Separation of ethylbenzene from para-xylene by azeotropic distillation
by Richard Lee Nelson

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
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Abstract:
This investigation was performed to study the separation of ethylbenzene from para-xylene by azeotropic distillation. The apparatus consisted mainly of a fractionating column with a Corad condensing head, a refractometer, and a gas chromatograph.

The entraining agents were chemical compounds that were available at a reasonable price, that boiled from about 40°C below to 20°C above the boiling point of ethylbenzene, and that contained active oxygen, nitrogen, or halogen atoms since compounds having these atoms are likely to azeotrope with ethylbenzene. For each entraining agent a mixture of the entraining agent and ethylbenzene was charged to the column and distilled. The overhead product, which should be the ethylbenzene-entrainer azeotrope, since all azeotropes formed were minimum boiling azeotropes, was analyzed to determine the azeotropic-composition, The usual method of analysis was reading the refractive index of the sample and then determining the composition from a previously prepared plot of refractive index versus composition. The charge to the column was then adjusted so that there was enough entrainer to azeotrope with all of the ethylbenzene present./Also, about as much para-xylene was added to the charge as there was ethylbenzene. This charge was distilled at total reflux for at least three hours. Then samples of the overhead and bottoms were analyzed for percent ethylbenzene and para-xylene on the gas chromatograph so that relative volatilities could be calculated using the Fenske equation.

If the entrainers did not azeotrope with ethylbenzene, or if the azeotropes were less than 10% ethylbenzene* the entrainers were not used for a relative volatility determination. This method for determining azeotrope compositions seems to be reasonably good. The azeotropic composition between ethylbenzene and cellosolve found by this method at 640 mm. of mercury was 59 weight percent ethylbenzene. The literature(8) gives this azeotropic composition at 735 mm. of mercury as 56.7 weight percent ethylbenzene.

The relative volatility between ethylbenzene and para-xylene using no entrainer was 1.037. The relative volatilities obtained from the best four entrainers were: 2-methyl butanol, 1.079; methyl isobutyl carbinol, 1.075; n-hexyl amine, 1.073; and methyl amyl alcohol, 1.073. The ratios of the number of plates needed to obtain 95% separation in the overhead and bottoms products using an entrainer to using no entrainer were .48, .50, .51, and .51, respectively for these entrainers.

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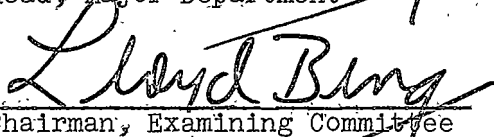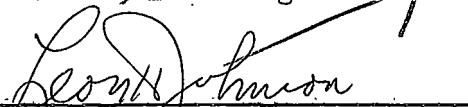fulfillment of the requirements for the degree

of

MASTER OF SCIENCE

in

Chemical Engineering

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MONTANA STATE COLLEGE
Bozeman, Montana

December, 1962

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ACKNOWLEDGEMENT

The author wishes to acknowledge the staff of the chemical
engineering department of Montana State College, and in particular
the research advisor Dr. Lloyd Berg, for their encouragement, sug-
gestions, and criticisms which have been helpful to the completion
of this research project.

The author also wishes to thank the National Science Foundation
for their financial assistance.

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ABSTRACT

This investigation was performed to study the separation of ethyl-benzene from para-xylene by azeotropic distillation. The apparatus consisted mainly of a fractionating column with a Corad condensing head, a refractometer, and a gas chromatograph.

The entraining agents were chemical compounds that were available at a reasonable price, that boiled from about 40 °C below to 20 °C above the boiling point of ethylbenzene, and that contained active oxygen, nitrogen, or halogen atoms since compounds having these atoms are likely to azeotrope with ethylbenzene. For each entraining agent a mixture of the entraining agent and ethylbenzene was charged to the column and distilled. The overhead product, which should be the ethylbenzene-entrainer azeotrope, since all azeotropes formed were minimum boiling azeotropes, was analyzed to determine the azeotropic composition. The usual method of analysis was reading the refractive index of the sample and then determining the composition from a previously prepared plot of refractive index versus composition. The charge to the column was then adjusted so that there was enough entrainer to azeotrope with all of the ethylbenzene present. Also, about as much para-xylene was added to the charge as there was ethyl-benzene. This charge was distilled at total reflux for at least three hours. Then samples of the overhead and bottoms were analyzed for percent ethylbenzene and para-xylene on the gas chromatograph so that relative volatilities could be calculated using the Fenske equation.

If the entrainers did not azeotrope with ethylbenzene, or if the azeotropes were less than 10% ethylbenzene, the entrainers were not used for a relative volatility determination. This method for determining azeotrope compositions seems to be reasonably good. The azeotropic composition between ethylbenzene and cellosolve found by this method at 640 mm. of mercury was 59 weight percent ethylbenzene. The literature (8) gives this azeotropic composition at 735 mm. of mercury as 56.7 weight percent ethylbenzene.

The relative volatility between ethylbenzene and para-xylene using no entrainer was 1.037. The relative volatilities obtained from the best four entrainers were: 2-methyl butanol, 1.079; methyl isobutyl carbinol, 1.075; n-hexyl amine, 1.073; and methyl amyl alcohol, 1.073. The ratios of the number of plates needed to obtain 95% separation in the overhead and bottoms products using an entrainer to using no entrainer were .48, .50, .51, and .51, respectively for these entrainers.

INTRODUCTION AND THEORY

The purpose of this investigation was to study the ease of separation of ethylbenzene and para-xylene by azeotropic distillation.

Ethylbenzene and para-xylene are two important commercial chemicals. Ethylbenzene is used to make styrene, and para-xylene is used to make terephthalic acid and plastics. The present method of separation of para-xylene and ethylbenzene from an ethylbenzene-xylene mixture is quite costly. Para-xylene is crystallized from a solution at about -63 °F with a yield of only about 65 percent. Ethylbenzene is then separated by distillation from the remaining xylenes, which includes some para-xylene. The distillation columns used for this separation require a large number of theoretical plates. This study was undertaken to see if the separation could be accomplished using a smaller number of plates by employing azeotropic distillation.

Distillation is a process of separation based on the difference in composition between a liquid and the vapor formed from it. Since the difference in composition between a liquid and the vapor formed is somewhat dependent on the difference in boiling points of the constituents, compounds with close boiling points such as ethylbenzene and para-xylene are difficult to separate by straight distillation. For this reason, azeotropic distillation was selected as one method to separate these two compounds.

The method selected to measure the separation between ethylbenzene

and para-xylene was their relative volatility. The volatility of a compound is a measure of its tendency to enter the vapor phase, and is equal to the mole fraction of the component in the vapor phase divided by the mole fraction of the component in the liquid phase. The ease of separation of a binary mixture by fractional distillation depends on the relative volatility of one component to the other component. /The purpose of azeotropic distillation is to change the relative volatilities of the components present.

Since all systems for this study were homogeneous, the discussion that follows will be for homogeneous systems only. An azeotrope is a constant boiling mixture and is usually the result of deviations from ideality caused by hydrogen bonds or internal pressure. A minimum boiling binary azeotrope is a mixture of the two pure compounds that has a boiling point which is less than the boiling point of any other mixture containing the pure components. In the sense that an azeotrope will distill with no change in composition, it acts like a pure compound. However, the composition of azeotropes rarely corresponds to any simple formula, and the azeotropic composition changes if the pressure of distillation changes. A maximum boiling azeotrope is a mixture of the two pure compounds that has a boiling point which is greater than the boiling point of any other mixture containing the two pure components. No maximum boiling azeotropes were encountered in this study. The reason there were none is discussed in the section CHEMICAL COMPOUNDS.

Azeotropic distillation has been used quite successfully to separate different classes of compounds. However, the separation of isomers or homologues generally presents a more difficult problem. One example of this type of separation is between 2,6-lutidine, 3-picoline, and 4-picoline(6) using acetic acid which forms a maximum boiling azeotrope with each of these compounds.

The equation used to calculate the relative volatility was the Fenske equation which can be written as follows:

$$\alpha^{n+1} = \frac{y_e}{y_p} \times \frac{x_p}{x_e}$$

where α = relative volatility

n = number of theoretical plates in column

y_e = percent ethylbenzene in overhead

y_p = percent para-xylene in overhead

x_p = percent para-xylene in bottoms

x_e = percent ethylbenzene in bottoms

This formula results from applying the definition of relative volatility to each theoretical plate in the column and to the still-pot which acts as one theoretical plate.

The method of analyzing samples to obtain quantitative values for the overhead and bottoms compositions was a gas chromatograph. Gas chromatography uses a gas as the mobile phase. The solute travels

through the column as a plug of gas which is partially dissolved in, or adsorbed on, the stationary phase. A sample of the mixture to be analyzed is flash-evaporated at one end of the column. The time required for each component to emerge from the column is known as its retention time. This retention time is characteristic of the compound. The chromatograph used had a thermal conductivity cell that detects each component as it emerges from the column.

A continuous recorder records each component as a peak on the recording paper. If two compounds have equal thermal conductivities but different retention times, the areas under the peaks for each of the compounds should be proportional to the volume percent of each compound in the sample. This method was used in this study since the thermal conductivities of ethylbenzene and para-xylene should be nearly equal. The accuracy of this method is evaluated in the DISCUSSION OF RESULTS section.

RESEARCH OBJECTIVES

The main objective of this project was to effect a separation
between ethylbenzene and para-xylene using azeotropic distillation
that would require a smaller number of plates than would be needed
to effect the same separation using straight distillation. The separ-
ation obtained was to be measured by relative volatility between ethyl-
benzene and para-xylene for each entrainer used.

A secondary objective was to determine azeotropic compositions
between ethylbenzene and various entraining agents.

EQUIPMENT

The equipment used in this study consisted of a fractionating column, Corad condensing head, still-pot, electrical heater, refractometer, Westphal balance, Ohaus balance, Christian Becker chainomatic balance, and gas chromatograph with a Minneapolis-Honeywell recorder.

The fractionating column was made from three concentric glass cylinders each 48 inches high. The diameters of the three cylinders were 1.0, 1.75, and 2.5 inches, respectively. The inside cylinder contained 45 inches of randomly packed, one-eighth inch stainless steel helice packing (Fenske rings) supported on a cone-shaped wire support. The middle column was wound with a Nichrome heating coil so that the column could be operated nearly adiabatically. The heat supplied was controlled with a Variac connected to the heating coil. A mercury thermometer was attached to the outside of the inner column. The inner column had ground glass joints at top and bottom so that the Corad condensing head and the still-pot could be connected easily but tight enough to prevent any vapor from leaking from the column to the air.

The still-pot used was a one-liter flask with a sidearm for sampling and a thermometer well. This still-pot was heated with a small electric heater connected to a Variac. The Variac was used to control the heat input to the column.

A Corad condensing head was used to condense the vapors rising from

the fractionating column. Using this head, reflux ratios of 2.5 to 1,

5 to 1, 10 to 1, 20 to 1, and 30 to 1 could be obtained. This head was

used at total reflux except when overhead samples were taken. During

this time, a 30 to 1 reflux ratio was used.

A diagram of this equipment is shown in Figure 1.

An Ohaus laboratory balance scale was used to weigh the amounts of

the various components charged to the column.

In determining azeotropic compositions, a Valentine refractometer

and a Westphal balance were used. A constant temperature water bath was

used to keep the temperature of the samples in the refractometer at 20

degrees Centigrade.

An Aerograph gas chromatograph made by the Wilkens Instrument

and Research Company was used to analyze the overhead and bottoms prod-

ucts for percent ethylbenzene and para-xylene. Two packed chromatograph

columns were used. One was a 1/4-inch copper tube, 12 feet long, packed

with 60-80 mesh Chromosorb P acid-washed packing, containing 20 percent

of 7,8-benzoquinoline substrate. This column was operated at 100 $^{\circ}$C

with a helium flow rate of about 90 milliliters per minute. The separa-

ation obtained between ethylbenzene and para-xylene for this column is

shown in Figure 2. The other column was a 1/4-inch copper tube, 8 feet

long, packed with 30-60 mesh Chromosorb P acid-washed packing, containing

15 percent of 1-chloronaphthalene substrate. This column was operated at

about 50 °C with a helium flow rate of about 175 milliliters per minute. The separation obtained between ethylbenzene and para-xylene for this column is shown in Figure 3. A Minneapolis-Honeywell recorder was used with the chromatograph.

A Christian Becker precision chainomatic balance was used to weigh the pieces of paper representing the areas under the peaks from the chromatograph.

CHEMICAL COMPOUNDS

Chemicals used for this investigation were the various entraining agents, ethylbenzene, and para-xylene. The ethylbenzene and para-xylene were obtained from Phillips Petroleum Company. These compounds were not less than 99 mole percent pure, and were not redistilled.

All liquids can be divided into the following five classes of compounds:(2)

1. "Liquids capable of forming three-dimensional networks of strong hydrogen bonds.

2. Other liquids composed of molecules containing both active hydrogen atoms and donor atoms.

3. Liquids composed of molecules containing donor atoms but no active hydrogen atoms.

4. Liquids composed of molecules containing active hydrogen atoms but no donor atoms.

5. All other liquids."

Ethylbenzene and para-xylene are class 5 liquids. Any liquid that azeotropes with a class 5 compound will always give positive deviations from Raoult's law which causes minimum boiling azeotropes.

The entrainers were selected for the following reasons:

1. be available at a reasonable price,

2. boil close to the boiling point of ethylbenzene,

3. contain oxygen, nitrogen, or halogen atoms, or groups containing these atoms.

The boiling points of the entrainers were usually from 40 °C below

to 15 °C above the boiling point of ethylbenzene. However, a few entrainers were tried that boiled below this range to check the effect this would have on the relative volatility. Entrainers that were water soluble and that did not azeotrope with water would be desirable for separation of the entrainer from the ethylbenzene, but the number of compounds having these properties in this boiling range is small.

The following list shows the entrainers that were used for this investigation:

2-methyl butanol	2,6-dimethyl morpholine
methyl isobutyl carbinol	isobutyl carbinol
n-hexyl amine	acetic acid
n-butanol	ethyl chloro acetate
amyl acetate	N-methyl piperazine
5-hexen-2-one	dimethyl ethanolamine
methyl propyl carbinol	2,4-pentanedione
1-nitro propane	1,3-diamino propane
methyl isoamyl ketone	n-propanol
2-ethyl butanol	n-amyl alcohol
2-methyl pentanol	2-chloro ethanol
2-nitro propane	nitroethane
diethyl carbinol	N-ethyl morpholine
methyl chloro acetate	methyl amyl acetate
dimethylamino propyl amine	dimethyl isopropanolamine

isobutanol

pyrrole

cellosolve

methyl cellosolve

propylene diamine

2-picoline

ethylene diamine

morpholine

allyl propionate

amyl formate

secondary butyl alcohol

tertiary butyl alcohol

chloro-2-propanone

1,3-dimethyl butyl amine

1,4-dioxane

ethyl butyl ketone

ethyl butyrate

p-fluoro toluene

isobutyl acetate

methanol

methyl ethyl ketone

methyl isobutyl ketone

N-methyl morpholine

2-methyl piperidine

piperazine

n-propyl propionate

pyrazine

tetrachloro ethylene

Table I gives the structures and boiling points of these entrainers at 760 mm. of mercury.

Most of the entrainers were obtained from Union Carbide Chemicals Company, Eastman Kodak Company, and Fisher Scientific Company. These entrainers were redistilled to remove high and low boiling impurities.

OPERATING PROCEDURE

During this investigation, nearly the same experimental procedure was used for each entrainer. Therefore, this section will present the general procedure used, with detailed descriptions of any variations in this procedure.

The first step in this investigation was to determine azeotropic compositions between the entrainer and ethylbenzene. A rough estimate of the azeotropic composition was made from the difference in boiling points of the entrainer and the ethylbenzene. A mixture of this composition was then charged to the column. Distillation at a 30 to 1 reflux ratio was used until the distillate temperature became constant. Since the azeotrope is the lowest boiling material, it should be the first material to come off as distillate. A distillate sample at this reflux ratio was then taken.

The distillate sample was then analyzed to determine azeotropic composition. For nearly all of the entrainers, the refractive index of the entrainer was much lower than the refractive index of the ethylbenzene. If so, the refractive index of the overhead from the column (the azeotrope) was found using the refractometer, and the composition of the azeotrope was determined from a previously prepared plot of refractive index versus composition.

In some cases the refractive index of the entrainer was too close to the refractive index of the ethylbenzene. Two methods were used to

determine the azeotropic composition of these samples. Some of the azeotropes were run through the chromatograph and analyzed by measuring the areas under the peaks as described in more detail later in this section for ethylbenzene and para-xylene. However, since the thermal conductivities of the entrainer and the ethylbenzene might be quite different, samples of known weight percent ethylbenzene and entrainer were run on the chromatograph. Then a plot of actual weight percent versus chromatograph area percent was made. From the area percent for the azeotrope, the azeotropic composition was then determined from this plot. This method was used for the following entrainers: 2-picoline, p-fluoro toluene, pyrazine and pyrrole.

The other method used when the refractive indices were too close was to measure differences in densities with the Westphal balance. This was used on only one entrainer. This entrainer was tetrachloro ethylene which did not azeotrope above 10 percent ethylbenzene.

After the azeotropic composition had been determined, enough additional entrainer or ethylbenzene was added to the column so that all of the entrainer would azeotrope with all of the ethylbenzene. Enough para-xylene was added to the column so that the amount of para-xylene was about equal to the amount of ethylbenzene in the column. However, the exact amount of para-xylene added is not important since the overhead and bottoms samples were analyzed on the chromatograph.

Distillation at a reflux ratio of 30 to 1 was used until the

temperature of the overhead became constant at the temperature of the azeotrope. The Corad condensing head was then turned to infinite reflux (all distillate returned to the column). The column was then operated at total reflux for at least three hours. At this time, a one milliliter sample of the overhead and bottoms were taken. The reflux ratio used was 30 to 1 to keep the column as close to total reflux as possible.

The samples of the overhead and bottoms products were then injected into the gas chromatograph with the column containing the 7,8-benzoquinoline substrate for analysis. If the entrainer did not come out at the same time as the ethylbenzene or para-xylene, the areas under the peaks for ethylbenzene and para-xylene were analyzed by tracing the peaks on a piece of paper. These tracings were then cut from the paper and weighed on the Christian Becker chainomatic balance. The areas under the respective peaks were taken as a measure of the relative amounts of ethylbenzene and para-xylene present. If the entrainer did come out at the same time as the ethylbenzene or para-xylene using this column, the column containing the 1-chloronaphthalene substrate was used. However, the separation on this column was not quite as good as the column containing the 7,8-benzoquinoline (see Figures 2 and 3). Since the chromatograph columns did not completely separate ethylbenzene from para-xylene, the lines were extrapolated as though only one component had been present as shown in Figures 2 and 3.

DISCUSSION OF RESULTS

The method used in this investigation to determine azeotropic composition is probably not the most accurate method since the column used cannot completely separate a homogeneous azeotrope from a pure component. However, if the boiling point of the ethylbenzene-entrainer azeotrope is more than a few degrees below the boiling point of the ethylbenzene, nearly complete separation should be obtained. The literature(8) gives the azeotropic composition between ethylbenzene and cellosolve as 56.7 weight percent ethylbenzene at 735 mm. of mercury. A value determined by the method used for this investigation gave a value of 59 weight percent ethylbenzene at 640 mm. of mercury. Considering the difference in pressure, this agreement seems quite good.

When the azeotropic composition was determined to be less than 10 percent ethylbenzene, the entrainer was not used for a relative volatility determination. The main reason these entrainers were not used is that the possibility of one of these entrainers making such a separation economical is small since so much entrainer would have to be used for a small amount of ethylbenzene. Also, if the azeotropic composition appears to be only three or four percent ethylbenzene, it is possible that the separation in the column was not good enough to separate completely the two pure components. This means that the compounds might not have even azeotroped.

The methods of analysis for azeotropic compositions were reasonably accurate. The temperature of the refractometer was controlled

at 20±0.5 °C. The refractive index method is probably the most accurate
method of analysis used. For the chromatograph, five samples of known
concentrations of ethylbenzene—para-xylene mixtures were analyzed on
the chromatograph. The average error for these determinations was one
percent. However, since the ethylbenzene and entrainers probably had
different thermal conductivities, plots of actual weight percent
entrainer to chromatograph area percent entrainer were made. Since
this introduces another source of error, the error in these analyses
was probably between one and two percent. Although using the Westphal
balance to determine densities should give reasonably accurate azeotropic
compositions, the accuracy of this method is not important in this
report since the only system that was analyzed this way did not seem
to indicate an azeotrope between the entrainer and the ethylbenzene.
The entrainer for this system (tetrachloro ethylene) has a density
of 1.623 gm/ml while the ethylbenzene has a density of 0.867 gm/ml.

The relative volatilities found in this investigation should be
close to, but not precisely equal to, actual relative volatilities
since the exact number of theoretical plates was not known. The value
used in this report, 23 theoretical plates, should be close to the
actual value. However, for comparing the various entrainers, the
calculated relative volatilities does give a valid rating of the
entrainers except for errors in measurements as discussed in the next
paragraph. Table III lists the relative volatilities for the entrainers
aiding separation while Table IV lists the relative volatilities for

the entrainers that did not enhance the separation. Also, the ratio of percent of plates needed using an entrainer to using no entrainer (Table V) should be correct even though the number of theoretical plates may not be exact. The following discussion of error will deal only with error assuming the column was found experimentally to have 23 theoretical plates.

The average error in area percents from the chromatograph, as determined from known samples, was one percent. An error of one percent in overhead and bottoms samples could have caused an error in the relative volatility of 0.004 units. Also, several factors such as boil-up rate in the column can change slightly the number of theoretical plates in the column. A change of one theoretical plate (as from 23 to 24 theoretical plates) would change the relative volatility by 0.003 units. As an example of the reproducibility of results, two separate trials using no entrainer were performed. The relative volatilities for these runs were 1.035 and 1.039. For calculations the average of 1.037 was used.

Two correlations of relative volatility with some property of the entrainers were examined. The first, boiling point, did not seem to have any correlation with relative volatility. This can be seen from the boiling points listed in Table I which has entrainers arrange in decreasing order of relative volatility. The second correlation examined was the type of compound. Several of the best entrainers

were alcohols. However, several of the other alcohols either did not

azeotrope or gave much smaller relative volatilities. Correlation of

alcohols by boiling points also did not seem to show any meaningful

trend.

CONCLUSIONS

It is possible to effect a given separation between ethylbenzene and para-xylene with about one-half as many theoretical plates using certain entraining agents as by straight distillation.

SAMPLE CALCULATIONS

Calculation of relative volatility

Fenske equation

$$\alpha^{n+1} = \frac{y_e}{y_p} \times \frac{x_p}{x_e}$$

where α = relative volatility

n = number of theoretical plates in column

y_e = percent ethylbenzene in overhead

y_p = percent para-xylene in overhead

x_p = percent para-xylene in bottoms

x_e = percent ethylbenzene in bottoms

Sample calculation using 2-methyl butanol run.

y_e = 0.785 mole fraction ethylbenzene

y_p = 0.215 mole fraction para-xylene

x_p = 0.627 mole fraction para-xylene

x_e = 0.373 mole fraction ethylbenzene

$$\alpha^{24} = \frac{0.785}{0.215} \times \frac{0.627}{0.373} = 6.14$$

$$= 1.079$$

Calculation of number of plates needed using entrainer divided by number of plates needed by straight distillation to obtain 95% separation at total reflux.

α_e = relative volatility using 2-methyl butanol (1.079)

α_s = relative volatility using no entrainer (1.037)

n_e = number of plates using 2-methyl butanol

n_s = number of plates using no entrainer

$$\alpha_e^{n_e+1} = \frac{0.95}{0.05} \times \frac{0.95}{0.05} = 361$$

$$1.079^{n_e+1} = 361$$

$$n_e+1 = 77.5$$

$$n_e = 76.5$$

$$\alpha_s^{n_s+1} = 361$$

$$1.037^{n_s+1} = 361$$

$$n_s+1 = 162$$

$$n_s = 161$$

$$\frac{n_e}{n_s} = \frac{76.5}{161} = 0.48$$

APPENDIX