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
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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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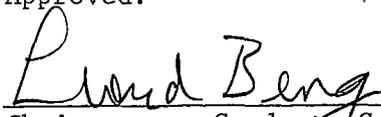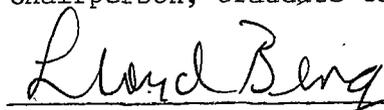of the requirements for the degree

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Chairperson, Graduate Committee

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TABLE OF CONTENTS

v

LIST OF TABLES

vi

LIST OF FIGURES

ABSTRACT

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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°C at one atmosphere pressure and para-xylene has a boiling point of 138.4°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°C while the other isomeric compounds all have freezing points below -25°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

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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

Relative Volatility	Theoretical Plates
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:

$$\alpha^n = \frac{Pl}{El} \times \frac{Ev}{Pv}$$

where

α = relative volatility

n = number of theoretical plates

Pl = percent para-xylene in bottoms

El = percent ethylbenzene in bottoms

Ev = percent ethylbenzene in distillate

Pv = 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
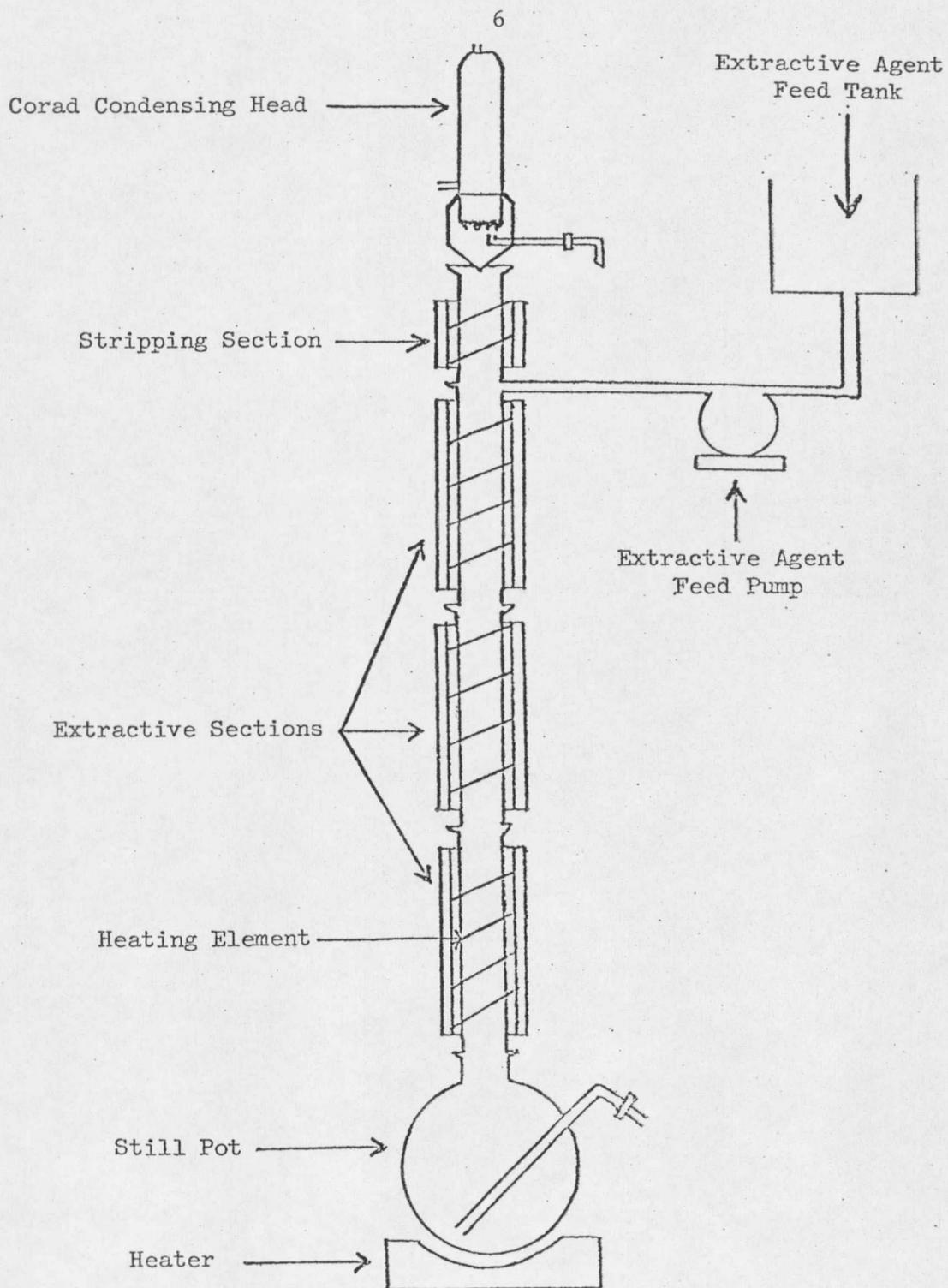
Figure 1. Large Distillation Column

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 distil-

lation 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 dis-

tillation column.

The distribution of the components in the bottoms and distillate

was determined using a gas chromatograph. The column in the chromato-

graph 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 com-

plex, National Lead Bariod Division) and dissodecyl phthalate deposited