



Separation of ethylbenzene from para-xylene by extractive distillation  
by Stephen Lynn Supola

A thesis submitted 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 application of extractive distillation to the separation of ethylbenzene from para-xylene .

\ \ The experimental work consisted of evaluating extractive agents in order to determine their effect on the relative volatility of ethylbenzene to para-xylene. During the course of the research, 12 different extractive agents were investigated. The extractive agents were composed of various oxygenated organic compounds. It was determined that the selection of the proper extractive agent components, the ratio of extractive agent to ethylbenzene-para-xylene mixture, and the dimensions of the column involved is vital to the success of the process.

The major pieces of equipment used in this study were two distillation columns having 18 and 44 theoretical plates respectively and a gas chromatograph.

Evaluation of an extractive agent was done by using the extractive agent in an actual extractive distillation of ethylbenzene and para-xylene. The extractive agents' effect on the relative volatility of ethylbenzene to para-xylene was determined by using the analytical data obtained from the gas chromatograph in the Fenske equation.

The relative volatility between ethylbenzene and para-xylene is 1.06. All of the extractive agents tested had yielded relative volatilities of at least 1.20 in vapor-liquid equilibrium stills. Of the 12 different extractive agents tested in a distillation column, the best result was obtained using an extractive agent composed of 40 wt% phthalic anhydride, 40 wt% maleic anhydride, and 20 wt% hexylene glycol diacetate. This agent increased the relative volatility to 1.152.

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*Stephen Lynn Lyzola*

*Feb. 16, 1979*

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BY EXTRACTIVE DISTILLATION

by

STEPHEN LYNN SUPOLA

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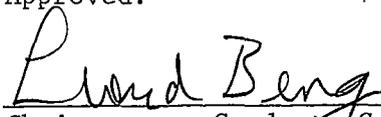
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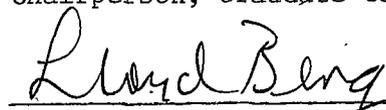
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## ABSTRACT

This investigation was performed to study the application of extractive distillation to the separation of ethylbenzene from para-xylene.

The experimental work consisted of evaluating extractive agents in order to determine their effect on the relative volatility of ethylbenzene to para-xylene. During the course of the research, 12 different extractive agents were investigated. The extractive agents were composed of various oxygenated organic compounds. It was determined that the selection of the proper extractive agent components, the ratio of extractive agent to ethylbenzene-para-xylene mixture, and the dimensions of the column involved is vital to the success of the process.

The major pieces of equipment used in this study were two distillation columns having 18 and 44 theoretical plates respectively and a gas chromatograph.

Evaluation of an extractive agent was done by using the extractive agent in an actual extractive distillation of ethylbenzene and para-xylene. The extractive agents' effect on the relative volatility of ethylbenzene to para-xylene was determined by using the analytical data obtained from the gas chromatograph in the Fenske equation.

The relative volatility between ethylbenzene and para-xylene is 1.06. All of the extractive agents tested had yielded relative volatilities of at least 1.20 in vapor-liquid equilibrium stills. Of the 12 different extractive agents tested in a distillation column, the best result was obtained using an extractive agent composed of 40 wt% phthalic anhydride, 40 wt% maleic anhydride, and 20 wt% hexylene glycol diacetate. This agent increased the relative volatility to 1.152.

## Introduction

The purpose of this investigation was to study the feasibility of separating ethylbenzene from para-xylene by means of extractive distillation and to test this separation in the high-purity range of ethylbenzene. Paul Kober, in 1974, at Montana State University did previous work in this area investigating various chlorinated compounds as extractive agents. (4) This investigation tested various oxygenated compounds as extractive agents. Also, Kober did not test this separation in the high-purity range of ethylbenzene.

There are three isomeric xylenes, the ortho, meta, and para isomers. Ethylbenzene is also isomeric with the xylenes. The four usually occur together as a result of thermodynamic equilibrium in their origin. These compounds are obtained from the petroleum industry where both are products of the reforming process used in the refining of oil. The principle use of ethylbenzene is in the conversion to styrene for synthetic rubber. Para-xylene is used to make terephthalic acid, which is used in the manufacture of synthetic fiber and plastics. Ethylbenzene and para-xylene have nearly the same vapor pressures and boiling points. Ethylbenzene has a boiling point of  $136.2^{\circ}\text{C}$  at one atmosphere pressure and para-xylene has a boiling point of  $138.4^{\circ}\text{C}$  at one atmosphere pressure. These similarities make their separation difficult and costly. The present method of separation is by fractional crystallization. Para-xylene can be crystallized from a solution of

xylenes since the freezing point of para-xylene is  $13.3^{\circ}\text{C}$  while the other isomeric compounds all have freezing points below  $-25^{\circ}\text{C}$ . This method recovers about 65% of the para-xylene from the mixture. The ethylbenzene is recovered from the remaining mixture of xylenes, which still has some para-xylene in it, by fractional distillation. Because of the large number of theoretical plates required to make this separation, extractive distillation is being investigated to determine if this separation could be accomplished with fewer plates. (1)

The degree of separation of two chemical compounds by means of fractional distillation depends on the difference in their volatilities. In a vapor-liquid equilibrium mixture, the more volatile compound will be in greater concentration in the vapor phase than in the liquid phase. The difference in volatilities of two compounds is determined by the difference in their boiling points. Since ethylbenzene and para-xylene have nearly the same boiling points, their tendency to vaporize is nearly the same, which means that they cannot be easily separated by straight fractional distillation. For this reason, extractive distillation was selected as a means to separate these two compounds. (2)

In extractive distillation, separation of two components is effected by the addition of a third component. Extractive distillation is fractional distillation in the presence of a solvent. This solvent must be relatively non-volatile compared to the compounds to be separated and act as a preferential solvent for one of the components. The solvent

is added near the top of the column and flows down the column washing the ascending vapors and absorbing one of the components preferentially. The vapor pressure of the dissolved material is lowered, thus raising the relative volatility of the two-component mixture to be separated. As can be seen in Table I, raising the relative volatility of a binary mixture decreases the number of theoretical plates required for a given separation. (3)

Table I. Relative Volatility vs. Theoretical Plates for 99% Purity of both Components of a Binary Mixture

<u>Relative Volatility</u>	<u>Theoretical Plates</u>
1.06	157
1.08	118
1.10	97
1.11	87
1.12	81
1.13	75
1.14	70
1.15	66
1.16	62
1.17	58
1.18	55
1.19	53
1.20	50

In this research, the method used to measure the degree of separation obtained between ethylbenzene and para-xylene was their relative volatility. Relative volatility is defined for an ideal mixture as the ratio of the vapor pressure of the more volatile component to the vapor pressure of the less volatile component. It is also defined as a

ratio of volatilities where volatility is equal to the mole fraction of the component in the vapor phase divided by the mole fraction of that component in the liquid phase. The volatility of the higher boiling component is usually used as the denominator of the ratio in order to give a relative volatility greater than one. The higher the value of the relative volatility, the easier the separation. (3)

The method used to calculate the relative volatility made use of the Fenske equation which can be written as follows:

$$\alpha^n = \frac{P_1}{E_1} \times \frac{E_v}{P_v}$$

where

$\alpha$  = relative volatility

n = number of theoretical plates

P<sub>1</sub> = percent para-xylene in bottoms

E<sub>1</sub> = percent ethylbenzene in bottoms

E<sub>v</sub> = percent ethylbenzene in distillate

P<sub>v</sub> = percent para-xylene in distillate

This equation, which applies at total reflux, came from applying the definition of relative volatility to every plate in the column. Because of the amount of liquid hold-up in the sampling ports of the column that had to be drained off to get a sample, the column could not be run at total reflux. For this reason the reflux ratio used was 30:1 both during the extractive runs to determine relative data and during the calibration runs to determine the number of theoretical

plates in the column.

The method of analyzing samples from the distillate and bottoms was a gas chromatograph. The samples were shot into the chromatograph and subsequent peaks, whose areas corresponded to quantitative values of ethylbenzene and para-xylene, were drawn out on the recorder. The recorder had an automatic integrater which measured the area under each peak and it was these areas that were used for the quantitative values in the Fenske equation.

#### Research Objectives

The objective of this research was to investigate as many extractive agents as possible to obtain relative volatility data for the separation of ethylbenzene from para-xylene. The ultimate purpose of this data is to supply the information needed for the design of a commercial ethylbenzene-para-xylene plant.

#### Experimental Procedures

##### Equipment

To carry out this research, two different distillation columns were used.

The first system used is shown in Figure 1, and it consisted of three six-foot sections and one two-foot section of distillation column each with an inside diameter of 1.97 inches. These sections were set

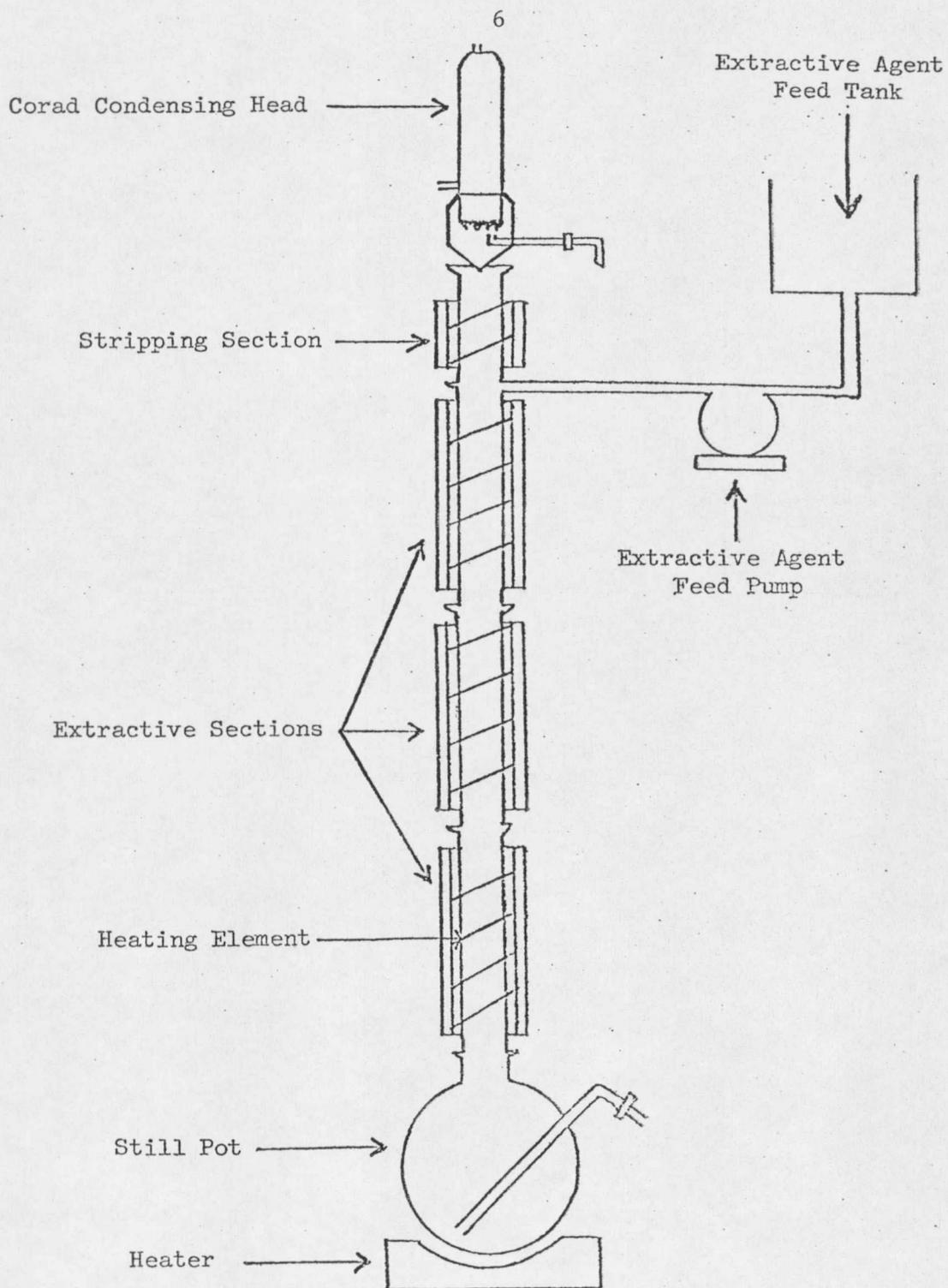


Figure 1. Large Distillation Column

one on top of the other with the two-foot section on top. Each section had a 65/40 male ball-and-socket joint on the bottom and a 65/40 female ball-and-socket joint on the top. The ground glass joints were used to connect to a 50 liter still pot and a corad condensing head. The still pot had a sidearm sampling port and a dry well temperature recorder. The six-foot sections each contained 40 Oldershaw perforated bubble plates, while the two-foot section contained 10, for a total of 130 actual plates. Around each section was a concentric glass tube with an outside diameter of 3.35 inches that was wrapped with nichrome heating wire. Each section had its heating wire hooked to a variac to allow the temperature of the air around each section to be controlled. Thermometers were attached to the outside of each inner section to allow for this air temperature to be measured. Around the second tube was another concentric glass tube with an outside diameter of 4 inches. This tube was there for the purpose of insulation and to prevent heat loss. A heating mantle whose heat input was controlled by two variacs was used to heat the still pot. The extractive agent feed system consisted of a 5-gallon stainless steel tank, a fluid metering pump, and a 3/8" copper line. The tank was heated with two slab-type surface heaters which were each controlled by variacs and the pump head and pump line were all insulated. There was a thermocouple located in the pump line to allow for temperature measurement of the extractive agent being fed into the column. The extractive agent was fed into the col-

umn below the two-foot section. The top of the tank was covered with a suction hose that expelled the vapors from the heated extractive agent to the atmosphere.

The second system used is shown in Figure 2 and consisted of two two-foot sections of vacuum jacketed one-inch inside diameter distillation columns. Each section contained 20 Oldershaw perforated bubble plates and had a 35/25 male ball-and-socket joint on the bottom and a 35/25 female ball-and-socket joint on the top. The ground glass joints were used to connect to a 1.5 liter still pot with sidearm sampling port and a Corad condensing head. A heating mantle whose heat input was controlled with a variac was used to heat the still pot. The extractive agent feed system consisted of a 200 ml steam jacketed separatory funnel, a fluid metering pump, and a 3/8" copper line. The fluid metering pump was the same pump that was used for the large column. The pump head and pump line were heated with nichrome heating wire. This system was the only system for which extractive agent data was obtained because of problems associated with running the large distillation column.

The distribution of the components in the bottoms and distillate was determined using a gas chromatograph. The column in the chromatograph was 15 foot long and was 1/8" in outside diameter. The column packing was made up of .5 gm each of Bentone 34 (an organo clay complex, National Lead Bariod Division) and disodecyl phthalate deposited

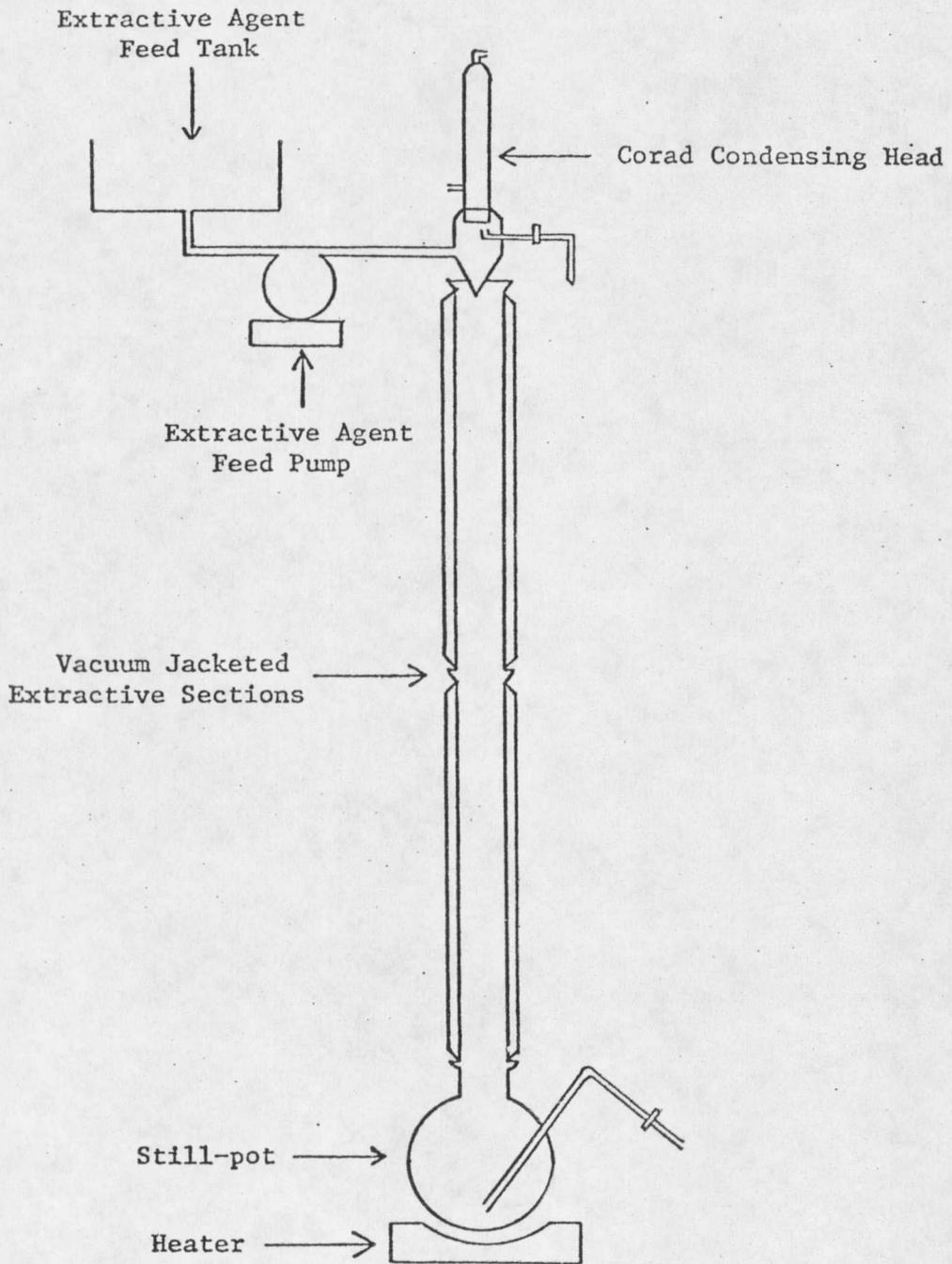


Figure 2. Vacuum Jacketed Distillation Column

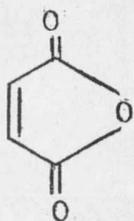
on 9.0 grams of chromosorb P,

The actual apparatus included an Aerograph 660 ionization gas chromatograph hooked to a Sargent recorder, Model SR. The operating conditions used were: column temperature, 75°C; injection port temperature, 200°C; detector temperature, 140°C; helium flow rate, 20-30 ml per minute; hydrogen flow rate, 20-30 ml per minute; air flow rate, 250-400 ml per minute.

#### Extractive Systems

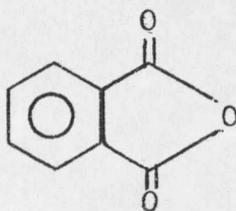
During the course of this research, 12 different extractive agents were investigated. All of the agents investigated contained at least two of the following three compounds: phthalic anhydride; maleic anhydride; and benzoic acid. The melting and boiling points of these three compounds at 640 mm of mercury are listed below:

maleic anhydride



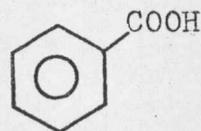
M.P.      B.P.  
60°C      195°C

phthalic anhydride



M.P.      B.P.  
131°C      290°C

benzoic acid



M.P.      B.P.  
122°C      245°C

A solvent was added to these compounds which had the result of lowering the melting point of the resultant mixture to about 80 to 85°C. This made it much easier to pump the extractive agent through the line.

### Operational Procedures

The operational procedure will be explained in two parts, one section on the operation of the large 1.97 inch diameter column that contains 130 Oldershaw perforated bubble plates and one section on the small vacuum jacketed one-inch diameter column with a total of 40 Oldershaw perforated bubble plates.

### Large 130 Plate Distillation Column

The large 130 plate distillation column was the first system investigated, so it will be explained first. To begin the research, the column was calibrated to determine the number of theoretical plates present in the column. The calibration was done at a reflux ratio of 30:1. This was also the reflux ratio used during the extractive runs, to insure a constant number of theoretical plates. The still pot was charged with a four liter mixture of 90 wt% para-xylene and 10 wt% ethylbenzene, which has a known relative volatility of 1.06. By knowing the relative volatility of the mixture and by analyzing samples from the still pot and condenser,  $n$ , the number of theoretical plates in the column could be calculated by using the Fenske equation which is:

$$\alpha^n = \frac{P_1}{E_1} \times \frac{E_v}{P_v}$$

which was explained in the introduction and in the sample calculations.

During the calibration, the effects of time and boil-up rate were evaluated to see if they had any effect on the number of theoretical

plates in the column. It was determined that the boil-up rate had no effect on the number of theoretical plates. As can be seen in Figure 3, the column had an equilibrium time of  $3\frac{1}{2}$  hours. This equilibrium time was determined by taking samples of the distillate and bottoms from the Corad condensing head and still-pot at regular hourly intervals, and shooting them into a gas chromatograph. When the number of theoretical plates in the column became constant, the equilibrium time had been reached.

Another variable that was tested was the wall temperature of the column. The column was in four sections and each section's temperature was controlled with a separate variac. At the start of the research, a dry well was installed in the still pot so that the temperature in the still-pot could be measured. There was also a thermometer in the Corad condensing head. The temperatures in the still-pot and condensing head when the column was operating were 141 and 131°C respectively. It was assumed that the column would run most efficiently with a temperature gradient from the still-pot to the condensing head of 141°C to 131°C so that adiabatic conditions could be best approached. It was later established that the column would run more efficiently at lower temperatures as can be seen in Table II.

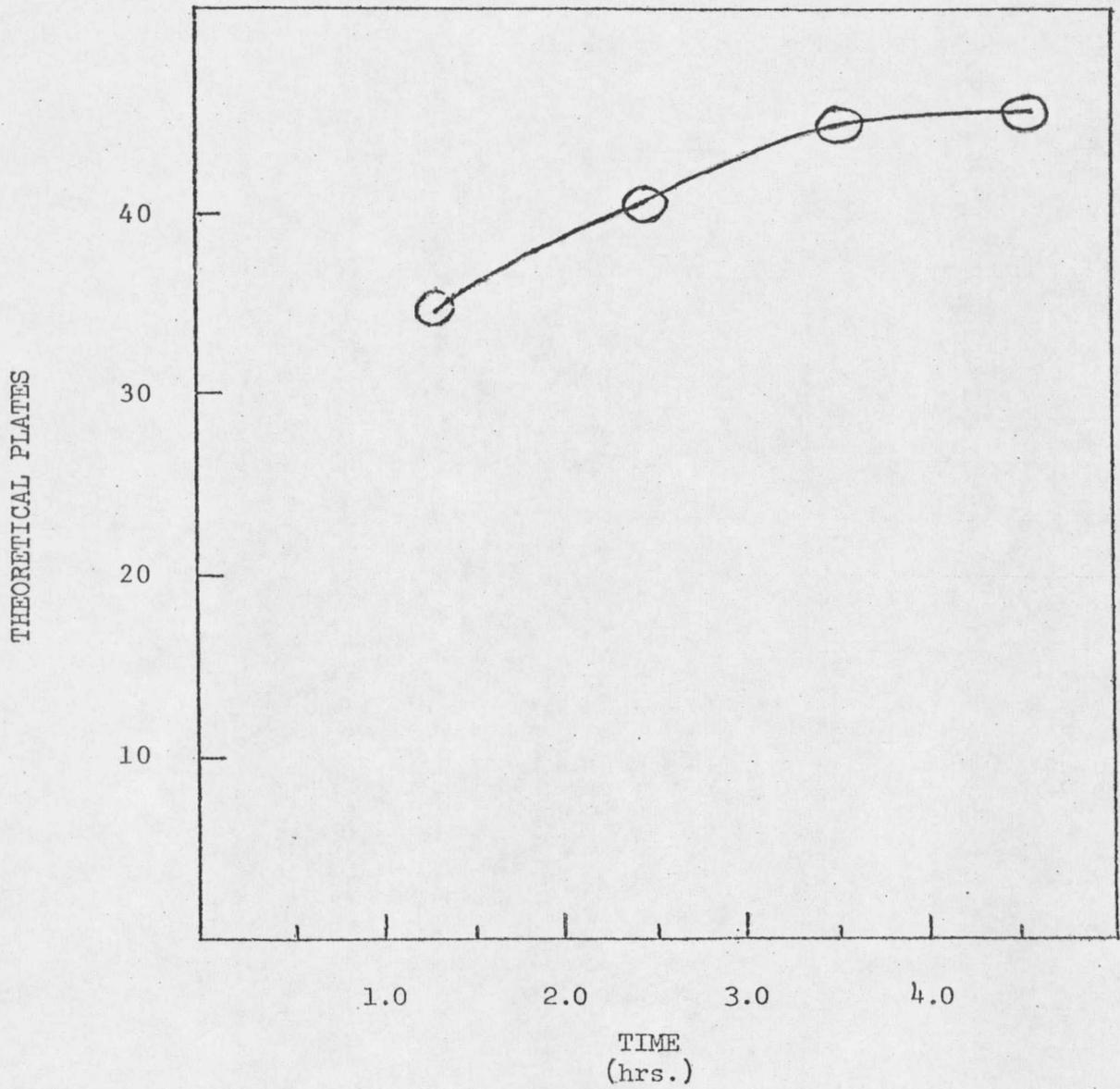


Figure 3. Theoretical Plates vs. Time for Large Distillation Column

Table II. Wall Temperatures and Efficiency for Large Distillation Column

Efficiency, %	Section Temperature, °C			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
22	136	134	132	130
18	138	135	133	130
27	130	128	126	125
34	128	126	125	125

It was finally established that the column had a maximum efficiency of 34%, which corresponds to 44 theoretical plates.

To begin an extractive run in the large column, the still-pot was charged with a four liter mixture of 90 wt% para-xylene and 10 wt% ethylbenzene. The heating mantle for the still pot was then turned on as were the heaters for the four column sections. The extractive agent, which was prepared on a weight percent basis, was then put in the feed tank and the tank, pump head, and pump line heaters were all turned on. When the column had liquid on each plate and liquid refluxing back into the column, the boil-up rate was calculated. By taking a timed sample of distillate from the condensing head and by knowing the reflux ratio, the boil-up rate could be calculated. The boil-up rate used in the runs was 15 ml/min. The pump was then set to feed at 30 ml/min. and was turned on. The temperature of the extractive agent being fed to the column was maintained at 140°C, while the temperature

of the extractive agent in the feed tank was  $100^{\circ}\text{C}$ . This increase in temperature was accomplished by heating the extractive agent as it passed through the line. If the feed entered the column much below this temperature, it would cause the ethylbenzene-para-xylene mixture in the column to condense and run back down the column. The temperature of the extractive agent in the feed tank could not be held at  $140^{\circ}\text{C}$  because at this temperature, a large amount of vapors would be given off, which would condense and solidify in the suction apparatus, making it inoperable. Also, these vapors were an irritant to the eyes and lungs, and if the tank was kept this hot, it was impossible to work by it, since the fan did not expel all the vapor to the atmosphere.

The first two extractive runs made in the large column resulted in such excessive foaming that the runs could not be continued. By decreasing the boil-up rate, the foaming would subside somewhat, but the boil-up rate had to be turned down so far that no vapor was reaching the condenser and the foam would still be going up the column. At this stage, it was decided to test the extractive agents first in the small vacuum jacketed column to screen out any potential foamers. The smaller column used only a fraction of the chemicals that the large column used and if the operation had to be shut down, not as much was lost as with the large column.

Small Vacuum Jacketed Column

The procedure for operating the small column was similar to the procedure for operating the large column. First the column was calibrated to determine the number of theoretical plates present in the column. The still pot was charged with a 500 ml mixture of 50 wt% para-xylene and 50 wt% ethylbenzene. The calibration was done at a reflux ratio of 30:1, and this was also the reflux ratio used for the extractive runs. As before, once liquid was refluxing back into the column, samples of distillate and bottoms were taken off hourly and shot into the gas chromatograph to determine when the maximum separation occurred between ethylbenzene and para-xylene. From these samples, it was determined that the equilibrium time for the small column was two hours and by use of the Fenske equation that the number of theoretical plates in the column was 18. This is shown in Figure 4.

To begin an extractive run in the small column, the still-pot was charged with a 500 ml mixture of 50 wt% para-xylene and 50 wt% ethylbenzene and the heating mantle turned on. Then the heaters for the feed tank, feed pump, and feed line were all turned on. While the heaters were warming up and the column filling with still-pot charge, the extractive agent was prepared. When the column had liquid on each plate and liquid refluxing back into the column, the boil-up rate was determined. The boil-up rate used for the small column was 5 ml/min. The pump was then set to run from 5 ml/min to 10 ml/min, depending

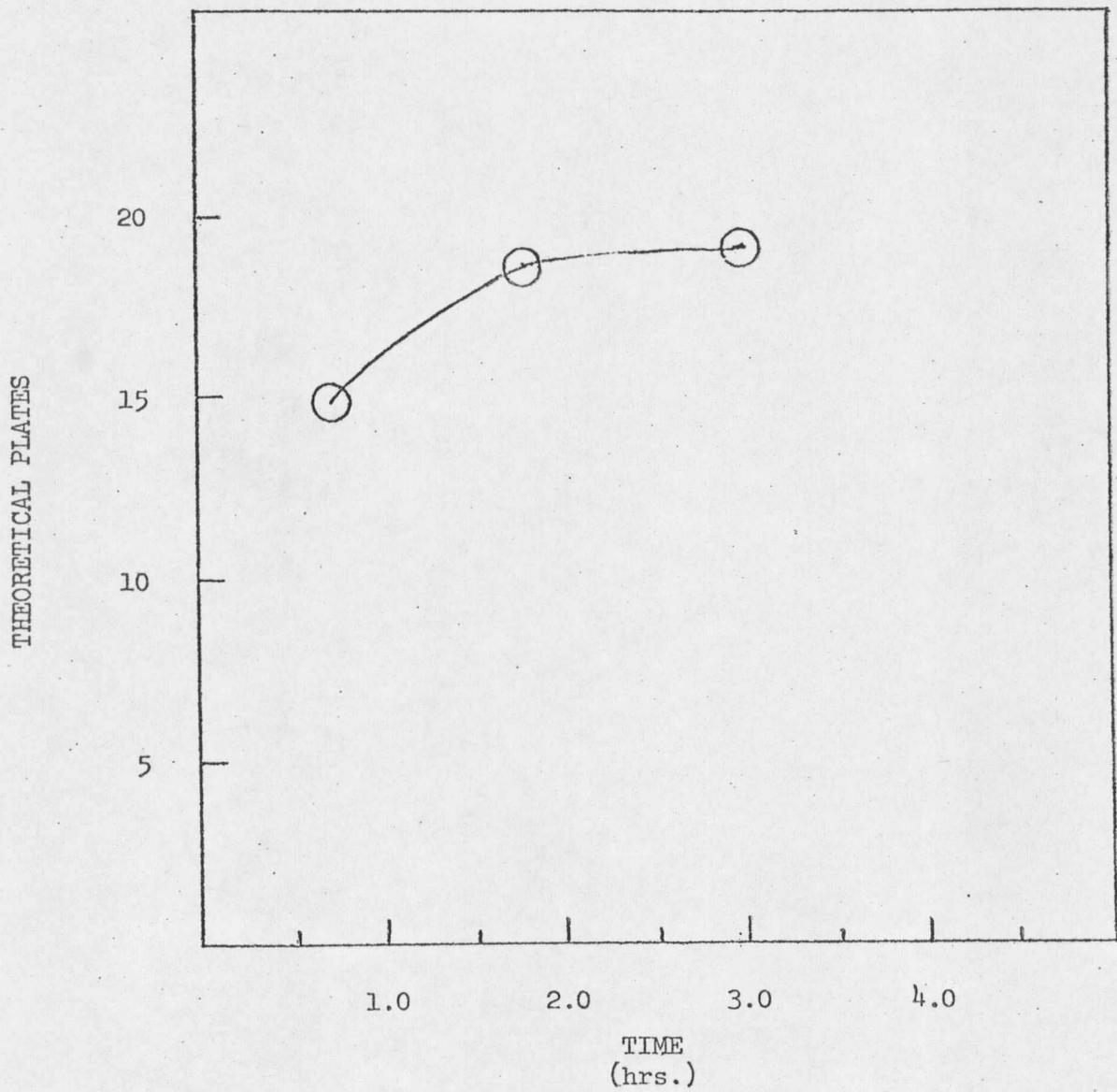


Figure 4. Theoretical Plates vs. Time for Vacuum Jacketed Column

on the run being made. This corresponded to a ratio of from 1:1 to 2:1 of extractive agent to ethylbenzene-para-xylene mixture.

As the run progressed, the condenser had to be carefully watched to make sure that distillate was constantly running out of the condensing head sampling port and that the proper boil-up rate was being maintained. To maintain a constant boil-up rate, the still pot mantle had to be gradually turned up during the run. The reason is that as more extractive agent reached the still-pot, the boiling point of the mixture went up and the quantity of material to be boiled increased and thus more heat was required to maintain the same boil-up rate.

Samples of distillate and bottoms were taken at hourly intervals and shot into a gas chromatograph. From the data obtained from the chromatograph and from the number of theoretical plates determined in the calibration runs, relative volatility data could be obtained. After an equilibrium time of two hours, the relative volatility became constant and the operation was shut down.

Once relative volatility data had been obtained for a few extractive agents, production of high-purity ethylbenzene was attempted. The first step was to decide how high of purity ethylbenzene was wanted. Then by knowing the relative volatility obtained from an extractive agent and the number of theoretical plates present in the column, the still-pot charge could be calculated by use of the Fenske equation. Details are in the sample calculations.

## Discussion of Results

### Small Vacuum Jacketed Column

During the course of this research, 12 different extractive agents were tested in the small column. These agents tested were the agents that had been tested in equilibrium stills by Dr. Berg and had been found to give acceptable relative volatilities. A relative volatility that was considered acceptable was 1.2.

A summary of the extractive agents, the relative volatility they gave, and the ratio of extractive agent to boil-up rate is found in Table III. The actual mole percentages of ethylbenzene and para-xylene in the distillate and bottoms used to calculate these relative volatilities is found in Table IV.

After the relative volatility data had been obtained, production of high-purity ethylbenzene was attempted. It was found that approximately 99% pure ethylbenzene could be produced and that the relative volatility of the ethylbenzene-para-xylene mixture was constant in this range. Details are in the sample calculations.

During the first part of the research, the ratio of extractive agent to boil-up rate was 1:1. Later on, the ratio was increased to 1.5:1 and finally to 2:1 to see if these increasingly higher ratios would increase the relative volatility obtained. As can be seen by the first extractive agent in the table, an increase in the ratio does

Table III. Relative Volatilities and Extractive Agent Ratios for the Vacuum Jacketed Column

<u>Extractive Agent</u>	<u>Extractive Agent/Boil Up</u>	<u>Relative Volatility</u>
40% phthalic anhydride	1:1	1.127
40% maleic anhydride	1.5:1	1.143
20% hexylene glycol diacetate	2:1	1.152
25% phthalic anhydride		
25% maleic anhydride		
25% benzoic acid	1.1	1.086
25% diethyl malonate		
25% phthalic anhydride		
25% maleic anhydride		
25% benzoic acid	1.5:1	1.095
25% diethyl carbinol		
25% phthalic anhydride		
25% maleic anhydride		
25% benzoic acid	1.5:1	1.09
25% diethylene glycol diethyl ether		
40% phthalic anhydride		
40% maleic anhydride	1.5:1	1.113
20% butyl cellosolve		
40% phthalic anhydride		
40% maleic anhydride	2:1	1.102
20% tri cresyl phosphate		
25% phthalic anhydride		
25% maleic anhydride		
25% benzoic acid	2:1	1.09
25% ethylene glycol methyl ether acetate		
25% phthalic anhydride		
25% maleic anhydride		
25% benzoic acid	2:1	1.1
25% tri cresyl phosphate		

Table III. (Cont.)

<u>Extractive Agent</u>	<u>Extractive Agent/Boil Up</u>	<u>Relative Volatility</u>
40% phthalic anhydride		
40% maleic anhydride	1:1	foamed too much to make run
20% butoxy propanol		
40% phthalic anhydride		
40% maleic anhydride	1:1	foamed too much to make run
20% propoxy propanol		
33% maleic anhydride		
33% meta-nitro-benzoic acid	2:1	foamed too much to make run
33% butoxy Propanol		

Table IV. Mole % Ethylbenzene and Para-Xylene in Distillate and Bottoms and Relative Volatilities for Vacuum Jacketed Column.

<u>% Para-Xylene in Bottoms</u>	<u>% Ethylbenzene in Bottoms</u>	<u>% Para-Xylene in Distillate</u>	<u>% Ethylbenzene in Distillate</u>	<u>Relative Volatility</u>
57	43	13.4	86.6	1.127
61.8	38.2	12.7	87.3	1.143
55	45	8.7	91.3	1.152
56	44	22.5	77.5	1.086
56.5	43.5	20.2	79.8	1.095
47	53	16	84	1.09
56.5	43.5	16	84	1.113
54	46	17	83	1.102
55.9	44.1	22	78	1.09
56.5	43.5	19	81	1.1
14.4	85.6	1.3	98.7	1.152
90.3	9.7	76.5	23.5	1.06*

\* This was the calibration run to determine the number of theoretical plates in the column.

increase the relative volatility obtained. The ratio could not be increased any further because the column was so small that the amount of liquid the column could handle was small and very critical. An increase in the extractive agent feed rate much above 10 ml/min resulted in flooding of the Oldershaw bubble plates.

Another situation that occurred when running the column was the problem of foaming. All of the extractive agents tested had a tendency to foam and the critical factor was the boil-up rate. If the boil-up rate was not kept at 5 ml/min or lower, foaming would occur. This foaming action would start in the lower section of the column and work its way up the column. The turbulent action of the foam on a lower plate would cause the plate above it to foam and this action would proceed on up the column. There seemed to be a small amount of foaming action in the lower section of the column during every extractive run. This was thought to be the reason for the low relative volatilities obtained.

Another factor that was thought to be involved with the low relative volatilities obtained was the use of the Fenske equation. The Fenske equation calculates the number of theoretical plates in a column by "stepping" them off between an operating line of  $45^\circ$ , which corresponds to total reflux, and the equilibrium curve on a McCabe-Thiele diagram. The column was run at a reflux ratio of 30:1 and therefore the operating line that should have been used to calculate the number of theoretical

plates should be the one that corresponds to a reflux ratio of 30:1. This operating line has a slope less than  $45^\circ$  and thus will cross the equilibrium curve somewhere. If the number of theoretical plates in a column are being stepped off on a McCabe-Thiele diagram and a "pinch point" is reached where the operating line crosses the equilibrium curve the number of theoretical plates will go to infinity. The relative volatility between ethylbenzene and para-xylene is 1.06 and thus the equilibrium curve is very close to the  $45^\circ$  line and it is very easy to reach a pinch point when calculating the number of theoretical plates. Since the method used to calculate the number of theoretical plates used the  $45^\circ$  operating line a significantly lower number of theoretical plates was obtained than if the operating line corresponding to a reflux ratio of 30:1 had been used. This lower number of theoretical plates was then used to calculate relative volatilities during the extractive runs and thus the relative volatilities reported are not accurate and are probably higher than reported. The problems associated with running the column at total reflux are explained in the introduction.

Another problem associated with running the small column was that some of the feed entering the column was carried up to the condenser by the vapor in the column. The feed would then condense and solidify in the sampling port and plug it up. This problem could be alleviated

by the addition of a few plates above the feed as was done with the large column.

#### Large 130 Plate Distillation Column

As mentioned previously in the operational procedure for the large column the first two runs in the large column resulted in such excessive foaming that the runs could not be continued. After testing the various extractive agents in the small column, another attempt was made to run the large column. This time the extractive agent that had given the greatest relative volatility in the small column was used. This extractive agent also caused excessive foaming in the column and the run could not be completed.

It could be seen when operating the large column that there was some condensation occurring on the walls of the column. This would be expected, considering the temperature of the air outside the wall which was always lower than the boiling point of the mixture. This condensation had the effect of there being a larger boil-up rate in the lower part of the column than in the condenser where the boil-up rate was calculated. This higher boil-up rate in the lower part of the column was thought to have caused the foaming. Because of this effect of foaming in the large column, it appears that the dimensions of a distillation column used for extractive distillation are a very important factor for successful separation.

The actual mole percentages of ethylbenzene and para-xylene in the distillate and bottoms used to calibrate the column are found in Table V.

Table V. Mole % Ethylbenzene and para-Xylene in Distillate and Bottoms and Theoretical Plates for Large Column

<u>% Para-Xylene in Bottoms</u>	<u>% Ethylbenzene in Bottoms</u>	<u>% Para-Xylene in Distillate</u>	<u>% Ethylbenzene in Distillate</u>	<u>Theoretical Plates</u>
92.5	7.5	67.2	32.8	34
95.2	4.8	79.1	20.1	28
91.5	8.5	73.5	26.5	23
94.1	5.9	80.5	19.5	23
80.5	19.5	23.9	76.1	44

Conclusions

1. It is possible to increase the relative volatility of ethylbenzene to para-xylene by using extractive distillation. The best extractive agent tested, which was a mixture of 40 wt% phthalic anhydride, 40 wt% maleic anhydride, and 20 wt% hexylene glycol diacetate, increased the relative volatility from 1.06 to 1.152.
2. The selection of the proper components of the extractive agent is vital to its success. An increase in the ratio of agent to hydrocarbon will increase the relative volatility.
3. The relative volatility obtained from an extractive agent in a vapor-liquid equilibrium still does not necessarily agree with the relative volatility obtained in a distillation column. This is because of the problem of foaming and running the column at a finite reflux ratio.
4. The dimensions of the column set a limit on the ratio of agent to hydrocarbon possible because of the negative effects of flooding and foaming.

APPENDIX

Sample Calculations

Calculation of relative volatility for the vacuum jacketed distillation set up.

Fenske Equation:

$$\alpha^n = \frac{P_1}{E_1} \times \frac{E_v}{P_v}$$

where

$\alpha$  = relative volatility

n = number of theoretical plates

P<sub>1</sub> = percent para-xylene in bottoms

E<sub>1</sub> = percent ethylbenzene in bottoms

E<sub>v</sub> = percent ethylbenzene in distillate

P<sub>v</sub> = percent para-xylene in distillate

Sample calculation using the following system:

25% phthalic anhydride

25% maleic anhydride

25% benzoic acid

25% diethylene glycol diethyl ether

P<sub>1</sub> = 0.475 mole fraction para-xylene

E<sub>1</sub> = 0.525 mole fraction ethylbenzene

E<sub>v</sub> = 0.85 mole fraction ethylbenzene

P<sub>v</sub> = 0.15 mole fraction para-xylene

n = 18 for the vacuum jacketed column.

$$\alpha^{18} = \frac{.475}{.525} \times \frac{.85}{.15}$$

$$\alpha = 1.095$$

Calculation of still-pot charge for vacuum jacketed column to produce high-purity ethylbenzene.

Fenske equation

$$\alpha^{18} = \frac{P_1}{E_1} \times \frac{E_v}{P_v}$$

Sample calculations for the following system.

40% phthalic anhydride

40% maleic anhydride

20% hexylene glycol diacetate

The relative volatility obtained from this system was 1.152. Production of 99% ethylbenzene was attempted which corresponds to  $E_v = .99$  and  $P_v = .01$ .

$$1.152^{18} = \frac{.99}{.01} \times \frac{P_1}{E_1}$$

$$\frac{P_1}{E_1} = .13$$

$$P_1 = .885$$

$$E_1 = .115$$

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