



Application of azeotropic distillation to the separation of para-xylene and meta-xylene
by Thomas Keith Wilkinson

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemical Engineering
Montana State University
© Copyright by Thomas Keith Wilkinson (1963)

Abstract:

This research was performed as a study of the application of azeotropic distillation to the separation of mixtures of para-xylene and meta-xylene.

The experimental work consisted of evaluating azeotropic entrainers to determine their influence on the relative volatility of the xylenes. The entrainers were chosen as compounds which boil within about 20°C of the xylenes and have in their molecular structure active oxygen* nitrogen or halogen atoms. Forty such compounds were evaluated.

- The major pieces of apparatus employed were two identically packed distillation columns with Corad heads, a refractometer and a gas chromatograph.

Evaluation of an entrainer was divided into determination of its azeotropic composition with para-xylene and determination of the relative volatility of the xylenes using the entraining agent. An estimate of azeotropic composition was made for each entrainer and a sample of that composition distilled. If the overhead from the column* which should be the azeotrope* had a composition within about 10% of that estimated* the actual composition as found by refractive index was taken as the azeotropic composition. The material in the column was then adjusted to this composition and an amount of meta-xylene* equal to the para- present, was added and this charge distilled at total reflux.

The distillation was continued for three hours to allow Steady—state to be reached and then small samples of overhead and bottoms taken for analysis with the gas chromatograph. The relative percentages of xylenes in these samples were used with the Fenske equation to calculate relative volatility. Comparison of this value and that using no entrainer was the basis of evaluation.

Duplicate runs were made for all but a few entrainers where sufficient material was not available. These runs seem to agree well within expected experimental error. The agreement with the literature (S) seems good. For acetic acid and cellosolve* the literature values for azeotropic compositions are 28 and 50 weight percent para-xylene and the values found here were 28 and 54- weight percent. Of the entrainers studied* 18 gave relative volatilities equal to or greater than the 1.019 found using no entrainer. Also, 16 gave values lower than 1.019 and 6 failed to azeotrope. The highest value found was that using 2-methyl butanol. This value was 1.029*.

APPLICATION OF AZEOTROPIC DISTILLATION TO THE SEPARATION
OF PARA-XYLENE AND META-XYLENE

by

THOMAS K. WILKINSON

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

of

MASTER OF SCIENCE

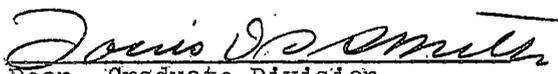
in

Chemical Engineering

Approved:


Head, Major Department


Chairman Examining Committee


Dean, Graduate Division

MONTANA STATE COLLEGE
Bozeman, Montana

June 1963

ACKNOWLEDGEMENT

The author wishes to thank Dr. Lloyd Berg, the research advisor, and the other members of the Chemical Engineering Department of Montana State College for their suggestions and criticisms which have been of great help in the completion of this research project and the writing of this thesis.

Also, the author would like to thank the National Science Foundation for its financial assistance.

TABLE OF CONTENTS

	page
Abstract	vi
Introduction and Theory	1
Research Objectives	9
Equipment	10
Azeotropic Entraining Agents	11
Experimental Procedure	13
Discussion of Results	16
Conclusions	23
Sample Calculations	24
Appendix	27
Literature Consulted	38

LIST OF TABLES AND FIGURES

	page
Figure 1 Distillation Apparatus	28
Figure 2 Para-xylene and Meta-xylene Peaks from Chromatographic Analysis	29
Figure 3 Correlation of Peak Height Percent with Actual Weight Percent	30
Table I Structures and Boiling Points of Entrainers	31
Table II Azeotropic Compositions	32
Table III Data for Correlation of Actual Weight Percent with Chromatograph Peak Height Percent	34
Table IV Relative Volatilities of Xylenes	36

ABSTRACT

This research was performed as a study of the application of azeotropic distillation to the separation of mixtures of para-xylene and meta-xylene.

The experimental work consisted of evaluating azeotropic entrainers to determine their influence on the relative volatility of the xylenes. The entrainers were chosen as compounds which boil within about 20°C of the xylenes and have in their molecular structure active oxygen, nitrogen or halogen atoms. Forty such compounds were evaluated.

The major pieces of apparatus employed were two identically packed distillation columns with Corad heads, a refractometer and a gas chromatograph.

Evaluation of an entrainer was divided into determination of its azeotropic composition with para-xylene and determination of the relative volatility of the xylenes using the entraining agent. An estimate of azeotropic composition was made for each entrainer and a sample of that composition distilled. If the overhead from the column, which should be the azeotrope, had a composition within about 10% of that estimated, the actual composition as found by refractive index was taken as the azeotropic composition. The material in the column was then adjusted to this composition and an amount of meta-xylene, equal to the para- present, was added and this charge distilled at total reflux. The distillation was continued for three hours to allow steady-state to be reached and then small samples of overhead and bottoms taken for analysis with the gas chromatograph. The relative percentages of xylenes in these samples were used with the Fenske equation to calculate relative volatility. Comparison of this value and that using no entrainer was the basis of evaluation.

Duplicate runs were made for all but a few entrainers where sufficient material was not available. These runs seem to agree well within expected experimental error. The agreement with the literature (6) seems good. For acetic acid and cellosolve, the literature values for azeotropic compositions are 28 and 50 weight percent para-xylene and the values found here were 28 and 54 weight percent. Of the entrainers studied, 18 gave relative volatilities equal to or greater than the 1.019 found using no entrainer. Also, 16 gave values lower than 1.019 and 6 failed to azeotrope. The highest value found was that using 2-methyl butanol. This value was 1.029.

INTRODUCTION AND THEORY

The objective of this investigation was to study the application of azeotropic distillation to the separation of mixtures of para-xylene and meta-xylene.

Para-xylene is a valuable material in plastics production through conversion to terephthalic acid. Meta-xylene, although in limited use aside from its use as a solvent and gasoline octane improver, shows considerable promise in plastics as the parent of isophthalic acid.

Obtaining these materials in purity from the complex petroleum mixtures in which they occur is a difficult task. The principal problem arises in the separation of these two compounds from one another and from the other two C₈ aromatic hydrocarbons, ethylbenzene and ortho-xylene. Because of the nearness of their boiling points, separation by straight distillation is not economical. This difficulty is usually approached by initially applying fractional crystallization. This is done to remove the major part of the para-xylene from the mixture. The remaining material is then distilled in columns employing an extremely large number of theoretical plates. Unfortunately, the crystallization does not remove all of the para-isomer and it becomes a troublesome impurity in the purification of the ethylbenzene and meta-xylene. Final purification of these isomers requires further crystallization or distillation.

Because of the inherent expense of refrigeration and of operating extremely tall distillation columns, methods of avoiding this expense are of interest. This interest has led to the study of azeotropic distillation to reduce the number of theoretical plates needed for a given separation and to possibly avoid the crystallization step.

Separation of chemical compounds by distillation depends upon differences in the tendencies of the compounds to vaporize. These differences cause the vapor to have a composition different from that of the liquid from which it was produced. That is, the vapor tends to be richer in those constituents which vaporize most readily. Separate collection of liquid and vapor permit a degree of separation of the compounds.

The simplest measure of the tendencies of pure compounds to vaporize is boiling point. The lower the boiling point, the greater the tendency to vaporize. Materials such as para-xylene and meta-xylene with nearly equal boiling points have nearly equal vaporization tendencies.

A single stage of vaporization, in which the vapor leaving is in equilibrium with the liquid, is called a theoretical plate. By using a series of theoretical plates, it is possible to increase the degree of separation of constituents. This is accomplished by condensing the vapor from each plate on that above with the plates arranged in a vertical column. This condensed vapor is then, in effect, partially

revaporized. As with a single theoretical plate, the vapor from each plate is richer in the lower boiling compounds than was the liquid on that plate or the vapor from the plate below. In general, the greater the number of theoretical plates in a distillation column, the greater the degree of separation of components.

For a binary mixture, the liquid leaving the bottom of the unit may approach the pure higher boiling compound and the vapor leaving the top may approach the pure lower boiling compound. For a multi-component mixture, the lowest boiling material tends to collect at the top of the column and the highest at the bottom. Intermediate boiling components distribute between top and bottom.

Because their boiling points are so close, a single theoretical plate gives little separation of the xylenes. In order to obtain high purity by straight distillation, a very large number of theoretical plates is required. This leads to expensive equipment and high operating costs. The aim of azeotropic distillation is to reduce the number of plates required for a given separation.

Often two (or more) compounds form mixtures of a certain composition that may be boiled to give a vapor with exactly the same composition as that of the liquid. Such mixtures are known as azeotropes or constant boiling mixtures. It should be emphasized that the composition of the vapor from a boiling azeotrope is not merely near that of the liquid, as with the xylenes, but exactly the same.

Azeotropes are of several types: homogeneous or heterogeneous and minimum boiling or maximum boiling. Homogeneous azeotropes are produced from completely miscible compounds; that is, from a single liquid phase. Heterogeneous azeotropes result from mixtures of partially soluble liquids and, thus, from a liquid consisting of more than one phase. Minimum boiling azeotropes are those which boil at a temperature lower than the boiling points of the pure components or any other mixture of them. Occasionally, certain compounds form constant boiling mixtures which boil higher than the pure compounds or any other mixture of them. These azeotropes are called maximum azeotropes. Maximum azeotropes are much less common than the minimum boiling variety.

Since, in distillation, an azeotrope acts as a single pure compound, it may be separated from other compounds or azeotropes provided that its boiling point is sufficiently different from those of the other materials present. This is the basis of azeotropic distillation.

In the case of the xylene separation, a third compound called an azeotropic entrainer would be added to a mixture of these isomers. Since the xylenes are so chemically similar, it is unlikely that such an entrainer would form an azeotrope with one and not the other. Therefore, it appears doubtful that an entrainer selective with respect to para-xylene and meta-xylene exists and we will have to be content with investigating non-selective entrainers for this azeotropic separation.

Of course, in commercial operation the separation of xylene and entrainer after distillation becomes an important consideration. This problem may be approached in several ways (1); however, for the purposes of this study it was not a primary consideration.

In evaluating the degree of separation of the xylenes in a distillation, the concept of relative volatility was used. Before defining this term, it may first be helpful to define the term 'volatility'. Volatility, defined for a single theoretical plate, is the ratio of the mole fraction of a component, A , in the vapor to the mole fraction of A in the liquid. This is a measure of the compound's tendency to vaporize. Separation by distillation depends upon differences in volatilities of the components of the mixture, or, for a binary mixture, on the relative volatility of the compounds.

The relative volatility of two compounds is simply the ratio of their volatilities. The volatility of the lower boiling compound is generally used as the numerator of the ratio to give a relative volatility greater than one. Comparison of the relative volatilities of the xylenes using azeotropic distillation with that using straight distillation was the basis for evaluation of entrainers in this study. Higher relative volatilities indicate a greater ease of separation,

For an actual distillation column, it is impractical to base relative volatility on compositions around a single theoretical plate. It is desirable to use compositions that can easily be measured and

these are usually those of the material from the top of the column (overhead) and that from the bottom (bottoms). By applying the relative volatility definition to each plate in a distillation column and considering the relative volatility constant from plate to plate, the following equation may be derived:

$$\alpha^{n+1} = \frac{y_A/x_A}{y_B/x_B} = \frac{y_A^x y_B}{y_B^x y_A} \quad \text{where}$$

α = relative volatility

n = number of theoretical plates in the column

y_A, y_B = mole fractions of the compounds A and B in overhead

x_A, x_B = mole fractions of A and B in bottoms

It might be noted that the exponent, $n + 1$, results from consideration of the still-pot of the column as one theoretical plate.

Analysis of the overhead and bottoms samples for the relative volatility calculation was done with a gas chromatograph. This instrument consists basically of two parts: the column and the detector cell. The chromatograph column consists of a length of small diameter tubing filled with a finely divided inert solid which supports a liquid absorbent. The inert solid provides a large surface area for contact between the absorbent and the material to be analyzed. In analysis, a small sample of an unknown is injected into the column and into a stream of inert gas which flows at a constant rate through the column. If liquids are to be analyzed, they are vaporized in the proper heating

zone before passing into the column packing. The column is maintained at constant temperature by coiling it within a heated chamber.

The sample flowing with the inert gas through the column distributes itself between the stationary absorbent and the moving gas stream. There is a continual process of absorption by the absorbent and elutriation by the moving gas stream. Because the strengths of absorption of the constituents of the sample will, in general, be different, the absorbent tends to selectively retard them. And for this reason, they move through the column at different rates and thus tend to segregate into bands within the gas stream. It is this separation which permits chromatographic analysis of mixtures.

As the sample constituents emerge from the column, they pass into the detector cell. The detector of the instrument used in this study is a bridge-type thermal conductivity cell. Different chemical compounds have, in general, different thermal conductivities. The thermal conductivity cell reacts to this property and is used to detect the changes as the various sample components leave the column. An electronic recorder is used with the instrument to record continuously the output signal of the cell as a series of peaks on the recorder chart. There is usually a separate peak for each constituent.

The recorder allows observation of both the magnitudes of the peaks and the length of time from sample injection until detection of each component. The magnitude of a peak (height and area) is a function of

the amount of the component present and the material's thermal conductivity. The time element, called retention time, is a characteristic of each chemical compound and may be used as a means of identification. It might be mentioned that the chromatograph is primarily a device for quantitative analysis and the word, unknown, as used in this study pertains to composition. However, the instrument may be used for qualitative analysis if a list of retention for expected compounds is available.

For compounds with nearly equal thermal conductivities, the areas under individual peaks may be used as a measure of the composition of the sample being analyzed. This method works well for compounds whose retention times differ enough to permit formation of entirely separate peaks. However, if the retention times are nearly equal for two compounds, the peaks will overlap, making area determination difficult or impossible. This is the case with para-xylene and meta-xylene. Fortunately, it was shown in this study that for these xylenes the heights of the peaks could be used as a measure of the composition. Establishment of a correlation of composition with peak heights is discussed in the Discussion of Results section.

RESEARCH OBJECTIVES

The objective of this investigation was to study the application of azeotropic distillation to the separation of mixtures of para-xylene and meta-xylene. This was to be based on improvement in relative volatility between the xylenes using azeotropic distillation over that using straight distillation.

EQUIPMENT

In this study the following equipment was used: two batch distillation columns fitted with Corad condensing heads, electric still-pot heaters, triple-beam balance, refractometer, and gas chromatograph.

The distillation columns were identical packed columns. These were 48-inch by 1-inch glass columns with a 45-inch packed height of 1/8-inch stainless steel Fenske rings. Corad heads allowed easy changes in reflux ratio between several discrete values. Those used were 30:1 and total reflux. One-liter, round-bottom still-pots with sampling taps were used for all distillations.

Other equipment was an Ohaus triple-beam balance for weighing material to be distilled, a Valentine refractometer with temperature control to $20 \pm 0.3^\circ\text{C}$, and an Aerograph gas chromatograph equipped with a Minneapolis-Honeywell continuous recorder. The chromatograph column was 1/4-inch by 12 feet and packed with 7,8-benzoquinoline supported on 60-80 mesh acid-washed Chromasorb P.

For a further description of this equipment, the reader is referred to Nelson (8). A diagram of the distillation column is shown in Figure 1.

AZEOTROPIC ENTRAINING AGENTS

Choice of entrainers was based primarily on boiling point and chemical character. Boiling point of the entrainer is a primary factor in the formation of azeotropes and the setting of azeotropic composition. Azeotropes are most likely to form if the entrainer boils at a temperature near the boiling points of the xylenes. Generally, compounds boiling within about 20°C were sought, but a few boiling outside this range were evaluated. Experience has shown that certain types of compounds containing oxygen, nitrogen or halogen atoms in their structures are likely to form azeotropes with the xylenes (1). Therefore, compounds of these types boiling in the proper range were sought. The compounds are generally acid, alcohol, amine, and ketone types.

The following is a list of these compounds evaluated in this study:

2-methyl butanol	2,6-dimethyl morpholine
isobutyl carbinol	methyl amyl acetate
methyl isoamyl ketone	N-methyl piperazine
acetic acid	dimethyl ethanol amine
ethylene diamine	pyrrole
2-ethyl butanol	1,3-propane diamine
N-butanol	methyl chloro acetate
isobutanol	ethyl chloro acetate
methyl isobutyl carbinol	N-amyl alcohol
amyl acetate	methyl cellosolve

2-methyl pentanol	morpholine
2-chloro ethanol	5-hexene-2-one
1-nitro propane	cellosolve
2,4-pentanedione	ethylene glycol
N-ethyl morpholine	cyclopentanol
propylene diamine	2-nitro propane
2-amino ethanol	N-propanol
2-pentanol	nitro ethane
3-methyl-1-pentyne-3-ol	3-pentanol
dimethyl amino propyl amine	dimethyl isopropanol amine

EXPERIMENTAL PROCEDURE

The procedure used in evaluating each of the entrainers may be divided into two phases: (1) determination of the azeotropic composition with para-xylene, and (2) determination of the relative volatility between the two xylenes. For each of the entrainers, duplicates were made of each of these determinations except in the case of the last few, where sufficient material was not available.

The azeotropic composition of the entrainer with para-xylene was first estimated from the relative boiling points of the entrainer and xylene. Two samples of this composition were prepared and distilled at 30 to 1 reflux until steady overhead temperatures were attained. Since the azeotrope would be the first material to leave the column, the overhead material should be the azeotrope. A sample of the overhead from each column was taken and its refractive index determined. These values were used with a previously prepared plot of composition versus refractive index for the particular entrainer to find the composition of the samples. If the composition so determined was nearly equal to that estimated, it would represent the azeotrope and was used as the composition of the azeotrope. If the values differed by over 10%, a second determination was made with the composition adjusted to that determined in the first trial.

It should be mentioned here that this method of analysis is satisfactory if the refractive index of the entrainer is sufficiently

different from that of the xylene to detect changes in the index with composition changes. For all of the entrainers except pyrrole, the refractive indices were sufficiently different. In the case of pyrrole, where its refractive index was too near that of para-xylene for accurate analysis, the analysis was done with the chromatograph using known samples as reference points to insure accuracy.

When a satisfactory value had been determined for the azeotropic composition, the composition of the material in the still-pot was adjusted to that value and an amount of meta-xylene equal to the para-present was added.

At this point, the determination of relative volatility was begun. The entrainer-xylene charge was distilled at 30 to 1 reflux until the overhead temperature stabilized and then at total reflux for three hours to ensure equilibrium throughout the column. At this point, samples of overhead and bottoms were taken for analysis and relative volatility calculation. Samples of about one ml. were taken to avoid upsetting equilibrium. For chromatographic analysis, even such small samples were more than ample.

The samples were analyzed with the gas chromatograph and the heights of the peaks produced on the recorder were measured. Using the peak-height-percent versus actual composition plot previously established, the actual relative weight-percentages of the xylenes was determined. This method of determining composition using peak

heights is discussed further in the Discussion of Results section.

The compositions thus found were used with the Fenske Equation to calculate the relative volatility.

DISCUSSION OF RESULTS

If, in the determination of azeotropic composition for each entrainer with para-xylene, the charge to the column is not at the precise azeotropic composition, the distillation will proceed as the separation of the azeotrope and the component which is in excess. Since a finite column cannot separate these completely, the overhead will be a mixture of the azeotrope and the component in excess. This gives a somewhat false picture of the azeotropic composition. However, if the estimated composition and that determined experimentally agree quite closely, the error is not serious. If the values differed by more than 10%, a second determination was made by charging to the column a mixture of the initial composition found.

For each of the entrainers evaluated, except for seven cases where sufficient material was not available, duplicates were made of each azeotropic composition determination. The azeotropic compositions agreed extremely well between duplicate runs and quite well with those that might be expected from Nelson's work (8). For all of the entrainers investigated, azeotropic compositions agree between duplicate runs within one weight percent. Agreement with the literature seems fair. Horsley (6) reports compositions with para-xylene for several of the entrainers evaluated here. Two of these are acetic acid and cellosolve. For these compounds, Horsley reports 28 and 50 weight percent, respectively, at 760mm while at 640 mm, the values found in this study were

28 and 54 weight percent. Considering the difference in pressure, the agreement seems satisfactory.

The use of refractive index as a measure of composition is accurate as long as the refractive indices of the entrainer and the xylene are sufficiently different to allow detection of changes in the refractive index of mixtures of the two with changes in composition. Of the entrainers evaluated, pyrrole was the only compound whose refractive index was too close to that of the xylene to permit use of this method. Chromatographic analysis was used in this case with the aid of known samples of pyrrole and xylene.

Refractive index has the advantage of easy and fast measurement and quite accurate results. In all measurements, the temperature of the refractometer was maintained at $20 \pm 0.3^\circ\text{C}$.

Five of the entrainers gave azeotropic compositions below 10% xylene. Evaluation of these entrainers was stopped at this point because of the difficulty in knowing if an azeotrope were formed or the mixture were merely the result of the inability of the column to separate the components. Also, such entrainers probably would not be of commercial interest because of the high entrainer to hydrocarbon ratio. One entrainer gave a composition well over 90% xylene. Although this is desirable economically, it is, as with low compositions, difficult to attribute such a composition to azeotrope formation and this entrainer was not evaluated further.

Three of the entrainers formed two-phase azeotropes. These were ethylene diamine, ethylene glycol and 2-amino ethanol. The compositions for these entrainers could not be measured with much accuracy but were estimated from the relative volumes of the phases. All azeotropic composition data are given in Table II.

Since the relative volatilities ranked so closely between entrainers, duplicate runs were made for each of the entrainers where sufficient material was available. This was done in hopes of better establishing the improvement in relative volatility given by each entrainer. However, the differences between duplicates combined with the close ranking did little to aid the situation. This will be discussed more extensively later.

The compositions of overhead and bottoms for use in the relative volatility calculations were found using the gas chromatograph. The common method of composition determination with the gas chromatograph is to use the areas of the peaks produced by the recorder as the measure. However, complete separation of the peaks produced by para-xylene and meta-xylene was not possible with any of the chromatograph columns which were available. The 7,8-benzoquinoline column gave the best separation (Figure 2), but even here the peaks were run together to the point where their separate areas could not be measured. For this reason a correlation of composition with peak height was sought. Maximum heights of the peaks were easily measurable.

The correlation was obtained by making several xylene samples of known composition and analyzing them with the chromatograph. The percentage compositions were then calculated by dividing the height of the para-xylene peak by the sum of the heights of that peak and the peak representing meta-xylene. These values were plotted versus the actual weight percent para-xylene. It was found that the points thus determined fell nearly on a straight line. To obtain a good fit of a line to the points, linear regression was used. The values of regression coefficients and intercepts of the lines established here are given with the sample points in Table III. It was found that as the average height of the two peaks increased at a given actual composition, the "peak percent" decreased. For this reason, three sets of points were established for three nearly constant values of average height. This was done by simply varying the size of samples injected into the chromatograph. The three curves represent average heights in the ranges 25.7 - 27.2, 45.0 - 47.2, and 60.5 - 67.0 units on the 100-unit recorder scale.

In actual analysis it was helpful to keep the average height within the limits designated by these values and as near one of them as possible. This was done by varying sample size and helped to avoid extensive interpolation. It was found, however, that for samples which gave average heights between two of the curves, linear interpolation between them located the point quite closely. Figure 3 shows a plot of these curves.

Unfortunately, this method of analysis is subject somewhat to the judgement of the analyst. But the results were found to be reproducible to within one weight percent. This was satisfactory and much higher precision could not be expected.

The compositions determined were used with the Fenske equation to calculate relative volatility between xylenes for each entrainer. The value of the relative volatility as calculated with this equation is dependent upon the number of theoretical plates in the column, the number n . Throughout his work, Nelson (8) used the same columns as were used in this study and took the number to be 23. The exact number is not known except that it is near 23. For this reason, the relative volatilities determined in Nelson's work and this study might be termed pseudo values. They are near the actual relative volatilities, however. This is not a significant problem since α^{n+1} is a valid measure of separation regardless of the value of n and this is the basic consideration in this work.

The highest relative volatility found was that using 2-methyl butanol as the entrainer. This is 1.029. Its duplicate run gave 1.028. The lowest values obtained were 1.012 and 1.008 with cellosolve as the entrainer.

Duplicate runs were made for 27 of the 40 entrainers evaluated. Of these, 15 gave average relative volatilities (average of the two runs) greater than the 1.0195 for straight distillation and 12 gave

values equal to or lower than 1.0195. Those giving values lower apparently hindered the separation. Of the 13 entrainers for which duplicates were not made, 6 gave azeotropic compositions lower than 10% or greater than 90% xylene and were not evaluated further. Also, of these 13, two gave relative volatility values higher than that for straight distillation, and five lower.

An error of one weight percent in both the overhead and bottoms compositions could cause an error of about 0.003 in the value of α . The number of theoretical plates represented by a given height of packing is dependent somewhat on boil-up rate and other factors. A change of one theoretical plate in the column would change α by approximately 0.001. These errors compare with 0.003, the average difference in the duplicated runs.

Although several of the entrainers showed improvement in the ease of separation of the xylenes over straight distillation, the values of relative volatilities are not encouraging for commercial application. The Fenske equation is not strictly valid for distillation at a finite reflux ratio which, of course, is necessary under production conditions, but it may be used to estimate the number of theoretical plates needed for a given composition of overhead and bottoms. At total reflux, the number of theoretical plates required to give 95% overhead and bottoms at a relative volatility of 1.019 is 312, while at a relative volatility of 1.029, the number is reduced to 205. This represents a considerable

improvement but 205 theoretical plates is probably still beyond commercial interest.

There seems to be little correlation of relative volatility with either the boiling point of the entrainer or with its structure. Table I which shows boiling points for the entrainers is arranged in order of decreasing relative volatility (average of the two runs). It is seen that boiling points change in a random fashion throughout the list. Also, it may be seen that structure and functional character of the entrainers show no apparent correlation with the relative volatility. Combination of the two also fails to give an indication of expected relative volatility. It was noted, too, that there is not good agreement in relative ranking of entrainers between Nelson's work (8) and this investigation. This does not necessarily indicate errors, however. Differences in systems caused by the changes in structure and other properties between ethylbenzene and meta-xylene could well cause such differences.

Of course, any attempt at correlation of results of this study with properties of the systems must take note of the extremely close ranking of the resulting relative volatilities and, in fact, the actual overlapping of duplicate runs. This overlapping tends to make the ranking somewhat arbitrary and the presence or absence of correlations dependent upon the ranking.

CONCLUSIONS

It is possible to separate para-xylene and meta-xylene with fewer theoretical plates using azeotropic distillation than using straight distillation. However, this improvement, depending of course of economic factors, is probably not enough to make the separation by azeotropic distillation commercially feasible.

SAMPLE CALCULATIONS

Determination of the peak percent versus actual percent curves
for chromatographic analysis--

Equation of sample regression line of y on x:

$$y^1 = a + bx$$

Regression Coefficient:

$$b = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2}$$

Y-intercept:

$$a = \frac{\sum y - b \sum x}{n}$$

x = actual weight percent para-xylene

y = percent para-xylene calculated from peak heights

y¹ = peak percent predicted by regression line

n = number of points (x,y) in the sample

For peaks with average* height between 25.7 and 27.0 units
(see Table III for data):

*Average height = (height of para-peak + height of meta-peak)/2

$$n = 6$$

$$\sum y = 292.7$$

$$\sum xy = 15021.05$$

$$\sum x^2 = 15091.58$$

$$\sum x = 293.2$$

$$(\sum x)^2 = 85966.24$$

$$b = \frac{6(15021.05) - (293.2)(292.7)}{6(15091.58) - (293.2)^2} = 0.937$$

$$a = \frac{292.7 - 0.937(293.2)}{6} = 3.03$$

SAMPLE CALCULATIONS (cont.)

Use of the Peak Percent vs. Actual Percent Correlation in obtaining actual compositions--

For 2-methyl butanol Run 1:

Overhead

Height para- peak = 31.5 units
Height meta- peak = 23.0 units
Peak % para- = 57.8
Average height = 27.25 units
Actual % para-
from Figure 3 = 59.4

Bottoms

Height para- peak = 38.5 units
Height meta- peak = 54.0 units
Peak % para- = 41.6
Average height = 46.25 units
Actual % para-
from Figure 3 = 42.3

Calculation of relative volatility--

For 2-methyl butanol Run 1:

$$\alpha^{n+1} = \frac{y_p x_m}{x_p y_m}$$

y_p & y_m = mole percent* para-xylene and meta-xylene in overhead

x_p & x_m = mole percent para-xylene and meta-xylene in bottoms

n = number of theoretical plates in the column.

* Because of equal molecular weights, mole % = weight %.

SAMPLE CALCULATIONS (cont.)

$$y_p = 59.4, y_m = 40.6$$

$$x_p = 42.3, x_m = 57.7$$

$$n = 23$$

$$\alpha^{24} = \frac{(59.4)(57.7)}{(40.6)(42.3)} = 1.995$$

$$\alpha = 1.029$$

Calculation of the number of theoretical plates needed to give a given overhead and bottoms composition--

For 95% para-xylene in the overhead and 5% in the bottoms using 2-methyl butanol as the entrainer:

$$1.029^{n+1} = \frac{(95)(95)}{(5)(5)} = 361$$

$$n+1 = \frac{\ln 361}{\ln 1.029} = 206$$

$$n = 205$$

Using no entrainer:

$$1.019^{n+1} = 361$$

$$n = 312$$

. APPENDIX

