The separation of ortho-xylene from meta-xylene by azeotropic distillation
by Joseph William Petrin

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:
The purpose of this investigation was to study the application of azeotropic distillation to the separation of meta-xylene from ortho-xylene.

The experimental work consisted of evaluating azeotropic en-trainers in order to determine their effect upon the relative volatility of the xylene isomers. Chemical compounds having a boiling point in the range between 40 C° below and 20 C° above the boiling point of meta-xylene, and possessing oxygen, nitrogen, or halogen atoms in their molecular structure were considered as possible en-trainers. Thirty-six such compounds were evaluated.

The major pieces of equipment used in carrying out this study were three packed distillation columns having 26, 25, and 16 theoretical plates , a refractometer, and a gas chromatograph.

Evaluation of an entrainer consisted of determining if the entrainer formed an azeotrope with meta-xylene, and if so the azeotropic composition, and the effect upon the relative volatility of the xylenes. If a 'mixture of the meta-xylene and the entrainer had a boiling point which was lower than the boiling points of the pure components, a minimum boiling azeotrope existed. The composition of this mixture was varied until the overhead and bottoms products from a distillation column had the same composition. This mixture was the azeotropic composition since the vapor and the liquid of an azeotrope' have the same composition. The effect upon the relative volatility of the xylenes was determined by distilling a charge consisting of the meta-xylene and entrainer azeotrope and an amount of orthoxylene equal to the amount of meta-xylene present. Quantitative analysis of the overhead and bottoms samples were obtained by the use of a gas chromatograph. The relative amounts of the xylenes in these samples were used with the Fenske equation to calculate the relative volatility. The basis of evaluation used was the comparison of the relative volatility obtained with and without an entrainer.

Duplicate relative volatility runs were made for all entrainers, and the values obtained agreed well within the expected experimental error. Twenty-One compounds increased the relative volatility of the xylenes, while seven decreased it. The relative volatility for the xylenes using no entrainer was 1.105. Formic acid, the best entrainer, increased the relative volatility, to 1.154, and its use would require only 70 percent of the theoretical plates needed when no entrainer was used.

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ABSTRACT

The purpose of this investigation was to study the application of azeotropic distillation to the separation of meta-xylene from ortho-xylene.

The experimental work consisted of evaluating azeotropic entrainers in order to determine their effect upon the relative volatility of the xylene isomers. Chemical compounds having a boiling point in the range between 40 C° below and 20 C° above the boiling point of meta-xylene, and possessing oxygen, nitrogen, or halogen atoms in their molecular structure were considered as possible entrainers. Thirty-six such compounds were evaluated.

The major pieces of equipment used in carrying out this study were three packed distillation columns having 26, 25, and 16 theoretical plates, a refractometer, and a gas chromatograph.

Evaluation of an entrainer consisted of determining if the entrainer formed an azeotrope with meta-xylene, and if so the azeotropic composition, and the effect upon the relative volatility of the xylenes. If a mixture of the meta-xylene and the entrainer had a boiling point which was lower than the boiling points of the pure components, a minimum boiling azeotrope existed. The composition of this mixture was varied until the overhead and bottoms products from a distillation column had the same composition. This mixture was the azeotropic composition since the vapor and the liquid of an azeotrope have the same composition. The effect upon the relative volatility of the xylenes was determined by distilling a charge consisting of the meta-xylene and entrainer azeotrope and an amount of ortho-xylene equal to the amount of meta-xylene present. Quantitative analysis of the overhead and bottoms samples were obtained by the use of a gas chromatograph. The relative amounts of the xylenes in these samples were used with the Fenske equation to calculate the relative volatility. The basis of evaluation used was the comparison of the relative volatility obtained with and without an entrainer.

Duplicate relative volatility runs were made for all entrainers, and the values obtained agreed well within the expected experimental error. Twenty-one compounds increased the relative volatility of the xylenes, while seven decreased it. The relative volatility for the xylenes using no entrainer was 1.105. Formic acid, the best entrainer, increased the relative volatility to 1.154, and its use would require only 70 percent of the theoretical plates needed when no entrainer was used.

INTRODUCTION AND THEORY

The purpose of this investigation was to study the application of azeotropic distillation to the separation of meta-xylene from ortho-xylene.

Meta-xylene is a C_8 aromatic hydrocarbon having a boiling point of 139.1 C at one atmosphere of pressure. Ortho-xylene is also a C_8 aromatic hydrocarbon with a boiling point of 144.4 C at one atmosphere of pressure.

The chief industrial use of ortho-xylene is in the synthesis of phthalic anhydride, which is used for the preparation of plastics. Meta-xylene is also used in the production of plastics through its conversion to isophthalic acid. However, the principal use of this material is in the synthesis of xylidine. Both of these isomers have considerable use as industrial solvents and as octane improvers in motor and aviation gasoline (1).

The principal sources of the xylenes are petroleum and bituminous coal. Commercial xylene, whether derived from petroleum or coal, contains all four of the C_8 aromatics in a mixture approximately equal to the composition of the thermodynamic equilibrium at 1000 K; ortho-xylene 23%, meta-xylene 43%, para-xylene 19%, and ethylbenzene 15% (1).

The para-xylene is removed from the other C_8 aromatic hydrocarbons by a series of fractional crystallization and distillation

processes. The ortho and meta-xylene are separated from each other by a straight distillation process. Because of the proximity of their boiling points, the separation of these two isomers requires the use of distillation columns having a considerable number of theoretical plates. The operation of such large distillation columns is expensive, and methods of decreasing this operating expense are of interest. This interest has led to the study of the application of azeotropic distillation in order to reduce the number of theoretical plates needed for a given separation of the ortho and meta isomers.

The separation of chemical compounds by fractional distillation depends upon the differences in the tendencies of the compounds to vaporize at a given pressure. These differences in volatility cause the composition of the vapor coming from the liquid mixture to be different from the composition of the liquid. The greater the difference between the composition of the vapor and that of the liquid, the easier is the separation. The vapor coming from the liquid mixture tends to be richer in those constituents which are the more volatile (2).

A measure of the tendency of a chemical compound to vaporize is its boiling point. The lower the boiling point, the greater is the tendency for the compound to vaporize. Since meta-xylene and ortho-xylene have boiling points which are near each other, the tendencies of these compounds to vaporize are very much the same.

The distillation process is essentially characterized by the following combination of operations: a liquid mixture is partially vaporized by the application of heat; the vapor leaving the liquid is condensed resulting in a liquid distillate which is richer in the more volatile components. If the liquid distillate from this first step were again partially vaporized, the condensed vapor would result in a distillate which would be richer yet in the more volatile components. By repeating this procedure it would be possible to split a given liquid mixture into any number of distillate fractions. (3).

A distillation column is the means by which the above procedure is fulfilled. A single stage of distillation, in which the vapor leaving this stage is in thermodynamic equilibrium with the liquid, is called a theoretical plate. Therefore, a distillation column consists of a number of theoretical plates arranged vertically in a column. The vapor leaving each plate is condensed on the plate directly above, where it is then, in effect, partially revaporized. The number of theoretical plates necessary in a column depends upon the desired separation of a liquid mixture. In general, the greater the number of theoretical plates present, the greater is the degree of separation of components.

In the case of a binary mixture, it is possible to approach complete separation of the two components by using a series of theoretical

plates. The number of theoretical plates needed would depend upon the components' tendencies to vaporize. Since the boiling points, and therefore the vaporization tendencies, of meta-xylene and ortho-xylene are close to being the same, a large number of theoretical plates are needed to separate these components. This leads to expensive equipment and high operating costs. The aim of azeotropic distillation is to reduce the number of theoretical plates required for a given separation.

Azeotropic is the term applied to distillations which involve constant boiling mixtures (4). Liquid mixtures consisting of two or more components, which when partially vaporized give a vapor with exactly the same composition as that of the remaining liquid, are known as azeotropes. Only binary azeotropes, those consisting of two components, were used in the separation of ortho-xylene and meta-xylene.

The formation of azeotropes is a function of the non-ideality of the resulting mixture when two liquid components are mixed, and a function of the difference in boiling points between these two components. The deviation from ideality is attributed to the effects of hydrogen bonding and internal pressure (4).

There are several types of azeotropes: heterogeneous or homogeneous and minimum boiling or maximum boiling. Homogeneous azeotropes

are formed from components which are completely miscible, while heterogeneous azeotropes result from mixtures of partially soluble components. Minimum boiling azeotropes are those azeotropes which have a boiling point lower than the boiling points of the pure components from which they are formed. When an azeotrope is formed which boils at a higher temperature than the boiling points of the pure components from which it is formed, the azeotrope is called a maximum boiling azeotrope. All partially soluble liquids from minimum boiling azeotropes.

Since an azeotrope boils as a single compound, it can be separated from other compounds or azeotropes by fractional distillation as long as the vaporization tendencies of it and the other compounds present are sufficiently different.

In the application of azeotropic distillation to the separation of ortho-xylene and meta-xylene, a third compound called an entrainer would be added to this isomer mixture. The desired result would be that the entrainer would form an azeotrope with one of the xylene isomers and that this azeotrope would have a boiling point which differed greatly from the boiling points of the pure compounds. Since the xylenes are very chemically similar, it seems doubtful that many entrainers would form an azeotrope with the meta-xylene and not with the ortho-xylene. The literature however shows that a few such selective entrainers for the xylenes exist (5), but for the

most part it is likely that most of the entrainers will be non-selective.

In a commercial operation, the separation of the entrainer from the xylene isomer would be an important consideration (6). Such methods as phase separation and water washing could be used to remove the entrainer from the xylene. However, the problem of separating the entrainer from the xylene is not included in the purposes of this study.

Hydrogen bond pheonomena has a large effect upon the formation of azeotropes. According to the literature (4), the xylene isomers do not have hydrogen-bond-forming capabilities. However, chemicals possessing hydrogen bonds were evaluated as possible azeotroping entrainers, since the breaking of these hydrogen bonds by the xylenes would contribute to the formation of an azeotrope.

In order to compare azeotropic distillation and straight distillation of ortho-xylene and meta-xylene, a measure of the degree of separation of the xylenes must be known. The volatility of a component is defined as the ratio of the mole fraction of a component in the vapor to the mole fraction of the component in the liquid. If the component is in the pure state, its volatility is identical with its vapor pressure (2). Therefore, volatility is a measure of a compound's tendency to vaporize.

Where the degree of separation of two components is to be evaluated, the concept of relative volatility is used. Relative volatility is simply the volatility of one component divided by that of another (2). The volatility of the higher boiling component is generally used as the denominator of the ratio in order to give a relative volatility greater than unity. The greater the relative volatility, the greater is the ease of separating two components.

The above definition of relative volatility holds ture only for a single theoretical plate. By applying this definition of relative volatility to each theoretical plate in a rectification column at total reflux, and considering the relative volatility to be constant, the following equation can be obtained:

$$\alpha_{AB}^{n+1} = \frac{Y_A X_B}{Y_B X_A}$$

where

α = relative volatility

n = number of theoretical plates

Y_A, Y_B = mole fractions of the compounds A and B in the vapor

X_A, X_B = mole fractions of A and B in the liquid (2)

By the use of the above equation, it is not possible to determine the relative volatilities by quantitatively analyzing the material at the top and at the bottom of a distillation column.

Azeotropic and straight distillation of the xylene isomers are compared by using relative volatility as the criteria. It should be

kept in mind, that the greater the relative volatility, the greater is the case of separation of two compounds by distillation.

RESEARCH OBJECTIVES

The purpose of this investigation was to study the application of azeotropic distillation to the separation of ortho-xylene from meta-xylene. Separation of the xylenes by straight distillation and azeotropic distillation is to be compared by using the relative volatility for ortho-xylene and meta-xylene as the criteria.

EQUIPMENT

In carrying out the proposed study, the following equipment was used: three batch distillation columns, electric still-pot heaters, four Powerstat transformers, triple-beam balance, analytical balance, refractometer, and gas chromatograph.

The three distillation columns were comprised of three concentric glass tubes, having outside diameters of 1.25 inches, 2.00 inches, and 2.62 inches. The inner tube was packed with 1/8-inch stainless steel Fenske rings and had a 35/25 male joint on one end and a 29/42 female joint on the other end. These ground glass joints were used to connect the column with the still-pot and the condensing head. The middle concentric tube was wrapped with Nichrome heating coil so that the column could be operated near adiabatic conditions. A Powerstat transformer controlled the heat supplied to this middle tube. The outer glass column served primarily as insulation to prevent the excessive loss of heat.

A one-liter flask with a sidearm for sampling was used as a still-pot. An electric heater controlled by a Powerstat transformer was used to supply heat to the still-pot.

Each of the three columns had a different amount of packing, and therefore, each column had a different number of theoretical plates. The three columns had 46.5, 45.5, and 25.5 inches of packing

which resulted in 26, 25, and 16 theoretical plates respectively.

A schematic diagram of such a distillation column as described above is shown in Figure 1.

An Ohaus triple-beam laboratory balance was used to weigh the various components charged to the distillation columns. Where more precise weighings were necessary, as for the preparation of calibration curves for the gas chromatograph and refractometer, a Christian Becker analytical balance was used.

Quantitative analysis of the samples from the distillation columns were achieved by the use of a Valentine refractometer and an Aerograph gas chromatograph made by the Wilkens Instrument and Research Company.

A 1/4-inch stainless steel tube, 7 feet long and packed with 60-80 mesh Chromosorb P acid-washed packing containing 20 percent of 7, 8-benzoquinoline substrate, was used as the column for the gas chromatograph. This column was operated at a temperature of 100°C with a helium flow rate of 70 milliliters per minute. A Minneapolis-Honeywell recorder was used in conjunction with the gas chromatograph. The separation obtained from the chromatograph column is shown in Figure 2.

AZEOTROPIC ENTRAINING AGENTS

As it was mentioned previously, the choice of chemicals to be used as azeotroping entrainers was based primarily on their possession of hydrogen bonds. Since the boiling point of the entrainer is also an important factor in the formation of azeotropes and the setting of the azeotropic composition, compounds boiling in a range of 40 C° below meta-xylene to 20 C° above meta-xylene were generally considered. However, a few compounds outside of this boiling range were also evaluated.

The following is a list of chemical compounds which were evaluated as possible azeotroping entrainers.

2-methoxy ethyl acetate
isoamyl alcohol
n-propanol
methyl chloro acetate
cellosolve
2-methyl butanol
isobutyl carbinol
methyl isobutyl carbinol
formic acid
2-amino ethanol
acetic acid
2-ethyl butanol
2-chloro ethanol
isobutanol
butanol
methyl cellosolve
propionic acid
1-nitro propane
amyl alcohol
water
ethylene glycol
ethyl chloro acetate
cyclopentanol
2,4-pentanedione

morpholine

ethyl lactate

dimethyl ethanol amine

amyl acetate

methyl isoamyl ketone

2-butanol

N-ethyl morpholine

N-methyl piperazine

ethylene diamine

2-methyl pentanol

2,6-dimethyl morpholine

1,2-dibromo propane

EXPERIMENTAL PROCEDURE

The experimental procedure was nearly the same for each entrainer that was evaluated. Therefore, the general procedure will be described with mention made of any variations.

The first step in the procedure was to determine if the meta-xylene formed an azeotrope with the entrainer. The boiling point of the more volatile of these two components was recorded. If a depression in this boiling point occurred when the less volatile component was added to the column, a minimum boiling azeotrope had been formed. Samples of the overhead and bottoms products were then quantitatively analyzed using a refractometer and a prepared calibration curve as shown in Figure 3. Since the azeotrope boils lower than either of the pure compounds from which it is formed, the overhead product from the column will be the azeotrope. A mixture, which had the composition of this overhead product, was then charged to the column and distilled at total reflux for two hours in order that a steady state condition would exist in the column. Samples of the overhead and bottoms products were again quantitatively analyzed and the above distillation procedure was continued until the composition of the overhead was the same as that for the bottoms. Since the vapor composition of an azeotrope is equal to that of the partially vaporized liquid from which it comes, the composition, at which the overhead and the bottoms from the column are the same, is the azeotropic composition.

Once the composition of the azeotrope had been determined in the above manner, a charge consisting of this composition and an amount of ortho-xylene equal to the amount of meta-xylene present was distilled. The column was again operated at total reflux for two hours, after which samples of the overhead and bottoms products were taken.

Samples from the above distillation were injected into the gas chromatograph, and the relative amounts of meta-xylene to ortho-xylene were obtained from the relative areas under the peaks produced on the recorder. These experimental weight percents were then converted to actual weight percents by using a calibration curve for the chromatograph column, of actual weight percent meta-xylene versus experimental weight percent meta-xylene for a system of meta-xylene and ortho-xylene.

By using the Fenske equation the relative volatility for the xylene isomers was obtained. A sample calculation of the relative volatility appears in a later section of this thesis.

In the cases where the entrainer had the same retention time in the chromatograph as either xylene isomer, a water wash was used to remove the entrainer if it was soluble in water. Only a few entrainers which were insoluble in water, had such non-satisfactory retention times and these entrainers were rejected.

Duplicate relative volatility runs were made for all of the entrainers.

DISCUSSION OF RESULTS

Thirty-six chemical compounds were evaluated as possible azeotropic entrainers. The majority of these compounds had a boiling point in the range of 20 C° above to 40 C° below the boiling point of meta-xylene. About one-half of these chemicals were composed of alcohols and ketones, while the other one-half consisted mainly of amines.

Of the thirty-six compounds evaluated, relative volatility data was obtained for twenty-eight. Amyl acetate, 2-butanol, and 1, 2-dibromopropane were the only compounds investigated which did not form minimum boiling azeotropes with meta-xylene. The literature states that 1,2-dibromopropane forms a minimum boiling azeotrope with meta-xylene (5), however at the barometric pressure of 640 mm. Hg., at which this investigation was carried out, the 1,2-dibromopropane was found to decompose for three different trails.

One of the major quantitative analytical problems was the presence of overlapping retention times for the 7, 8-benzoquinoline chromatograph column. A number of entrainers had the same retention time as one or the other of the xylene isomers. In those cases where the entrainer was soluble in water, the entrainer was removed from the xylenes with a water wash. However, relative volatility data was not obtained for methyl isoamyl ketone, 2-methyl pentanol, and ethyl chloro acetate, since these chemicals had non-satisfactory

retention times and they were not soluble in water. This made the quantitative analysis of these samples a difficult task with the equipment which was available.

Relative volatility data was not obtained for 2,6-dimethyl morpholine because of a lack in the supply of this compound.

Five compounds formed two phase azeotropes with the meta-xylene. These compounds were water, formic acid, 2-aminoethanol, ethylene glycol, and ethylene diamine.

As was stated in an earlier section of this thesis, a minimum boiling azeotrope has a boiling point which is lower than the boiling points of the pure components from which it is formed. The difference in temperature between the boiling point of the azeotrope and the boiling point of the lowest boiling pure component was found to range from 1 C° to 14 C°.

The manner in which the azeotropic compositions were determined seemed to be very reliable. If the overhead product from a meta-xylene and entrainer mixture was considered as the azeotropic composition, it is possible that considerable error could be present. A column having only 25 theoretical plates could have difficulty in separating the azeotrope from the component in excess, therefore it is possible that the overhead product contained more of the component in excess than actually appears in the composition of the

azeotrope. As it was explained in earlier section of this thesis, the azeotropic composition was taken for the mixture of meta-xylene and entrainer which gave an overhead having the same composition as the bottoms. This procedure eliminated the possible error described above.

Table II lists the compositions of the azeotropes that were formed with meta-xylene. The amount of meta-xylene present in the azeotropes ranged from 8.8 weight percent, with propanol as the entrainer to 94.7 weight percent with ethylene glycol as the entrainer. From a commercial point of view, the less entrainer needed to form an azeotrope with the meta-xylene, the less is the expense for chemical materials.

Quantitative analysis for the compositions of the azeotropes was accomplished by using a refractometer with a constant temperature bath. The temperature was controlled at 20 ± .2°C. Plots of refractive index versus weight percent meta-xylene for systems of meta-xylene and entrainers were used in conjunction with the refractometer to determine the azeotropic composition. Such a plot is shown in Figure 3 of the Appendix. The accuracy of these plots depends upon the difference in the refractive indexes between the meta-xylene and the entrainer. In all the cases used in this study, the refractive indexes of the two components were sufficiently different to assure good accuracy.

The compositions of the two phase azeotropes were determined by a volumetric analysis. The volume percentages were converted to weight percentages by using the densities of the compounds taken from the literature (7).

The effect of the entrainers upon the relative volatility for meta-xylene and ortho-xylene is shown in Table III. The relative volatility for the xylenes using no entrainer was found to be 1.105. This value is the average of four determinations which ranged from 1.102 to 1.110. Values for the relative volatility when entrainers were used ranged from 1.154, with formic acid, to 1.064, with 2-chloro ethanol. Twenty-one entrainers increased the relative volatility for the xylenes, thus aiding in the separation of the isomers, while seven decreased the relative volatility and hindered the separation.

Duplicate relative volatility runs were made for all the entrainers. The values obtained from these duplicate runs agreed well. In Table III, the values obtained for the relative volatility for the two runs are listed, along with the average value of these two runs. The deviation between these duplicate runs ranged from 0.000 to 0.020 units for the value of the relative volatility, with only two entrainers exceeding the deviation of 0.0009 on the duplicate runs. Therefore, it is felt that the values from the duplicate runs agreed well within the expected experimental error.

Table IV compares the relative volatility results of azeotropic and straight distillation on the basis of the number of theoretical plates required to make a given separation. Since the meta-xylene and ortho-xylene used in this investigation had a purity of 99 weight percent, the number of theoretical plates was calculated on a basis of the separation of the xylene isomers to 99% purity. Using no entrainer, 97.2 theoretical plates are required to give the desired separation. When formic acid is used as an entrainer, 67.5 theoretical plates are necessary. Therefore the presence of formic acid as an entrainer with meta-xylene requires only 70 percent of the theoretical plates needed for straight rectification of the xylene isomers.

The Fenske equation, as shown in the sample calculations, was used to calculate the number of theoretical plates required for the above separation. Since this equation is valid only at conditions of total reflux, and since commercial operations would require something less than an infinite reflux ratio, the number of theoretical plates required would increase with a decrease in reflux ratio. However, the ratio of theoretical plates needed for azeotropic distillation to that needed for straight rectification at total reflux shows the effect of azeotropic distillation on the separation.

The values of the relative volatilities listed in Table III are subject to a small amount of error. By examining the Fenske

equation, page 7, it is seen that the relative volatility is dependent upon the number of theoretical plates in a column, and the amounts of the xylenes present in the overhead and bottoms. An error in the number of theoretical plates could result from changing boil-up rates for different runs. The boil-up rate was maintained as close as experimentally possible at a constant value. If the boil-up rate did change enough to cause an increase of one theoretical plate in the column, the relative volatility would be in error by 0.004 units from the relative volatility calculated using the number of plates obtained from the column's calibration.

Errors in the quantitative analysis of the overhead and bottoms products would also produce an error in the value for the relative volatility. A certain amount of error exists within the gas chromatograph and recording unit, however, it is felt that this error in the equipment is negligible in the comparison of the relative volatilities. A possible error exists in calculating the weight percents of the xylenes from the areas under the chromatogram peaks. An error of one weight percent in the quantitative analysis of the xylenes causes an error of 0.003 units in the relative volatility. By using samples of known composition, it was experimentally determined that a maximum error of one weight percent resulted in the quantitative analysis.

By experimentally varying the boil-up rate, it was determined that the number of theoretical plates in the column varied by three plates depending on the boil-up rate used. This change of three plates in the column would cause an error of 0.012 units in the relative volatility. Therefore it seems that the results obtained from this investigation possess only small amounts of error which do not alter the conclusions of the study.

There seems to be no correlation of the molecular structure and the boiling points of the entrainers with the relative volatilities listed in Table III. The difference in the boiling points of the azeotrope and the pure components from which it was formed did not give a correlation with the obtained relative volatilities.

CONCLUSIONS

By applying the principle of azeotropic distillation to the separation of meta-xylene from ortho-xylene, it is possible to separate these isomers using fewer theoretical plates than would be required for a straight rectification process.

SAMPLE CALCULATIONS

Calculation of relative volatility - using Fenske equation

$$\alpha^{n+1} = \frac{y_m x_o}{x_m y_o}$$

where α = relative volatility

n = number of theoretical plates in the column

Y_m & Y_o = mole percent* of meta-xylene and ortho-xylene in the overhead product

X_m & X_o = mole percent of meta-xylene and ortho-xylene in the bottoms product

Sample calculation for formic acid Run 1:

$$y_m = 96.0 \qquad y_o = 4.0$$

$$x_m = 34.0 \qquad x_o = 66.0$$

$$n = 25$$

$$\alpha^{26} = \frac{(96.0)(66.0)}{(4.0)(34.0)} = 46.5$$

$$\alpha = 1.159$$

Calculation of the number of theoretical plates needed to give an overhead composition of 99 weight percent m-xylene, and a bottoms composition of 1 weight percent m-xylene.

Sample calculation using no entrainer:

$$1.105^{m+1} = \frac{(99)(99)}{(1)(1)} = 9801$$

$$n + 1 = \frac{\ln 9801}{\ln 1.105} = 98.2$$

$$n = 97.2$$

*Because of equal molecular weights, mole percent equals weight percent for systems involving the two xylene isomers.

Sample calculation of the Number of theoretical plates needed using formic acid as the entrainer:

$$1.154 = 9801$$

$$n + 1 = \frac{\ln 9801}{\ln 1.154} = 68.5$$

$$n = 67.5$$

Calculation of the ratio of the number of theoretical plates needed for azeotropic distillation to that needed for straight distillation--

Sample calculation using formic acid as the entrainer:

$$\text{ratio} = \frac{\text{plates for azeotropic distillation}}{\text{plates for straight distillation}}$$

$$= \frac{67.5}{97.2}$$

$$= .70$$

APPENDIX

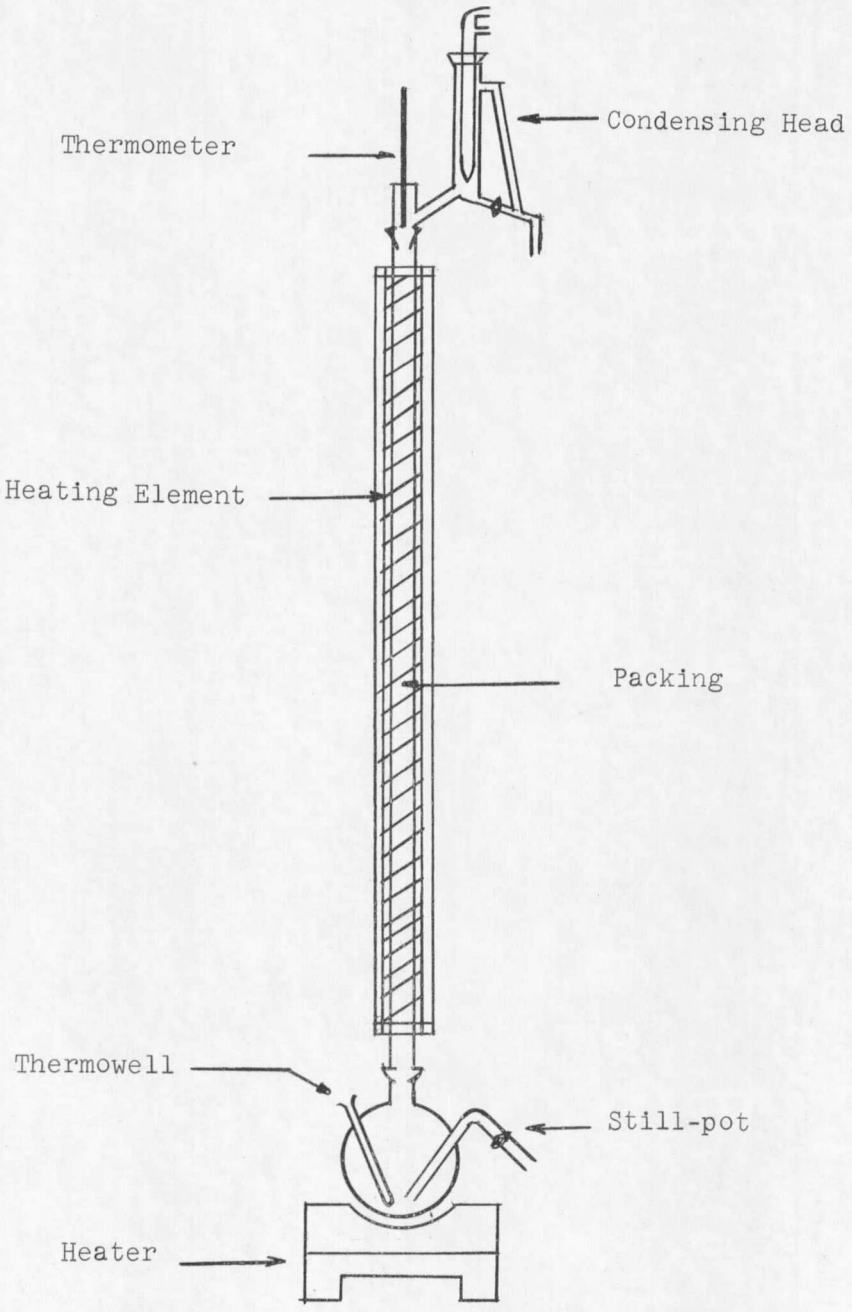


Figure 1. Distillation Apparatus

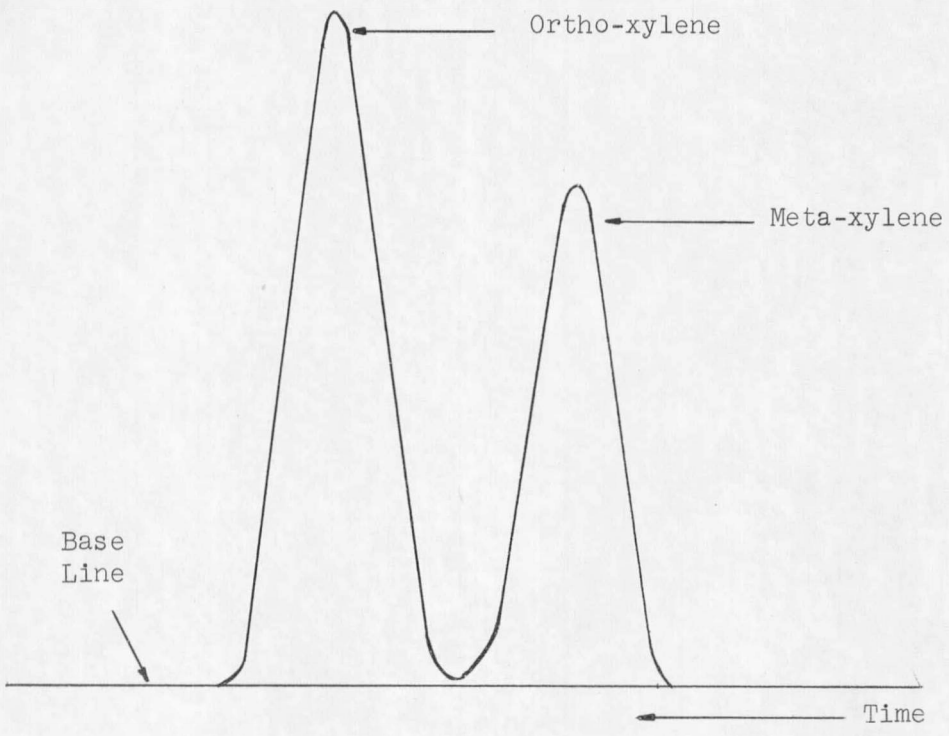


Figure 2. Meta-xylene and Ortho-xylene Peaks from Chromatographic Analysis

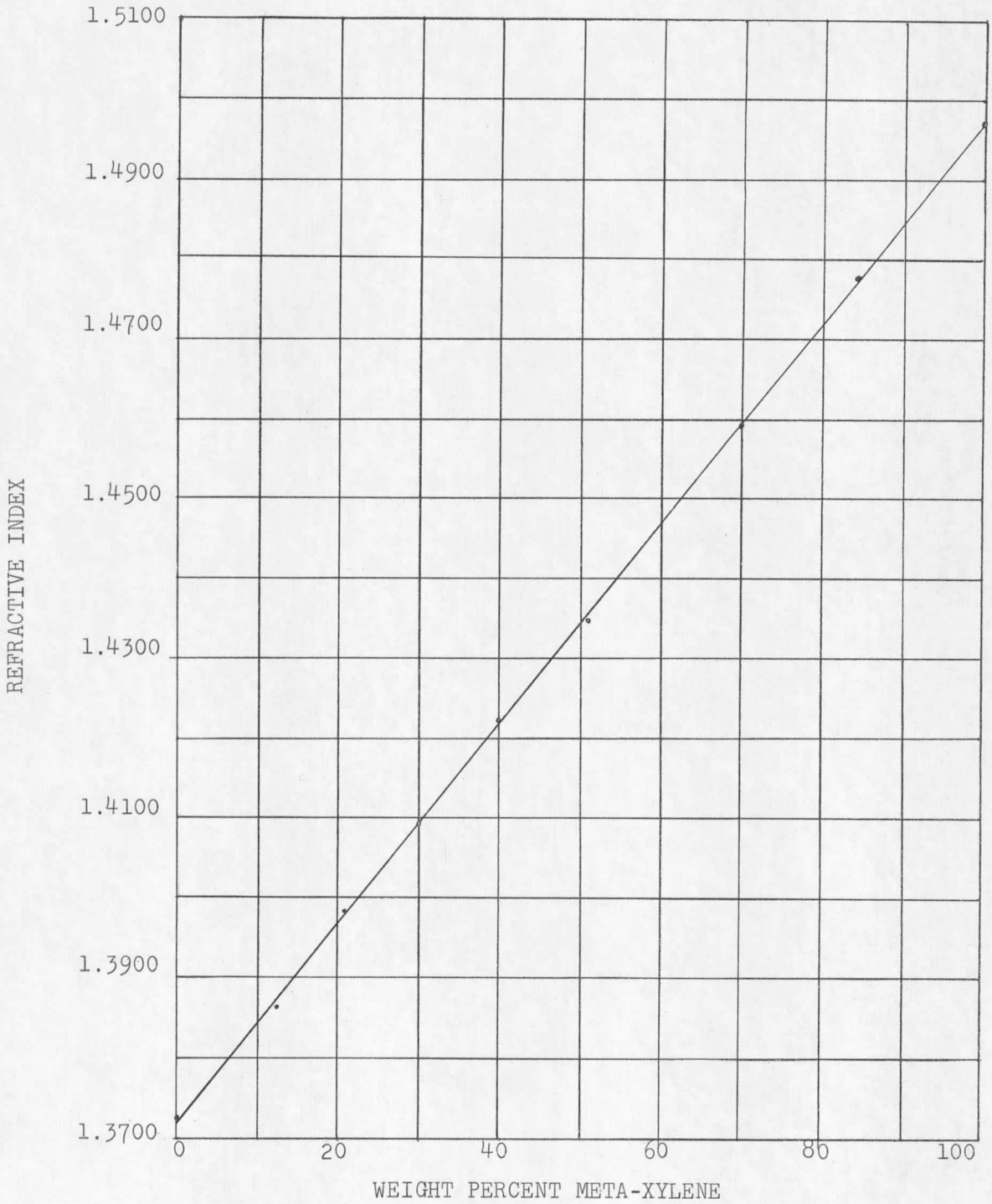


Figure 3. Refractive Index Versus Weight Percent Meta-xylene for a System of Acetic Acid and Meta-xylene

TABLE I

STRUCTURES AND BOILING POINTS OF ENTRAINERS

ENTRAINER	STRUCTURE	BOILING POINT °C*
2-methyl butanol	$CH_3CH_2CH(CH_3)CH_2OH$	128
methyl isobutyl carbinol	$(CH_3)_2CHCH_2CHOHCH_3$	131.4
isobutyl carbinol	$(CH_3)_2CH(CH_2)_2OH$	130.5
methyl isoamyl ketone	$CH_3COCH_2CH_2CH(CH_3)_2$	144
acetic acid	CH_3COOH	118.1
ethylene diamine	$H_2NCH_2CH_2NH_2$	116.1
2-ethyl butanol	$CH_3CH_2CH(C_2H_5)CH_2OH$	149.5
n-butanol	$CH_3CH_2CH_2CH_2OH$	117.7
isobutanol	$(CH_3)_2CHCH_2OH$	108.4
amyl acetate	$CH_3COO(CH_2)_4CH_3$	148
2-methyl pentanol	$CH_3(CH_2)_2CH(CH_3)CH_2OH$	148
2-chloro ethanol	$ClCH_2CH_2OH$	128.8
1-nitro propane	$CH_3CH_2CH_2NO_2$	132
2,4-pentanedione	$CH_3COCH_2COCH_3$	139
N-ethyl morpholine	$C_2H_5NCH_2CH_2OCH_2CH_2$	138.3
2,6-dimethyl morpholine	$NHCH_2CH(CH_3)OCH(CH_3)CH$	146.6
N-methyl piperazine	$CH_3NCH_2CH_2NHCH_2CH_2$	138
dimethyl ethanol amine	$(CH_3)_2NCH_2CH_2OH$	134.6
methyl chloro acetate	$ClCH_2COOCH_3$	131.5

*Boiling point at one atmosphereof pressure.

TABLE I (continued)

ENTRAINER	STRUCTURE	BOILING POINT °C
ethyl chloro acetate	$ClCH_2COOC_2H_5$	144.2
n-amyl alcohol	$CH_3(CH_2)_4OH$	138
methyl cellosolve	$CH_3OCH_2CH_2OH$	124.3
morpholine	$NHCH_2CH_2OCH_2CH_2$	126-30
cellosolve	$C_2H_5OCH_2CH_2OH$	135.1
ethylene glycol	$HOCH_2CH_2OH$	197.2
cyclopentanol	$CH_2CH_2CH_2CH_2CHOH$	139-40
2-amino ethanol	$H_2NCH_2CH_2OH$	172.2
n-propanol	$CH_3CH_2CH_2OH$	97.2
2-butanol	$CH_3CH_2CHOHCH_3$	99.5
2-methoxy ethyl acetate	$CH_3COOCH_2CH_2OCH_3$	142
isoamyl alcohol	$(CH_3)_2CHCH_2CH_2OH$	131
formic acid	$HCOOH$	100.7
propionic acid	CH_3CH_2COOH	141.1
water	H_2O	100
ethyl lactate	$CH_3CHOHCOOC_2H_5$	154(50-2)
1,2-dibromo propane	$CH_2BrCHBrCH_3$	141.6(40)

TABLE II

AZEOTROPIC DATA OF META-XYLENE WITH ENTRAINERS
AT 640 mm. Hg.

ENTRAINER	AZEOTROPIC COMPOSITION (wt. % m-xylene)	AZEOTROPIC BOILING POINT C
2-methoxy ethyl acetate	71.0	131
2-chloro ethanol	45.0	116
isoamyl alcohol	50.4	121
isobutanol	12.1	101
n-propanol	8.8	92
butanol	30.5	111
methyl chloro acetate	29.2	121
methyl cellosolve	43.5	112
cellosolve	53.5	121
propionic acid	64.4	125
2-methyl butanol	41.8	119
1-nitro propane	33.0	122
isobutyl carbinol	45.0	121
amyl alcohol	56.6	123.5
methyl isobutyl carbinol	38.9	122
water	61.2	87
formic acid	23.2	88
ethylene glycol	94.7	128
2-amino ethanol	83.8	126

TABLE II (continued)

ENTRAINER	AZEOTROPIC COMPOSITION (wt. % m-xylene)	AZEOTROPIC BOILING POINT C
ethyl chloro acetate	65.5	131
acetic acid	25.8	109
cyclopentanol	61.6	126
2-ethyl butanol	77.9	131
2,4-pentanedione	36.5	123
morpholine	21.0	119.5
N-ethyl morpholine	18.3	128
ethyl lactate	71.0	129
N-methyl piperazine	32.0	127
dimethyl ethanol amine	49.7	121

TABLE III

RELATIVE VOLATILITIES OF THE XYLENES*

ENTRAINER	RELATIVE VOLATILITY Run 1	Run 2	Ave.
formic acid	1.150	1.159	1.154
methyl isobutyl carbinol	1.15	1.145	1.150
2,4-pentanedione	1.148	1.150	1.149
water	1.150	1.130	1.140
amyl alcohol	1.137	1.136	1.136
isobutyl carbinol	1.132	1.130	1.131
2-amino ethanol	1.125	1.131	1.128
n-propanol	1.128	1.125	1.126
ethylene glycol	1.122	1.118	1.120
1-nitro propane	1.125	1.111	1.118
N-ethyl morpholine	1.118	1.116	1.117
isobutanol	1.112	1.119	1.116
2-ethyl butanol	1.115	1.113	1.114
ethyl lactate	1.116	1.113	1.114
isoamyl alcohol	1.113	1.114	1.114
morpholine	1.106	1.119	1.112
dimethyl ethanol amine	1.110	1.110	1.110
methyl chloro acetate	1.111	1.107	1.109
2-methyl butanol	1.111	1.106	1.108

*When no entrainer is used, the relative volatility is 1.105

TABLE III (continued)

ENTRAINER	Run 1	Run 2	Ave.
propionic acid	1.108	1.107	1.108
cellosolve	1.110	1.102	1.106
cyclopentanol	1.097	1.098	1.098
N-methyl piperazine	1.099	1.095	1.097
methyl cellosolve	1.096	1.094	1.095
n-butanol	1.093	1.093	1.093
2-methoxy ethyl acetate	1.091	1.092	1.092
acetic acid	1.082	1.078	1.080
2-chloro ethanol	1.063	1.064	1.064

TABLE IV

COMPARISON OF AZEOTROPIC AND STRAIGHT DISTILLATION FOR THE SEPARATION OF THE XYLENES*

ENTRAINER	THEORETICAL PLATES	RATIO +
no entrainer	97.2	1.00
formic acid	67.5	.70
methyl isobutyl carbinol	69.2	.71
2,4-pentanedione	69.7	.72
water	74.0	.76
amyl alcohol	75.6	.78
isobutyl carbinol	78.7	.81

*The composition of the overhead is 99 weight percent meta-xylene, and that of the bottoms is 1 percent meta-xylene.

+The ratio of theoretical plates needed for azeotropic distillation to that needed for straight distillation.

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