



Separation of ethylbenzene from para-xylene by extractive distillation
by Paul John Kober

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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, 27 extractive agents were investigated. The extractive agents were composed of various chlorinated organic compounds. It was determined that the selection of the proper extractive agent components and ratio of extractive agent to ethylbenzene-para-xylene mixture is vital to the success of the process.

The major pieces of equipment used in this study were three distillation column set ups having 12, 15, and 19.5 theoretical plates 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 agent's effect on the relative volatility of ethylbenzene-para-xylene was determined by using the separation data obtained from the gas chromatograph in the Fenske equation.

The relative volatility between ethylbenzene and para-xylene is 1.06. The value of relative volatility that was considered acceptable for further development was 1.20. Of the 27 different extractive agents investigated, 15 yielded relative volatilities greater than 1.20, with the best result being a relative volatility of 1.276.

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Date 12/3/74

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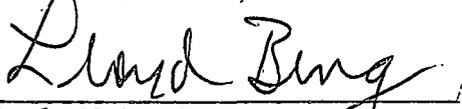
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This investigation was performed to study the application of extractive distillation to the separation of ethylbenzene from para-xylene.

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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.

Para-xylene and ethylbenzene are both eight carbon-atom aromatic compounds of the benzene family. Both are commercially important compounds with ethylbenzene being used to make styrene and para-xylene used to make terephthalic acid and plastics. The principal source of both of these compounds is the petroleum industry, both are products of the reforming process used in the refining of oil. Ethylbenzene and para-xylene are similar not only in that they are both eight-carbon aromatics but also in that they have practically the same vapor pressures at all temperatures and they both have nearly the same boiling points. Para-xylene has a boiling point of 138.4°C at one atmosphere pressure and ethylbenzene has a boiling point of 136.2°C at one atmosphere pressure. All of these similarities make their separation difficult and costly. The present method of separation is that para-xylene is crystallized from a solution of xylenes at a temperature between -80°F to -100°F with a yield of only about 65%. Ethylbenzene is then separated by distillation from the remaining xylene mixture which contains some para-xylene. The distillation columns required to make these separations must contain a large number of theoretical plates. This research was done for the purpose of determining if the separation could be accomplished with fewer plates by employing extractive distillation. (1)

The separation of two chemical compounds by the means of fractional

distillation depends on the difference in their volatilities. If one compound is more volatile than the other then the vapor in equilibrium with a liquid mixture of the two chemicals will be richer in the more volatile compound than is the respective liquid mixture. The difference in the volatilities of two compounds is determined by the difference in their boiling points. Since ethylbenzene and para-xylene have boiling points which are near each other the tendencies of these compounds to vaporize is very much 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 compounds. (2)

Extractive distillation is simply fractional distillation in the presence of a solvent. In extractive distillation separation of two compounds is effected by the addition of a third chemical or component near the top of the distillation column. This third component is one with a high boiling point and is nonvolatile relative to the compounds that are to be separated. The extractive agent is introduced near the top of the column so that it can flow down through the column washing the ascending vapors and absorbing one of the components. The temperature of the system is such that the liquid and vapor phases can exist. The vapor pressure of the absorbed or dissolved compound is lowered which raises the relative volatility of the two component mixture that is to be separated. By this change in relative volatility a separation can be more easily obtained. (3)

In this research the method used to measure the separation obtained between the ethylbenzene and para-xylene was their relative volatility. As explained previously volatility is simply the measure of a compound's tendency to vaporize and 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 ease of separation of a mixture by fractional distillation depends on the relative volatility of one compound to another. The relative volatility of a binary mixture is determined by dividing the volatility of one component by the volatility of the other component. 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 one. The higher the value of the relative volatility the greater the ease of separation. (3)

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

$$\alpha^n = \frac{Y_e}{Y_p} \times \frac{X_p}{X_e}$$

where

α = relative volatility

n = number of theoretical plates

Y_e = percent ethylbenzene in distillate

Y_p = percent para-xylene in distillate

X_p = percent para-xylene in bottoms

X_e = percent ethylbenzene in bottoms

This equation comes from applying the definition of relative volatility to every theoretical plate in the column. This same equation was used to do the calibration of the columns so everything was done on a consistent comparable basis.

The method of analyzing samples from the distillate and bottoms in order to obtain quantitative values usable in the equation was a gas chromatograph. The chromatograph has a column 15-20 feet long with a packing of diisodecyl phthalate. The values or mole percentages were obtained from a recorder hooked to the gas chromatograph which had an automatic integrater which accurately measured the area under each peak; it was from these areas that the composition of the bottoms and distillate were determined.

RESEARCH OBJECTIVES

The objective of this research was to investigate as many extractive agent systems 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 the proposed study basically three different distillation column set-ups were used. Each column set-up was similar but there is enough difference between each one that they will each be individually described here.

The first system, the physically smallest system used consisted of the following equipment: two sections of vacuum jacketed 1 inch inside diameter distillation columns, each column contained 10 Oldershaw perforated bubble plates, Corad condensing head, extractive agent feed tank, fluid metering extractive agent feed pump, 1.0 liter still-pot with sidearm for sampling, and a still-pot heater. A diagram of this apparatus is shown in Figure 1. This set-up was used at the outset of the research to make sure that the extractive distillation process would work before a large sum of money was spent on larger equipment. This set-up was also used during the later stages when there were shortages of some of the components used in the various extractive agents and when the larger system was inoperative.

The second system used is shown in Figure 2 and it consisted of a 6 foot section of distillation column with an inside diameter of 1.97 inches that contained 40 Oldershaw perforated bubble plates. The column has 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 the column to a 50 liter still-pot with sidearm sampling port and a Corad condensing head. Around the distillation

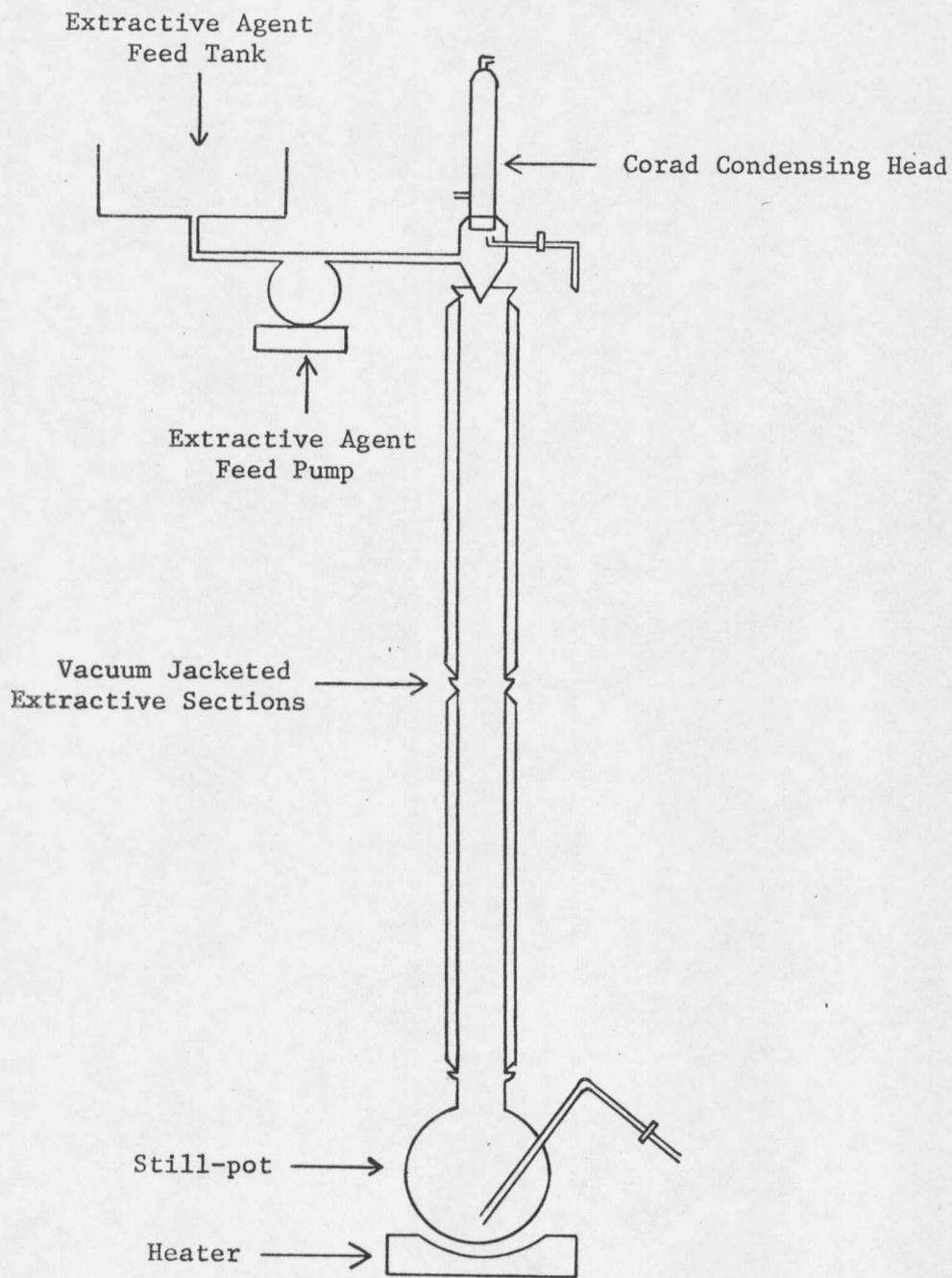


Figure 1. Vacuum Jacketed Distillation Set-Up

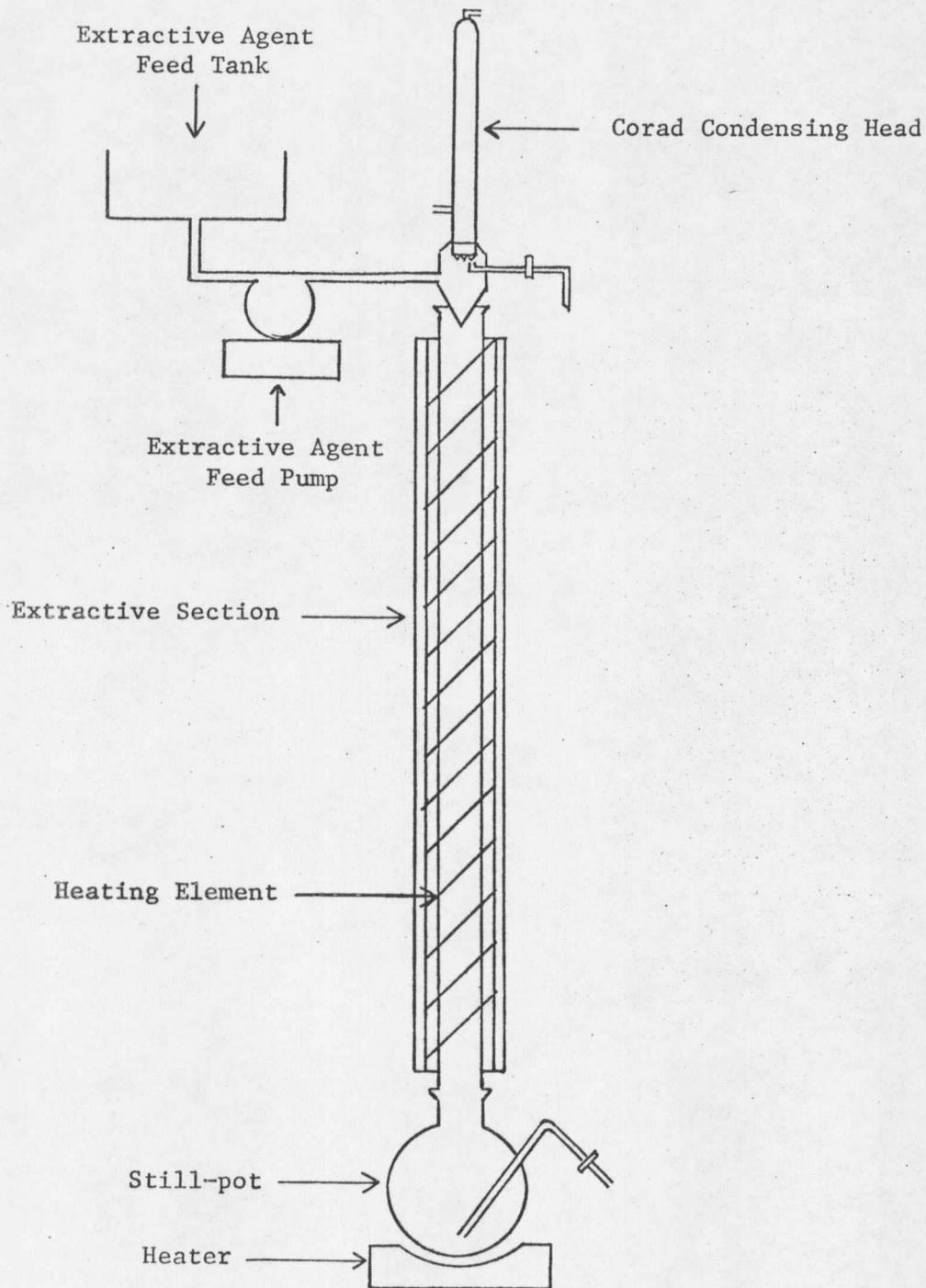


Figure 2. Large Column Distillation Set-Up

column was a concentric glass tube with an outside diameter of 3.35 inches that was wrapped with a nichrome heating wire that was hooked to a variac that allowed the column to be operated at adiabatic conditions. Around this second tube was another concentric glass tube with an outside diameter of 4.0 inches. This third concentric tube was there for the purpose of insulation to prevent excessive heat loss. The extractive agent feed system consisted of a 5 gallon stainless steel feed tank that was heated by two slab-type surface heaters that were controlled with variacs. The feed pump was the same fluid metering pump used in the first system. The pump head and pump line were wrapped with a nichrome heating wire and well insulated to keep the extractive agent heated and in the liquid state.

The third system used was exactly the same as the second system described above except that a stripping section was added between the 6 foot section of distillation column and the Corad condensing head. This stripping section was 2 feet long and had an outside diameter of 1.25 inches and was packed with 1/4 inch carbon steel Berl saddles. Like the large 6 foot section it had two concentric glass tubes around it each with outside diameters of 2.00 inches and 2.62 inches respectively. The middle tube was wrapped with nichrome wire that was hooked to a variac to provide adiabatic conditions in the stripping section. This distillation set-up is shown in Figure 3.

The distribution of the components in the bottoms and distillate was determined using a gas chromatograph. The column in the chromatograph

