an ideal gas at one-atmosphere pressure. The component enthalpies were combined to obtain the mixture enthalpy,

$$H^V = \sum y_i H_i^V \tag{14}$$

The saturated liquid enthalpy was obtained by subtracting the heat of vaporization from the saturated vapor enthalpy,

$$H_i^L = H_i^V - H_{vap_i} \tag{15}$$

Heats of vaporization were calculated from the Clapeyron equation,

$$\frac{dP^0}{dT} = \frac{H_{vap}}{T(V^G - V^L)} \tag{16}$$

These values agreed well with heats of vaporization calculated via the Kistiakowsky equation. The enthalpy of the saturated liquid solution was calculated from

$$H^L = \sum x_i H_i^L \tag{17}$$

The detailed methods of calculation of equilibrium and heat of vaporization values are presented in Appendix A.

CHAPTER IV

EXPERIMENTAL APPARATUS

The experimental apparatus consisted primarily of an Oldershaw column, a reboiler, a vapor-dividing head, and a pressure control system (see Figures 2, 3 and 4).

The distillation column used for this investigation was a glass Oldershaw column. Oldershaw columns have been shown to be useful as general research tools, especially for analytical distillations (9). The uniformity of its operating characteristics makes the column highly satisfactory for distillations of hydrocarbon mixtures.

The Oldershaw column consisted of a series of ten glass plates sealed into a five-eighths inch tube. Each perforated plate was equipped with a weir to maintain a liquid level on the plate. Downcomers provided for the flow of liquid reflux from plate to plate. The vapor rose through 0.035 inch diameter holes in the plates. The entire column was enclosed by an integral Dewar jacket to minimize heat losses. There were no provisions for sampling liquid and vapor streams within the column.

A reflux and holdup measuring trap was connected between the column and the reboiler. The trap was equipped with a sampling valve to permit measurement of column holdup and liquid reflux composition.

The reboiler for the column was essentially a glass pot. A dip leg in the reboiler enabled a bottom product to be withdrawn. A Chromalox C-622 heating element provided the heat to the reboiler. The heat input

AIR SUPPLY

MANOSTAT

TO VENT

AUXILIARY
CONDENSER

OVERHEAD CONDENSER

MANOMETER

VAPOR-
DIVIDING
HEAD

FEED
CONTROL
VALVE

FEED
CIRCULATION
STREAM

FEED SECTION

COOLER

DISTILLATE
GRADUATED
RECEIVER

DISTILLATE
SAMPLING

FEED
SAMPLING

OLDERSHAW
COLUMN

FEED
FILTER

BOTTOMS
GRADUATED
RECEIVER

REFLUX
MEASURING
TRAP

STORAGE
TANKS

POWERSTAT

BOTTOMS
COOLER

COOLER

REBOILER

BOTTOMS
SAMPLING

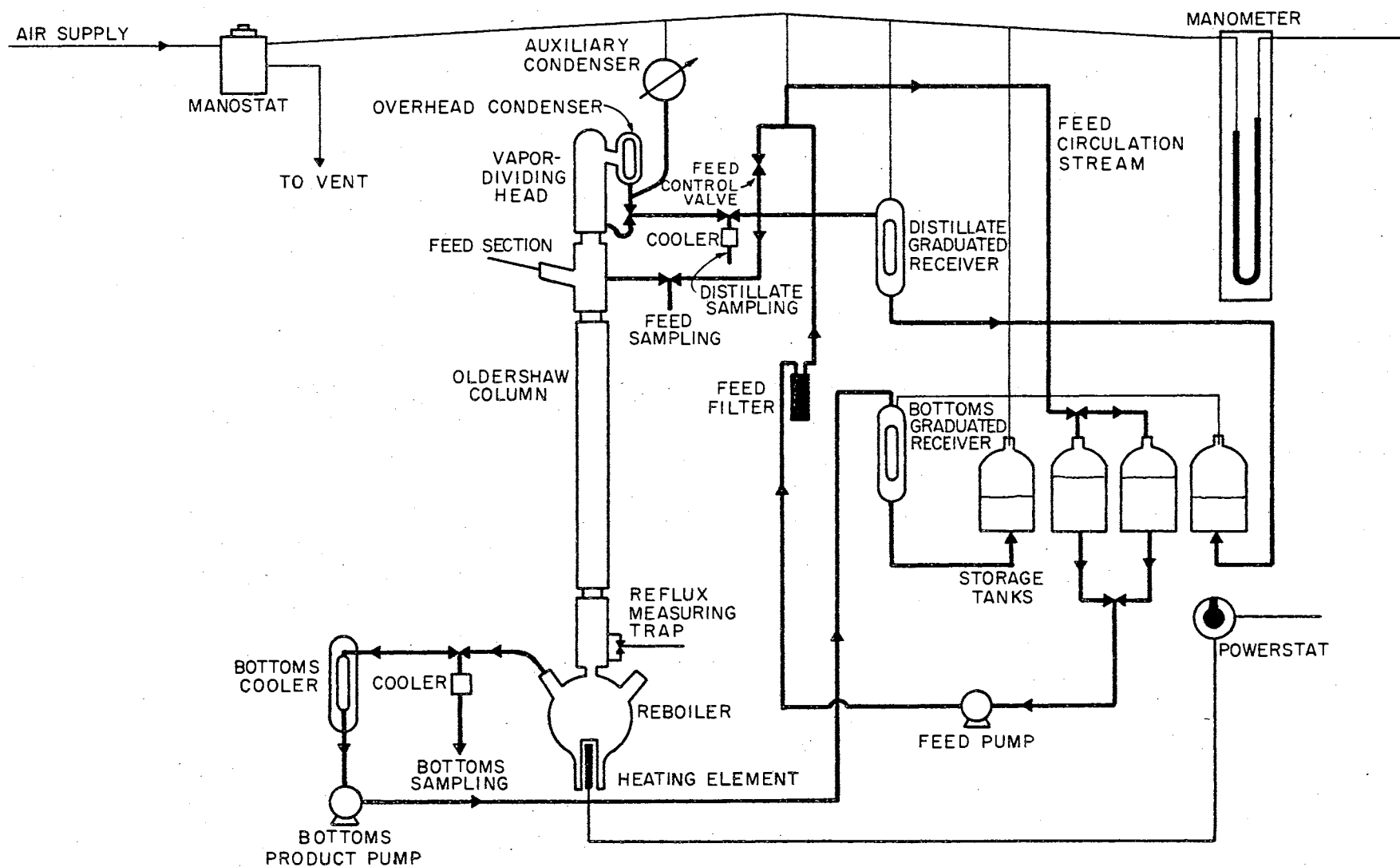HEATING ELEMENT

FEED PUMP

BOTTOMS
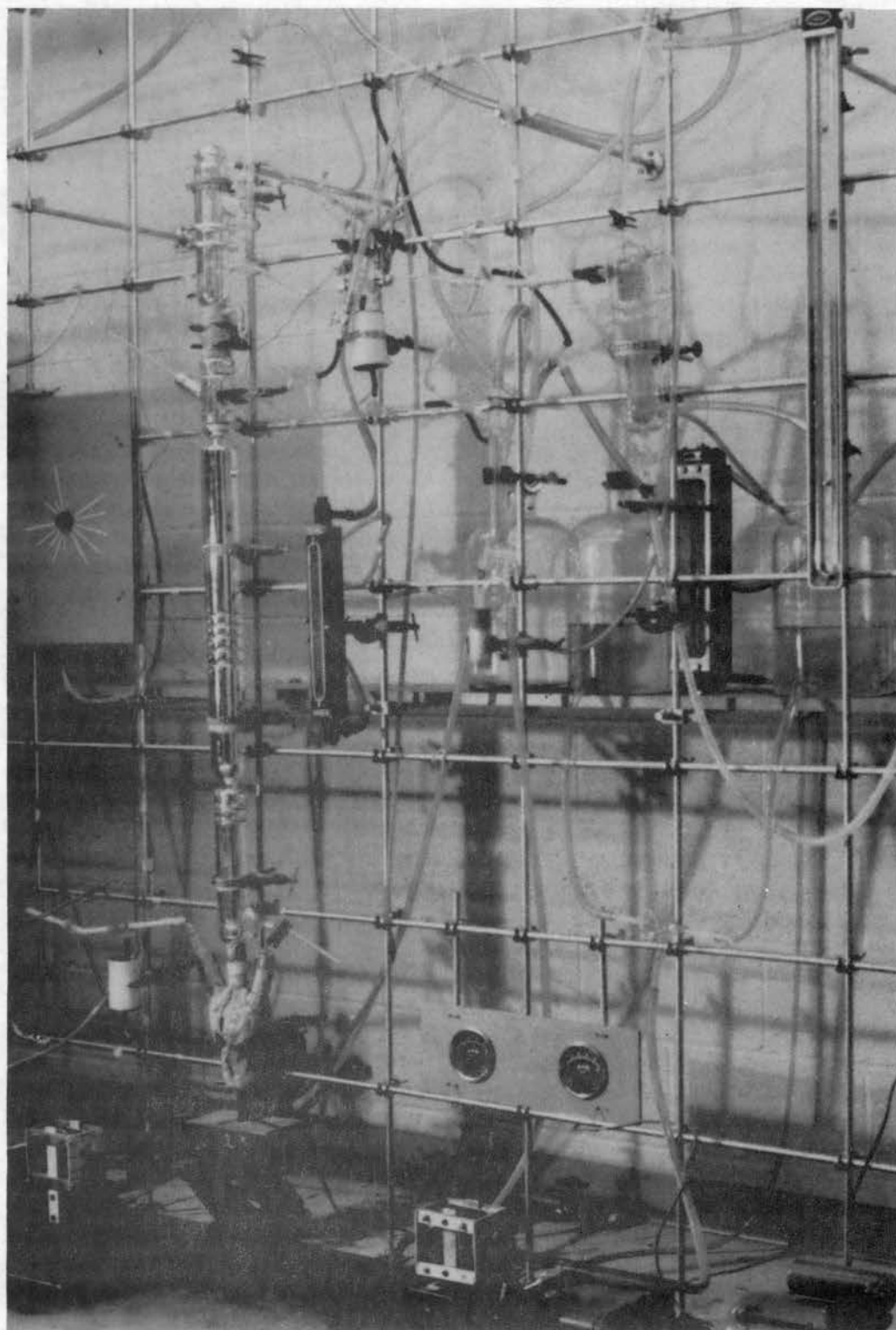PRODUCT PUMP

Figure 2. THE EXPERIMENTAL APPARATUS

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Figure 3. Photograph of the Experimental Apparatus
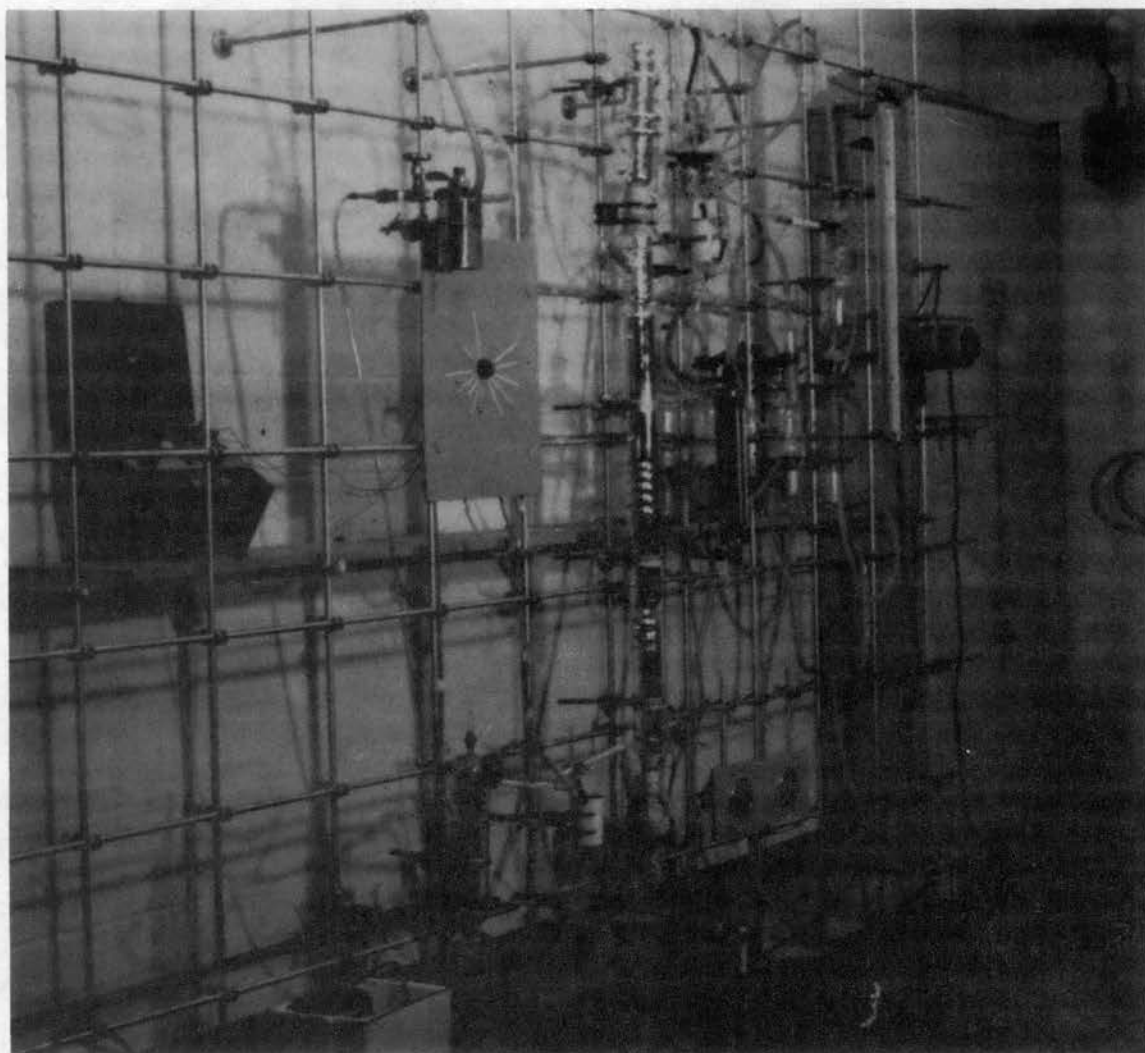
Figure 4. Photograph of the Experimental Apparatus

was controlled by a Powerstat. The heating element fitted into a slot in the reboiler so that the element did not contact the liquid. This arrangement provided safety features and the ability to distill the charge without charring.

The bottoms product was pumped to a combined cooler and receiver. After measurement of the volumetric bottoms rate, the bottoms product was pumped to a storage tank.

A glass feed section, surrounded by a Dewar jacket, was mounted on top of the column. The feed entered the feed plate after being pumped from feed storage through a constant head tank. A three-way stopcock in the feed line permitted measurements of the feed rate and feed composition.

A vapor-dividing head directed the flow of the vapor stream to the product condenser. The head was mounted above the feed section and was equipped with a Dewar jacket. The vapor passed through the dividing head into the overhead condenser. A three-way stopcock in the external reflux line directed the flow of the condensed vapor back to the column or to the product receiver, or to both.

An auxiliary condenser was connected to the overhead condenser. The additional condenser was needed to condense all the overhead vapor. Dry ice was packed around the top of the auxiliary condenser as a precaution to prevent loss of vapor.

A manostat controlled the pressure in the column and the system. The pressure was maintained at 760 mm Hg. Constant-pressure operation was considered important for several reasons:

1. For comparison purposes, most laboratory data in the literature are reported for one atmosphere pressure.

2. The same pressure for all runs gives these runs a common
denominator.

3. Unless the column is operated at constant pressure, there is
little reason to assume that the data will be reproducible.

Air was introduced to the system through the manostat when the pressure
was less than the desired pressure. Pressure lines connected the manostat
to the storage tanks, the product and feed streams, and the column
through the overhead condenser.

A manometer vented to the atmosphere was used to adjust the system
pressure to 760 mm Hg. pressure. The difference between atmospheric
pressure and 760 mm Hg. was found. Air was fed to the system and the
pressure difference was set on the manometer.

The liquid storage system included four eight-liter glass bottles.
Two tanks were provided for the feed and one for each of the products.

An F & M Model 500 Programmed High-Temperature Gas Chromatograph
was used to determine liquid sample compositions. The chromatograph
utilized a thermal conductivity unit, and helium was used as the carrier
gas. A Honeywell-Brown integrator measured the area under the peaks of
the curves traced from the thermal-conductivity response. Standard
samples were used to calibrate the response from the thermal-conductivity
detector of the chromatograph. A regression analysis was used to convert
area fractions to mole fractions. The calibration is listed in Appendix
B.

Sigma motor metering pumps were used to pump the feed from feed
storage to the feed plate and to pump the bottoms product from the reboiler
to the storage tank. Variable-speed Zeromax transmissions, attached to
the motors, were used to control the flow rates.

Copper-constantan thermocouples were used to sense column and product stream temperatures. Leads from a thermocouple selector switch were connected to a Leeds and Northup potentiometer. Standard thermocouple calibration tables were used to convert millivolt readings to degrees Fahrenheit.

CHAPTER V

EXPERIMENTAL PROCEDURE

The startup procedure consisted first of filling the reboiler with the feed mixture. The Powerstat voltage was set to give the desired heat input to the reboiler. The manostat was adjusted to make the system pressure 760 mm Hg.

The column was then operated at total reflux. The feed valve and product valves were closed. The column was allowed to operate at total reflux until a steady state had been reached. The steady-state operation was characterized by constant column temperatures and constant product compositions. Previous experiments showed that at total reflux approximately ninety minutes were required to achieve product compositions that did not change. The column was usually operated at total reflux for two hours to assure steady-state operation.

Once the total-reflux steady state had been realized, the column operation was changed to total-takeoff of the overhead product. The bottoms product and feed valves were opened and both pumps were started. The distillate product valve was opened to the position corresponding to no external reflux. In this manner the column was operated as a non-refluxed stabilizer, or stripping column. For columns of this type, the cold feed is sufficient to produce the necessary internal reflux to give a sharp separation.

Rate measurements were made of the feed and product streams. The

feed rate had been established during total-reflux operation. The feed valve to the column was closed at total reflux. A stop watch was used to record the time necessary to collect a volume of feed in a graduated cylinder. Feed rate measurements were continued until a reproducible feed rate was established. During the run, the product rate measurements were made. In a similar way, the time necessary to fill the graduated product receivers was recorded. The bottoms product rate could be altered by changing the speed on the pump transmission. There was no provision, other than the Powerstat setting for the heat input, to control the distillate rate.

The column was run at total-takeoff of the overhead product until another steady state was obtained. Steady-state operation was defined by the conditions:

1. Constant temperatures in the column

2. Constant product compositions

3. Constant product rates.

Usually the time required to satisfy conditions (2) and (3) was thirty minutes. Samples were taken every fifteen minutes for an hour to check for constant product compositions.

The attainment of the steady state marked the end of the run.

A sampling technique was developed to make the results as accurate as possible. Additional product condensers were installed in the product lines to further cool the streams. Samples were taken by turning three-way stopcocks in one direction to flush the tubing and then turning the stopcocks in the reverse direction to fill the sample vials. Small sample vials were chosen to keep the vapor-phase volume above the liquid sample as small as possible. The samples were immediately placed in a

dry-ice cooler. For analysis the sample vial was removed from the cooler, and the sample was immediately injected into the chromatograph.

CHAPTER VI

RESULTS AND DISCUSSION OF RESULTS

Experimental runs were made for both binary and ternary systems of benzene, toluene, and p-xylene. Binary systems were studied for the purpose of determining the binary efficiencies of each component. The binary mixtures included the benzene-toluene, benzene-p-xylene, and toluene-p-xylene systems. The ternary tests consisted of runs designed to determine the multicomponent efficiencies. Another objective of the ternary experiments was to examine what, if any, effect a third component would have on the efficiencies of the other components.

The scope of the experimental runs was determined by the range of feed compositions, feed rates, and column vapor rates. Feed compositions were selected in the middle portion of the composition range. A concentration of at least 20 mole per cent was necessary to have measurable compositions of all components in both products. The feed rate ranged from 0.036 to 0.048 pound-moles per hour. The vapor rate, essentially controlled by the feed rate and the heat input to the reboiler, varied from 0.011 to 0.022 pound-moles per hour. The upper limits on the feed and vapor rates corresponded to column operation below column flooding.

The experimental results in terms of the component splits are presented in Table I.

Product rates, component feed rates, and other necessary data were applied to the tray-by-tray program. The resulting calculated splits are

TABLE I

EXPERIMENTAL VALUES OF COMPONENT SPLITS

Run Number	Component Split, d/b		
	Benzene	Toluene	p-Xylene
1	1.232	0.158	0.055
2	3.958	0.224	0.068
3	1.969	0.163	0.058
4	8.512	0.352	0.102
5	0.929	0.128	0.040
6	2.188	0.229	-
7	-	3.984	0.305
8	10.800	-	0.108

presented in Table II.

Table III provides a comparison of the experimental and calculated splits for each component. The reader can see, for example, for Run 3 that the calculated split for benzene increases as the number of theoretical plates is increased. Figure 5 shows that the calculated split approaches an asymptotic value. An increase in the number of theoretical plates beyond a certain value of N_T will not yield any better separation. The results in Table III for Run 3 also show that the calculated splits for toluene and p-xylene decrease as the number of theoretical plates is increased. Figures 6 and 7 illustrate that increasing the number of plates beyond an N_T again results in a limiting value of the split.

According to the proposed method, the basis for the determination of the component efficiency was equal splits from the ideal and the actual columns. However, the results in Table III illustrate that the experimental values of the component splits lie outside the range of the calculated values of the splits. The limiting value, which is the largest value, of the calculated benzene split is lower than the experimental value of the benzene split. The experimental value is plotted in Figure 5. Also, the calculated values of the toluene and the p-xylene splits are always higher than the experimental values, as illustrated in Figures 6 and 7, respectively. Thus, the efficiency could not be calculated, since a value of N_T corresponding to the experimental split could not be obtained.

The above discussion indicates that the experimental results cannot be interpreted in terms of the theoretical model. The probable explanation is that fractionation was occurring above the feed plate. During the experimental runs vapor appeared to come in contact with condensed

TABLE II

CALCULATED VALUES OF COMPONENT SPLITS

Run Number	N_T	Component Split, d/b Benzene	Toluene	p-Xylene
1	8	1.184	0.183	0.062
2	8	2.648	0.259	0.084
3	3	1.304	0.205	0.065
	6	1.439	0.186	0.062
	9	1.458	0.183	0.061
4	6	5.010	0.346	0.107
	10	5.117	0.337	0.104
5	6	0.786	0.147	0.051
	10	0.786	0.147	0.051
6	6	1.924	0.273	-
	10	1.926	0.270	-
7	6	-	2.829	0.331
	10	-	2.884	0.323
8	6	6.180	-	0.111
	10	6.213	-	0.111

TABLE III

COMPARISON OF EXPERIMENTAL AND CALCULATED SPLITS

Run Number	N_T, or Experimental	Benzene	Component Split, d/b Toluene	p-Xylene
1	8	1.184	0.183	0.062
	exp.	1.232	0.158	0.055
2	8	2.648	0.259	0.084
	exp.	3.958	0.224	0.068
3	3	1.304	0.205	0.065
	6	1.439	0.186	0.062
	9	1.458	0.183	0.061
	exp.	1.969	0.163	0.058
4	6	5.010	0.346	0.107
	10	5.117	0.337	0.104
	exp.	8.512	0.352	0.072
5	6	0.786	0.147	0.051
	10	0.786	0.147	0.051
	exp.	0.929	0.128	0.040
6	6	1.924	0.273	-
	10	1.926	0.270	-
	exp.	2.188	0.229	-
7	6	-	2.829	0.331
	10	-	2.884	0.323
	exp.	-	3.984	0.305
8	6	6.180	-	0.111
	10	6.213	-	0.111
	exp.	10.800	-	0.108
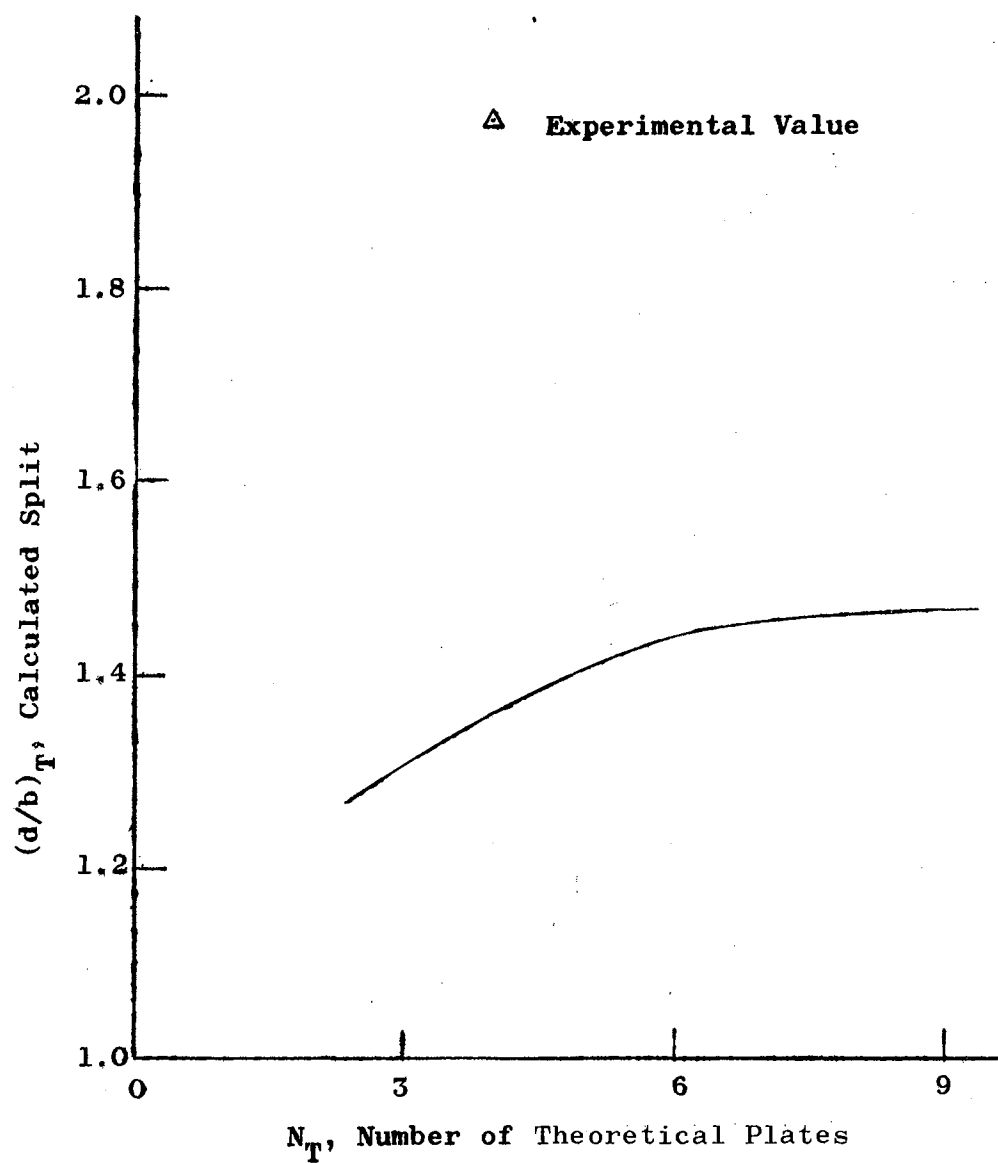
Run 3

Figure 5. Calculated Splits for Benzene
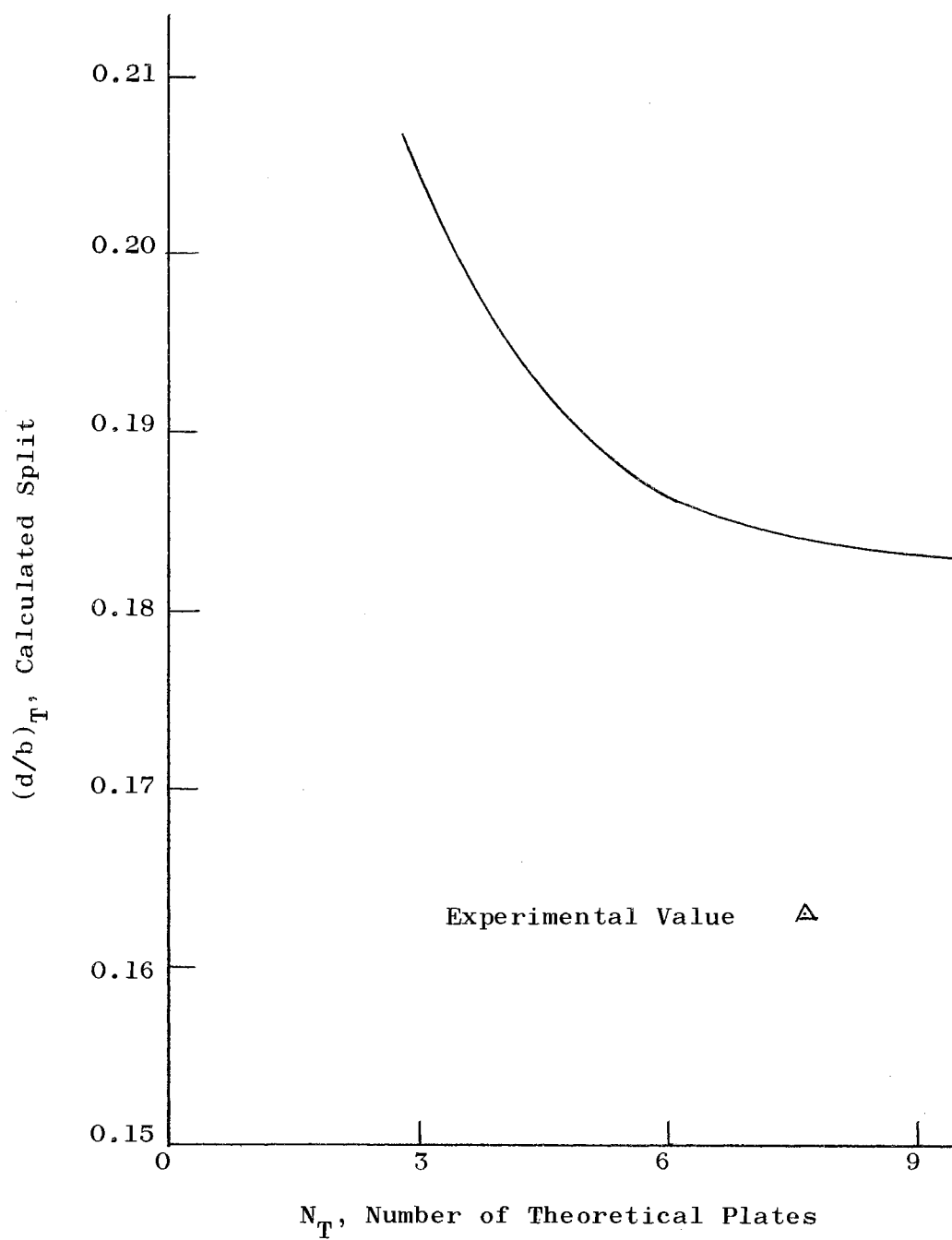
Run 3

Figure 6. Calculated Splits for Toluene
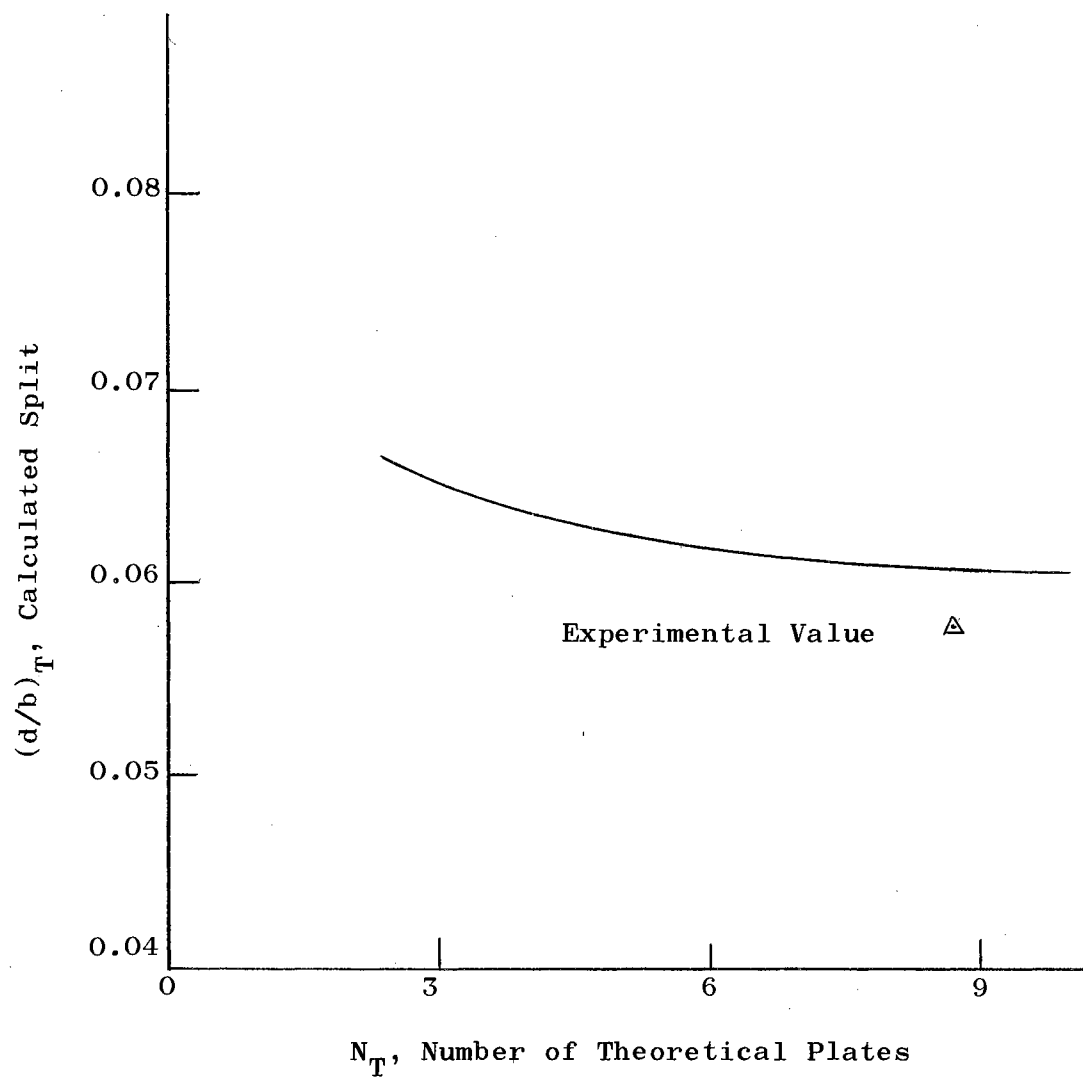
Run 3

Figure 7. Calculated Splits for p-Xylene

vapor in the vapor-dividing head. A diagram of the vapor-dividing head
is shown in Figure 8. The vapor leaving the feed section rises through
the dividing head around a liquid trap. During the runs vapor condensed
on the walls of the dividing head and liquid appeared to overflow from
the trap back to the column. The net result would be equivalent to
introducing a reflux stream to the column. Thus the vapor from the top
tray would be enriched in the more volatile component.

The tray-by-tray program, which describes the behavior of the ideal
column, assumes that there is no reflux returning to the column. The
quantity of reflux would be difficult to determine experimentally. In
addition, the question arises as to how many trays are represented by
the fractionation above the feed plate. However, the possibility of
additional separation by means of refluxing for the ideal column might
prove meaningful. Therefore, a theoretical tray was considered above
the feed with a reflux rate of 0.1 (ratio of reflux to distillate rate).
The purpose was to see if refluxing would yield calculated results that
approach the experimental values, and thus account for the high experi-
mental compositions of the distillate.

The results from the tray-by-tray program with refluxing are pre-
sented in Table IV. The split for benzene increased from the previous
limiting value (see Figure 5), but the calculated split is still below
the experimental value. For the refluxed case the split for toluene
decreased, but it did not reach the experimental value. However, the
p-xylene split did drop below the experimental value.

The results from Table III and Table IV, plus the visual observation
of column operation, indicate that fractionation above the feed plate is
a reasonable explanation for the lack of agreement between the calculated
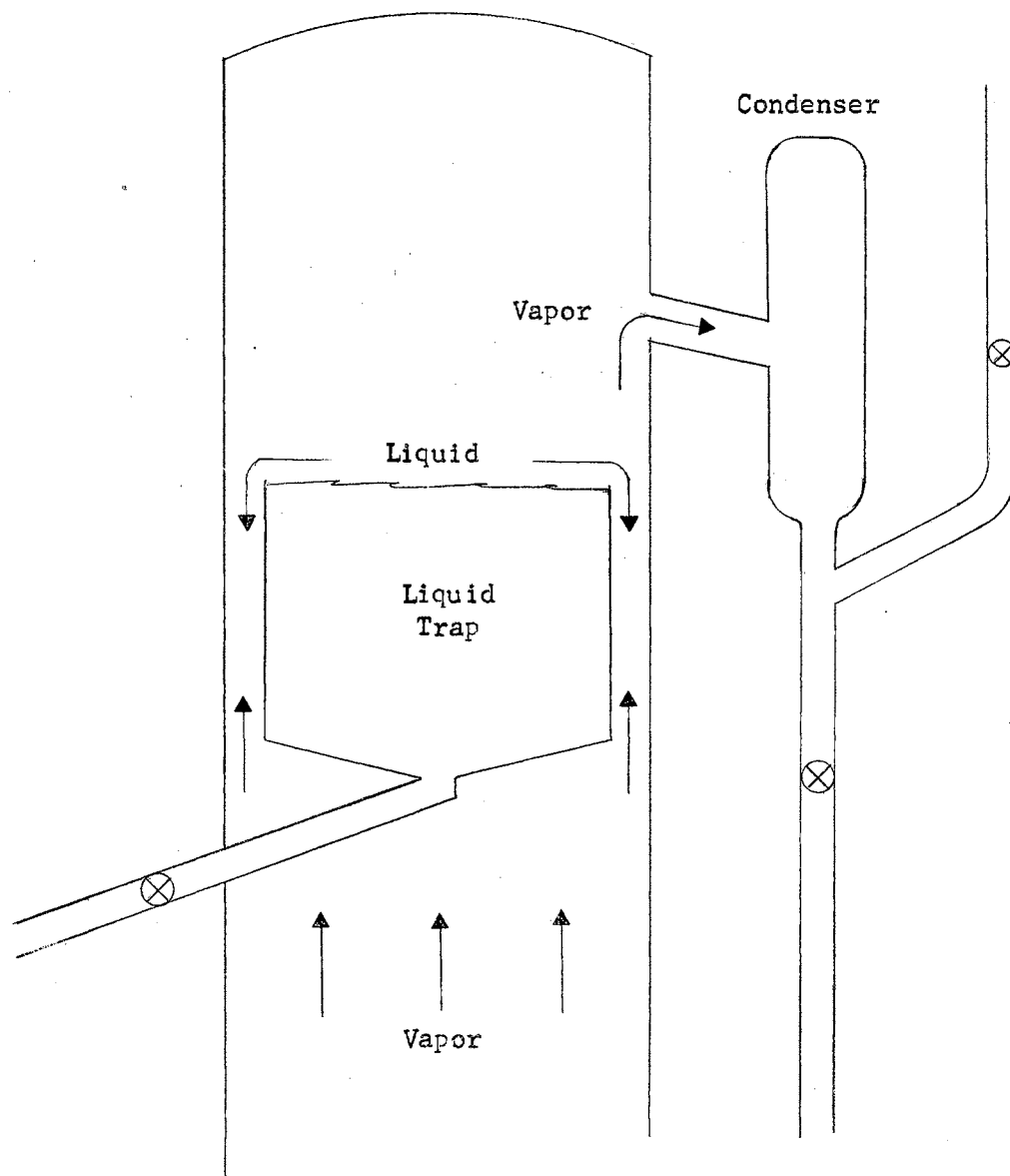
Figure 8. The Vapor-Dividing Head

TABLE IV

CALCULATED SPLITS FOR REFLUX OF L/D = 0.1

Run Number	N_T	Component Split, d/b		
		Benzene	Toluene	p-Xylene
1	9	1.276	0.170	0.045
2	9	3.044	0.241	0.061
3	10	1.627	0.176	0.048
4	11	6.190	0.302	0.102
5	11	0.833	0.136	0.037

and the experimental splits. This would explain why over-all column efficiencies could not be obtained.

Additional vapor-liquid interfacial area may be the cause of the apparent mass transfer above the feed plate. The condensation of vapor on the walls of the vapor-dividing head forms a liquid film. The liquid film increases the interfacial area available for vapor-liquid contact. Vapor from the top tray coming in contact with the liquid film will give rise to a distillate product higher in concentration of the light component.

At a recent symposium on distillation, Danckwerts and others (11) proposed a theory to explain why observed values of efficiencies were higher than predicted. The thermal distillation model links heat transfer with mass transfer. Both may have to be taken into account in efficiency experiments. In a distillation column, the vapor is hotter than the liquid with which the vapor comes into contact. Danckwerts and his associates suggested that partial condensation of vapor may occur at the vapor-liquid interface. The liquid close to the interface may boil or even become superheated, and subsequently flash when exposed to the vapor. Such thermal distillation would lead to efficiencies greater than those expected from conventional mass transfer-models.

The presence of thermal distillation effects seems very possible in the present study. The condensation of vapor in the vapor-dividing head provides an interface at which the liquid may become heated and flash when exposed to the rising vapor.

There are several ways to prevent condensation of vapor in the vapor-dividing head and thus permit measurement of efficiencies:

1. A solution would be to wrap the dividing head with a heating

element. Heat losses and subsequent condensation would be eliminated. The heat supplied by the element would have to be controlled so that the temperature would be the same as inside the column. If the temperature were too high, there would be a heat gain in the column.

2. A shoulder fitted around the dividing head would reduce heat losses and condensation. This method would not be as good as the first one, since there would still be heat losses in the dividing head.

3. Condensation of the overhead vapor stream away from the column is another solution. This type of design would eliminate the problem of condensed vapor flowing back to the column (see Figure 9).

Wrapped Heating Element

Pressure Control
Line

Condenser

Feed Section

Oldershaw Column
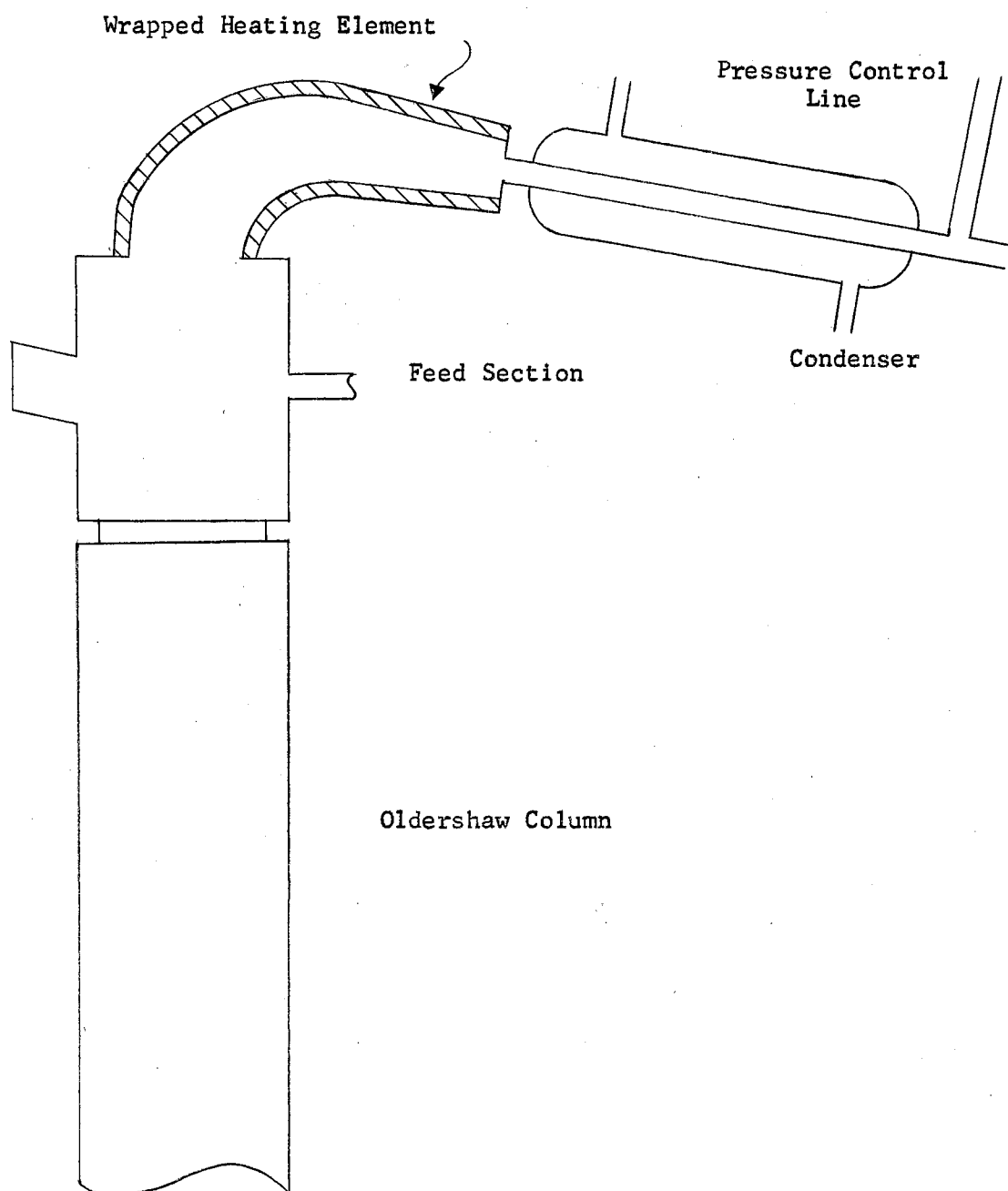
Figure 9. Proposed Change for Condensation of Overhead Vapor

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The objectives of this investigation were not achieved. The column configuration did not lend to the measurement of over-all column efficiencies.

The difficulties in obtaining efficiency data were attributed to fractionation occurring above the feed plate in the vapor-dividing head. The method developed for determining the efficiencies is limited to fractionation occurring only in the plate column.

The results that were obtained appear to indicate that the method is substantially sound for the calculation of efficiencies. However, equipment modifications must be made in order to obtain efficiency data.

Recommendations

For future studies of this type, apparatus changes should be made to prevent condensation of vapor in the vapor-dividing head. Heating the dividing head will prevent heat losses and subsequent condensation. Removal of the dividing head and the insertion of a condenser that will prevent the condensed vapor from flowing back to the column should similarly eliminate the problem of fractionation above the feed plate.

Experiments designed to determine the heat losses in laboratory columns should prove useful in assessing the analytical usefulness of such columns.

NOMENCLATURE

English Letters

A   -   regression coefficient in K-value equation

    -   coefficient in Antoine equation

A_f -   area fraction

a   -   regression coefficient in chromatograph calibration

B   -   coefficient in Antoine equation

    -   regression coefficient in K-value equation

    -   molar flow rate in total bottoms product

    -   second virial coefficient

b   -   molar flow rate of component in bottoms

    -   regression coefficient in chromatograph calibration

C   -   regression coefficient in K-value equation

    -   coefficient in Antoine equation

D   -   regression coefficient in K-value equation

    -   molar flow rate in total distillate product

d   -   molar flow rate of component in distillate

E   -   over-all column efficiency

E^O -   Lewis over-all column efficiency

E^O_{MV} -   vapor-phase Murphree plate efficiency

E^O_{ML} -   liquid-phase Murphree plate efficiency

E^O_{ji} -   modified vaporization efficiency

$\ddot{E}^O$ -   component efficiency in Holland method

f   -   standardization coefficient in chromatograph calibration

H^V -   molar enthalpy of saturated vapor

H^L -   molar enthalpy of saturated liquid

H_{vap} -   heat of vaporization

K   -   equilibrium ratio

N   -   number of plates

P   -   system pressure

p^o -   component vapor pressure

R   -   universal gas constant

T   -   absolute temperature

T_b -   normal boiling point

v^L -   molar liquid volume

v^o -   reduced expansion factor

V_r -   reduced volume

v^G -   molar vapor volume

w_f -   weight fraction

x   -   liquid composition, mole fraction

x*   -   equilibrium liquid composition

Y   -   sum of vapor mole fractions in Holland method

y   -   vapor composition, mole fraction

y*   -   equilibrium vapor composition

Greek Letters

β -   plate factor

γ^L -   liquid-phase activity coefficient

γ^V -   vapor-phase activity coefficient

θ -   imperfection pressure correction

θ -   convergence variable in Holland method

δ -   solubility parameter

δ_M -   mixture value of solubility parameter

ω -   acentric factor

Subscripts

A   -   actual column

B   -   bottoms

c   -   critical property

D   -   distillate

F   -   feed

i   -   component index

j   -   plate index

r   -   reduced property

T   -   theoretical column

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APPENDIX A

METHODS OF CALCULATION

METHODS OF CALCULATION

Equilibrium Values

Equilibrium values for benzene, toluene, and p-xylene were calculated from a method presented by Stuckey (32),

$$K_i = \frac{1}{\theta_i} \frac{P_i^o}{P} \frac{\gamma_i^L}{\gamma_i^V} \qquad (12)$$

γ_i^V, the vapor activity coefficient, was assumed to be unity at the low system pressure.

The liquid activity coefficient, γ_i^L, was calculated from the Scatchard-Hildebrand equation,

$$\ln \gamma_i^L = \frac{V_i^L}{RT} (\delta_m - \delta_i)^2 \qquad (18)$$

V_i^L in equation (18) is the molar liquid volume of component 'i.' The molar liquid volume was determined from the equation

$$V_i^L = \frac{RT_{c_i} V_{r_i}}{P_{c_i}} \qquad (19)$$

V_{r_i}, the reduced volume of component 'i,' was found from the following relation,

$$V_{r_i} = v_i^{\circ} (5.7 + 3.0 \, T_r) \qquad (20)$$

v_i° is the reduced expansion factor, and is related to the acentric factor, ω, by the following equation,

$$v_i^{\circ} = 0.01361 - 0.00328\,\omega - 0.0244\,\omega^2 + 0.0599\,\omega^3 - 0.0308\,\omega^4 \qquad (21)$$

δ_m is the liquid volume average solubility parameter for the entire mixture,

$$\delta_m = \frac{\sum x_i V_i^L \delta_i}{\sum x_i V_i^L} \tag{22}$$

Values of the solubility parameter are available from the tabulation of Hildebrand and Scott (22).

The imperfection pressure correction, θ, is designed to permit evaluation of correction factors to be applied to the ideal K-value. The imperfection pressure correction in generalized form is

$$\ln \theta_i = \frac{1}{T_r} \left(\frac{BP_c}{RT_c} - \frac{V^L P_c}{RT_c} \right) (P_r - P_r^{\,0}) \tag{23}$$

$P_r^{\,0}$ is the reduced vapor pressure. The term $\frac{BP_c}{RT_c}$ is a reduced second virial coefficient and is a function of the reduced temperature and the acentric factor,

$$\frac{BP_c}{RT_c} = (0.1445 + 0.073\,\omega) - (0.330 - 0.46\,\omega)T_r$$
$$- (0.1385 + 0.50\,\omega)/T_r^{\,2} - (0.0121 + 0.097\,\omega)/T_r^{\,3} \tag{24}$$
$$- (0.0073\,\omega)/T_r^{\,8}$$

Vapor pressures were calculated from the Antoine equation (29)

$$\log P^0 = A - \frac{B}{C + T} \tag{25}$$

A, B, and C are experimentally determined coefficients. The coefficients are available for several components (29).

Ideal K-values were used to check the K-values that were calculated by the above method. Ideal K-values were calculated from the vapor pressure and the system pressure,

$$K = \frac{P^0}{P} \tag{26}$$

The K-values from the two methods agreed within one per cent over the entire composition range.

Heats of Vaporization

The Clausius-Clapeyron equation was used to calculate heats of vaporization,

$$\frac{dP}{dT} = \frac{H_{vap}}{T \ (V^G - V^L)} \tag{16}$$

The vapor pressure data needed for equation (16) were obtained via the Antoine equation, equation (25). Differentiation of equation (25) gives

$$\frac{dP}{dT} = \frac{2.303 \ BP}{(C + T)^2} \tag{27}$$

Equation (16) and equation (27) were combined to obtain an expression for the heat of vaporization

$$H_{vap} = PT \ \frac{2.303 \ B}{(C + T)^2} \ (V^G - V^L) \tag{28}$$

The liquid molar volume is much smaller than the gas molar volume and can therefore be neglected. The molar gas volume was calculated from

$$V^G = \frac{RT}{P} + B \tag{29}$$

B is the second virial coefficient. Values of experimentally-determined second virial coefficients were taken from the works of several researchers (1, 6, 10, 24).

The resulting equation used for the calculation of the heat of vaporization was

$$H_{vap} = PT \left[\frac{2.303 \ B}{(C + T)^2}\right] (\frac{RT}{P} + B) \tag{30}$$

The Kistiakowsky equation was used to check the values calculated from the above method. The Kistiakowsky equation evaluates the heat of

vaporization at the normal boiling point,

$$H_{vap} = (7.58 + 4.571 \log T_b) T_b \qquad (31)$$

The heats of vaporization at temperatures other than the normal boiling point were found using the Watson equation,

$$\frac{H_{vap}}{(H_{vap})_{T_b}} = \left(\frac{T_c - T}{T_c - T_b}\right)^{0.38} \qquad (32)$$

The results obtained from the Kistiakowsky-Watson method agreed with the results calculated via the Clapeyron equation within less than one per cent.

APPENDIX B

CHROMATOGRAPH CALIBRATION

CHROMATOGRAPH CALIBRATION

Liquid sample compositions were determined by the use of an F & M Model 500 Programmed High-Temperature Gas Chromatograph. The output from the chromatograph consisted of curves traced from the thermal-conductivity detector response. The areas under the peaks of these curves are proportional to the amount of each component in the sample.

The area fraction for each component can easily be calculated. However, the area fraction by itself is not a very common indication of composition. Compositions are generally reported on the basis of mole fraction or weight fraction. Therefore, the purpose of the calibration was to convert the area fractions obtained from the chromatograph analyses to a more meaningful weight-fraction basis..

The procedure used in calibrating the gas chromatograph consisted first in the preparation of standard samples. The amount of each component in the sample was carefully weighed using an analytical balance. The weight of each component was determined to the nearest one-tenth of a milligram. Nine samples were prepared. The compositions covered the full range of weight fractions for each component. The compositions of the standard samples are presented in Table V.

The samples were refrigerated before analysis to prevent loss by evaporation. Each sample was analyzed on the chromatograph an average of five times to make the analyses as accurate as possible. The areas under the peaks of the response curves were measured, and the area fractions for the components were calculated. The chromatograph results are shown

TABLE V

COMPOSITION OF STANDARD SAMPLES

Sample	Benzene	Weight Fraction Toluene	p-Xylene
A	0.10391	0.87180	0.02428
B	0.62039	0.07129	0.30832
C	0.64855	0.16785	0.18359
D	0.12000	0.84568	0.03437
E	0.49378	0.35773	0.14847
F	0.22236	0.23943	0.44789
G	0.14428	0.24125	0.61446
H	0.11820	0.12071	0.76109
I	0.31268	0.12754	0.65010

in Table VI.

The next step in the calibration procedure involved the correlation of area fractions with weight fractions. The first method attempted was internal normalization. By this method the weight fraction is expressed as

$$w_{f_i} = \frac{f_i A_{f_i}}{\sum f_i A_{f_i}} \tag{33}$$

w_{f_i} and A_{f_i} are the weight and area fractions respectively, and f_i represents the standardization coefficient for component 'i.' The results predicted from this type of correlation did not agree very closely with the standard sample analyses.

The next attempt to arrive at a correlation involved the use of a linear model. The linear model is given by

$$w_{f_i} = a_i + b_i A_{f_i} \tag{34}$$

a_i and b_i are regression coefficients. The results obtained with this method were much better than those of the first method. Most of the error associated with the prediction of weight fractions from area fractions was due to the error in the determination of the data points. The results are presented in Table VII.

The other method of correlation that was tried was a quadratic model,

$$w_{f_i} = a_i + b_i A_{f_i} + c_i A_{f_i}^2 \tag{35}$$

The results, shown in Table VII, obtained from this method were not significantly better than those obtained from the linear model.

A comparison of the correlations indicated that the linear model, equation (34), best represented the data. The linear model was used to convert area fractions determined via chromatograph analyses to weight fractions. Then the mole fractions were calculated from the weight

TABLE VI

ANALYSIS OF CHROMATOGRAPH RESULTS

Sample	Benzene		Toluene		p-Xylene	
	Mean Area Fraction	Standard Deviation	Mean Area Fraction	Standard Deviation	Mean Area Fraction	Standard Deviation
A	0.09330	0.004848	0.89488	0.007350	0.01323	0.004322
B	0.68731	0.013999	0.04309	0.006697	0.26958	0.008952
C	0.69230	0.009316	0.16786	0.002411	0.13984	0.008041
D	0.11404	0.003269	0.86281	0.007293	0.02316	0.004439
E	0.49385	0.013862	0.35755	0.019822	0.14860	0.008637
F	0.22149	0.011027	0.23776	0.006067	0.43232	0.005950
G	0.14668	0.003678	0.23753	0.002361	0.61579	0.003182
H	0.11808	0.005021	0.10996	0.010055	0.77196	0.012386
I	0.32992	0.006312	0.11758	0.005335	0.66093	0.014166

TABLE VII

REGRESSION COEFFICIENTS AND STANDARD ERROR

Linear Model

Component	Regression Coefficients a	b	Standard Error of Estimate
Benzene	0.01671	0.90922	0.01500
Toluene	0.01622	0.95599	0.00951
p-Xylene	0.02463	0.96051	0.01717

Quadratic Model

Component	Regression Coefficients a	b	c	Standard Error of Estimate
Benzene	0.00195	0.01032	-0.15692	0.01419
Toluene	0.02552	0.88481	0.07053	0.00882
p-Xylene	0.01292	1.09518	-0.17977	0.01437

fractions.

The evaluation of the error in the predicted weight fractions provides an estimate of the accuracy of the reported compositions. The difference, or error, between the true weight fraction and the predicted weight fraction can be considered as a sum of several errors. These errors are listed:

1. Error in weighing the standard samples.

2. Experimental, or random, error.

3. Error in measurement of areas from the curves on the chromatogram.

4. Error associated with lack of fit of the linear model.

The first error can be neglected, since the accuracy of the weighing measurements was carried out to the nearest tenth of a milligram. The total error is then given by the standard error of the estimate, which is presented in Table VII. The standard error of the estimate was calculated as follows. The measured values of the weight fractions, that is, the true weight fractions, were regressed as a function of the calculated area fraction, according to the linear model. Then the linear model was used to calculate weight fractions, which were then compared with the true weight fractions. The differences were treated in the same manner as the conventional statistical method used to determine the standard deviation. The listed second and third types of errors were estimated by the standard deviation given in Table VI. A comparison of Tables VI and VII illustrate that the standard error of the estimate, representing the total error, is not significantly greater than the standard deviation, representing the error in the determination of the data points. Thus the conclusion was reached that most of the error associated with the prediction of weight fractions from area-fraction data was due to the error in the

determination of the area fractions. The error appears to be within two
per cent over the entire composition range.

APPENDIX C

RAW AND CALCULATED DATA

TABLE VIII

RAW COMPOSITION DATA

Run	Feed Area Fractions			Bottoms Area Fractions			Distillate Area Fractions		
	Benzene	Toluene	p-Xylene	Benzene	Toluene	p-Xylene	Benzene	Toluene	Benzene
1	0.359	0.232	0.409	0.243	0.241	0.516	0.827	0.106	0.067
2	0.352	0.212	0.436	0.090	0.284	0.626	0.817	0.116	0.067
3	0.220	0.381	0.399	0.076	0.421	0.503	0.666	0.246	0.082
4	0.467	0.222	0.311	0.068	0.354	0.578	0.825	0.125	0.050
5	0.388	0.284	0.328	0.220	0.335	0.445	0.818	0.140	0.042
6	0.699	0.301	-	0.433	0.567	-	0.893	0.107	-
7	-	0.507	0.493	-	0.172	0.828	-	0.757	0.243
8	0.543	-	0.457	0.070	-	0.930	0.924	-	0.076

TABLE IX

COMPOSITION DATA CALCULATED FROM RAW DATA

Run	Feed Mole Fractions			Bottoms Mole Fractions			Distillate Mole Fractions		
	Benzene	Toluene	p-Xylene	Benzene	Toluene	p-Xylene	Benzene	Toluene	p-Xylene
1	0.402	0.237	0.361	0.254	0.258	0.487	0.823	0.107	0.070
2	0.397	0.219	0.384	0.117	0.303	0.579	0.812	0.119	0.069
3	0.258	0.385	0.357	0.105	0.436	0.459	0.680	0.233	0.087
4	0.506	0.222	0.272	0.097	0.373	0.530	0.820	0.124	0.056
5	0.429	0.281	0.290	0.260	0.341	0.399	0.814	0.136	0.050
6	0.717	0.283	-	0.464	0.536	-	0.892	0.108	-
7	-	0.537	0.463	-	0.202	0.798	-	0.768	0.232
8	0.599	-	0.401	0.107	-	0.893	0.923	-	0.077

TABLE X

STREAM RATE RAW DATA

Run	Feed Rate ml/sec	Distillate Rate ml/sec	Bottoms Rate ml/sec
1	0.648	0.162	0.484
2	0.570	0.186	0.382
3	0.663	0.134	0.500
4	0.467	0.215	0.244
5	0.606	0.130	0.469
6	0.466	0.241	0.224
7	0.576	0.284	0.294
8	0.533	0.266	0.266

TABLE XI

STREAM RATES CALCULATED FROM RAW DATA

Run	Feed Rate lb mole/hr	Distillate Rate lb mole/hr	Bottoms Rate lb mole/hr
1	0.048	0.013	0.035
2	0.042	0.015	0.027
3	0.047	0.011	0.036
4	0.036	0.018	0.018
5	0.046	0.011	0.034
6	0.038	0.020	0.018
7	0.040	0.020	0.020
8	0.040	0.022	0.018

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