



Application of azeotropic distillation to the separation para-cresol and meta-cresol
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Abstract:

The purpose of this thesis was to study the feasibility of separation of the meta and para isomers of the cresols by azeotropic distillation. Both minimum and maximum boiling azeotropes were studied.

Distillation studies were carried out in laboratory columns of about 28 theoretical plates. Analysis was accomplished by use of a constant temperature refractometer and a gas chromatograph.

The experimental procedure for this work has been subdivided into three parts. The first, initial entrainer evaluation, was a test to determine if a proposed entrainer would form an azeotrope with either or both cresol isomers being studied. The indication of azeotrope formation was taken as depression of the mixture's boiling point below the lowest boiling component for a minimum azeotrope and for a maximum azeotrope an elevation of the mixture's boiling point above the highest boiling component in the mixture.

The second part of the investigation was the determination of azeotropic composition. This was accomplished by trial and error distillations with intermediate changes in charge composition until tops and bottoms samples were of the same refractive index. Composition of these samples was determined using entrainer-cresol refractive index curves.

The third part of the procedure, the relative volatility determinations, involved a 3 hour distillation of a calculated charge of entrainer with both cresol isomers and analysis of tops and bottoms products. Analysis of data was accomplished by use of gas chromatography. Application of the Fenske Equation yielded the relative volatility of para to meta cresol in the presence of the entrainers used.

Of the sixty-five compounds studied, fourteen were found to form azeotropes with the cresols. Eleven of these were maximum boiling azeotropes, the remaining three were minimum azeotropes. Agreement with the literature as to formation of azeotropes was excellent. Composition data agreed as well as can be expected with variations being explained in the differences in pressure at locations where the data was gathered. None of the minimum azeotropes appreciably enhanced the isomer separation while nine of the maximum boiling azeotropes gave reductions of from 40% to 63% in the number of theoretical plates needed to effect a 95% separation of the isomers by straight rectification. However since a total of 1053 plates would be needed for this separation by straight rectification, the decrease in theoretical plates required probably does not make the separation of meta and para cresol by azeotropic distillation economically feasible using any of the entrainers investigated in this work.

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PARA-CRESOL AND META-CRESOL

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ROBERT EMMETT YLINEN

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TABLE OF CONTENTS

	page
Abstract	vi
Introduction	1
Terminology and Theory	5
Research Objectives	11
Equipment	12
Chemical Materials	15
Procedure	17
Discussion of Results	23
Conclusions	28
Sample Calculations	29
Appendix	31
Literature Cited	45

LIST OF TABLES AND FIGURES

		page
Figure 1	Diagram of Distillation Apparatus	
Figure 2	Chromatograph Separation Using Di-n-octyl phthalate Column	
Figure 3	Relative Volatility of Cresols versus Cresol Mixture Composition	
Table I	Compounds Evaluated as Entrainers with Cresols	35
Table II	Azeotropic Composition Data of Effective Entrainers	40
Table III	Relative Volatilities of Investigated Minimum Azeotropes	41
Table IV	Relative Volatilities of Investigated Maximum Azeotropes (Lower boiling entrainer -para isomer azeotrope)	42
Table V	Relative Volatilities of Investigated Maximum Azeotropes (Lower boiling entrainer -meta isomer azeotrope)	43
Table VI	Theoretical Plate Ratio between Azeotropic Distillation and Straight Rectification for 95% Separation	44

ABSTRACT

The purpose of this thesis was to study the feasibility of separation of the meta and para isomers of the cresols by azeotropic distillation. Both minimum and maximum boiling azeotropes were studied.

Distillation studies were carried out in laboratory columns of about 28 theoretical plates. Analysis was accomplished by use of a constant temperature refractometer and a gas chromatograph.

The experimental procedure for this work has been subdivided into three parts. The first, initial entrainer evaluation, was a test to determine if a proposed entrainer would form an azeotrope with either or both cresol isomers being studied. The indication of azeotrope formation was taken as depression of the mixture's boiling point below the lowest boiling component for a minimum azeotrope and for a maximum azeotrope an elevation of the mixture's boiling point above the highest boiling component in the mixture.

The second part of the investigation was the determination of azeotropic composition. This was accomplished by trial and error distillations with intermediate changes in charge composition until tops and bottoms samples were of the same refractive index. Composition of these samples was determined using entrainer-cresol refractive index curves.

The third part of the procedure, the relative volatility determinations, involved a 3 hour distillation of a calculated charge of entrainer with both cresol isomers and analysis of tops and bottoms products. Analysis of data was accomplished by use of gas chromatography. Application of the Fenske Equation yielded the relative volatility of para to meta cresol in the presence of the entrainers used.

Of the sixty-five compounds studied, fourteen were found to form azeotropes with the cresols. Eleven of these were maximum boiling azeotropes, the remaining three were minimum azeotropes. Agreement with the literature as to formation of azeotropes was excellent. Composition data agreed as well as can be expected with variations being explained in the differences in pressure at locations where the data was gathered. None of the minimum azeotropes appreciably enhanced the isomer separation while nine of the maximum boiling azeotropes gave reductions of from 40% to 63% in the number of theoretical plates needed to effect a 95% separation of the isomers by straight rectification. However since a total of 1053 plates would be needed for this separation by straight rectification, the decrease in theoretical plates required probably does not make the separation of meta and para cresol by azeotropic distillation economically feasible using any of the entrainers investigated in this work.

INTRODUCTION

The three isomeric monomethylphenols (or hydroxytoluenes) are called cresols, $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$, formula weight 108.13. Of interest in this thesis are the meta and para isomers of the cresols. Meta cresol is a colorless to light amber oily liquid, while para cresol is colorless and crystalline in form at room temperature. Both isomers of the cresols have an odor resembling that of phenol. They are soluble in dilute sodium hydroxide and in most organic solvents, but are only slightly water soluble. In general, the properties of the cresols are similar to those of phenol.

Occurrence and Manufacture.

Cresols are found in admixture with other phenolics in the products of coal carbonization, in alkali extracts from the washing of certain cracked petroleum distillates, in the "middle oil" from the hydrogenation of coal, in shale oil and in some wood tars. The percentage of total cresols and the relative proportions of the individual isomers vary to a great extent in the phenolic mixtures obtained from the above mentioned sources.

The primary source of commercial cresols is the tar produced by the high temperature coal carbonization industry. (15) Coal tar is distilled to yield an oil fraction containing nearly all of the simpler monohydric phenolics with boiling points below 230°C . This phenolic group is known collectively as "tar acids" and is mostly a

mixture of phenol, the cresols, and the xylenols.

This tar acid is treated with a caustic wash, and the extract known as "sodium cresylate" is gravity separated from the nonaqueous layer. Steam stripping and/or vacuum distillation are used to remove nitrogen bases and dissolved or entrained oils. The purified sodium cresylate solution is then treated with carbon dioxide and the phenolic compounds are released and separated by decantation from the aqueous carbonate layer.

After the phenolic compounds have been dehydrated by distilling off the water, they are submitted to vacuum distillation to yield concentrates of phenol, cresols and xylenols. Further rectification of these concentrates gives phenol, ortho-cresol, the xylenols and a close-boiling fraction containing the meta and para isomers of the cresols in the approximate ratio of 3:2. Of a mixture of the three cresol isomers the ortho isomer is the only one directly recoverable from the mixture by simple rectification. The boiling points of meta cresol, 202.8°C, and para cresol, 202.5°C, (8) are too nearly alike to permit separation of these isomers by fractional distillation. Consequently, meta and para cresol are used as a mixture or are subjected to further separation techniques if the pure isomers are desired.

Separation of Meta and Para Cresol Mixtures.

Numerous processes are described in the patent and chemical literature for the separation of pure meta and para isomers of the cresols from a commercial mixture of the two. Most of the methods listed for separating these two isomers are based on the formation of selective addition compounds. The following is a listing by reaction or reagent of nine chemical separation processes for meta and para cresol: alkylation (18), hexa-methylenetetramine (3), oxalic acid (10), phenol (2), phosphate (11), pyridine base (4), sodium nitrite (5), sulfonation (17), and urea (19). Physical methods of separation dependent on differences in solubility in specific solvents or crystallization point are also reported. These methods include liquid-liquid extraction, fractional solvent extraction, and extractive crystallization. (7)

It was the purpose of this thesis study to investigate the possibility of the separation of the meta and para isomers of the cresols by azeotropic distillation.

Uses of Cresols.

A major use of cresols is in the manufacture of phenolaldehyde condensation products or phenolic resins. Para cresol is used in the manufacture of oil-soluble phenolic resins, whereas phenolic resins made from meta cresol are generally not soluble in varnish oils. (6)

Mixtures of the cresols are also used in the manufacture of resins, plastics, and tricresyl phosphate (a plasticizer, hydraulic fluid, gasoline and lubricating oil additive). Cresols find further use as disinfectants and as ore-flotation agents.

High purity meta cresol is used primarily for fine chemical manufacture. Such uses include the manufacture of pharmaceuticals, fungicides, special disinfectants, flavor and perfume chemicals. (12)

High purity para cresol is used for production of antioxidants such as 2,6-di-tert-butyl-para cresol (TBPC), an antioxidant used to protect petroleum products, foods, and rubber from deterioration on exposure to air. (7)

TERMINOLOGY AND THEORY

Separation by distillation is accomplished because of the difference in composition between a multicomponent liquid and the vapor in equilibrium with it. These differences in composition are due to differences in the volatilities of the components of the mixture undergoing distillation. The volatility of a compound is a measure of the tendency for that compound to enter the vapor phase. Here it is desirable to define the volatility of any substance in a liquid mixture as the ratio of the substance's partial vapor pressure to its mole fraction in the liquid.

$$v_a = \frac{\bar{p}_a}{x_a} \quad \text{Eqn. 1}$$

where: v_a = Volatility of component a.
 \bar{p}_a = Partial pressure of component a in mixture.
 x_a = Mol. fraction component a in liquid.

For pure substances or ideal mixtures, the volatility is equal to the vapor pressure of the pure material since direct comparison with Raoult's Law,

$$\bar{p}_a = p_a x_a \quad \text{Eqn. 2}$$

shows that if Equation 1 is valid then for pure components or ideal mixtures

$$v_a = p_a \quad \text{Eqn. 3}$$

where: p_a = Vapor pressure of pure component a.

In the case of non-ideal solutions, changes in composition will be accompanied by changes in the volatilities of the components involved. In this case the volatility of a component may be related to its vapor pressure through the use of the activity coefficient, δ , as follows:

$$v_a = p_a \delta_a \quad \text{Eqn. 4}$$

with the activity coefficient being defined as:

$$\delta_a = p y_a / p_a x_a \quad \text{Eqn. 5}$$

where: p = Total gaseous pressure

A relationship may be formed between the volatilities of compounds undergoing separation by distillation which is useful in the analysis of the separation. This relation is known as the relative-volatility equation and is simply the ratio of the higher volatility to the lower. The relative volatility of a substance A to a substance B is designated as:

$$\alpha_{AB} = v_A / v_B \quad \text{Eqn. 6}$$

where A is the most volatile component.

Composition of liquid and vapor may be related to volatility by use of Equations 1 and 5 as follows:

$$\frac{v_a}{v_b} = \frac{\bar{p}_a/x_a}{\bar{p}_b/x_b} = \frac{\bar{p}_a x_b}{\bar{p}_b x_a} = \alpha_{ab}$$

Application of Dalton's Law of partial pressures,

$$p_a/p_b = y_a/y_b \quad \text{Eqn. 7}$$

results in an expression for the relative volatility in terms of component concentrations in liquid and vapor.

$$\alpha_{ab} = y_a x_b / y_b x_a \quad \text{Eqn. 8}$$

In the case of pure substances or ideal mixtures, Raoult's Law applies and the relative volatility is the ratio of the vapor pressures:

$$\alpha_{ab} = p_a / p_b \quad \text{Eqn. 9}$$

A measure of the separating power of a distillation apparatus is the theoretical plate. A theoretical plate may be defined as one which produces the same difference in composition as exists at equilibrium between a liquid mixture and its vapor. The magnitude of the change in composition for one theoretical plate varies with the mixture under consideration, and for any one mixture this magnitude of change also varies with the composition.

By applying the relative volatility equation, Equation 8, to the stillpot and then to each of n theoretical plates in a column, the relative volatility for the components being distilled in a column of n theoretical plates is expressed as:

$$\alpha_{ab}^{n+1} = \frac{y_a x_b}{y_b x_a} \quad \text{Eqn. 10}$$

where: n = the number of theoretical plates in the column

n+1 = plates in column plus one theoretical plate for separation in still pot.

The relationship expressed in Equation 10 is known as the Fenske equation. In application, the validity of this equation is dependent on the fulfillment of certain restrictions. The Fenske equation restrictions are:

1. The vapor equilibrium for the system of components a and b with component a being the most volatile should follow the relative volatility relationship expressed in Equation 8.
2. The relative volatility should be at least approximately constant over the range of concentrations and temperatures involved.
3. The data used in the Fenske Equation should be gathered from a column of n theoretical plates operating at total reflux with a total condenser.

The derivation of the Fenske equation is the analytical equivalent to graphical methods for determining the number of theoretical plates in a column. For this derivation the reader is referred to Rose, et al. pp 39-41. (16)

Liquid mixtures may be classified into two broad groups, those which can be separated, at least theoretically, by simple distillation and those which cannot. The latter classification is of interest in this work as mixtures in this group are known as azeotropes. An azeotropic mixture will boil or distill without change in composition at a constant temperature under a constant pressure. That is to say, the vapor and liquid compositions of an azeotropic mixture at equilibrium are identical. Constant boiling mixtures known as azeotropes are usually the result of deviations from ideality caused by internal

pressures or hydrogen bonding. (1) Azeotropes may be categorized into two main groups, minimum boiling azeotropes and maximum boiling azeotropes.

Minimum boiling azeotropes are those constant boiling mixtures which have boiling points below any pure component or any other mixture of the pure components of the system. Minimum azeotropes show positive deviations from Raoult's Law. These minimum boiling azeotropic mixtures may be further subdivided into two classifications, homogeneous and heterogenous minimum azeotropes.

A homogeneous minimum boiling azeotrope is a single liquid phase mixture which has the same composition as the vapor in equilibrium with it and boils below the boiling point of any of the pure components in the mixture. A heterogenous minimum boiling azeotrope may be obtained by the distillation of a binary mixture having two phases. If an azeotrope is formed, the vapor leaving the two phase mixture in the stillpot will be of constant composition as long as two phases are present in the liquid. A common example of this is steam distillation where a water phase is present.

The second group of azeotropes are constant boiling mixtures which have boiling points higher than any pure component or nonazeotropic mixture of components in the system. Maximum boiling azeotropes are always homogeneous in nature and show negative deviations

from Raoult's Law. (1) Maximum boiling azeotropes represent less than 8% of all reported azeotropic systems but are of interest theoretically and have been patented for commercial application in at least one instance. (13) Typical examples of maximum boiling azeotropes are those of water with highly ionized acids and of phenols with amines, alcohols or donor liquids containing oxygen e.g., o-cresol and ethyloxalate. (1)

Application of the Fenske Equation to analysis of effectiveness of separation of the cresols by azeotropic distillation with various entrainers is made in this thesis. Both minimum and maximum boiling azeotropes are investigated. Calculations involving use of this relationship may be seen in the Sample Calculation section of this work.

RESEARCH OBJECTIVES

The main objective of this research was investigation of the feasibility of using azeotropic distillation as a method of separating the meta and para isomers of the cresols.

A secondary objective of this research was the determination of a number of azeotropic compositions for various cresol-entrainer combinations.

EQUIPMENT

Equipment used in the research and analysis of data for this thesis included, two laboratory distillation columns, auxiliary equipment, a chain balance, a triple beam balance, a refractometer, and a gas chromatograph.

The laboratory distillation columns used were constructed of three concentric glass tubes held in place with asbestos tape and epoxy cement. The innermost tube consisted of a #6288 Ace Glass Distillation Apparatus, 23 mm ID by 120 cm (condensate return to packing support). The Ace apparatus was packed to a height of 115 cm. with one-eighth inch stainless steel helices packing (Fenske rings) supported on a cone shaped stainless steel screen. A thermometer was attached to the outside of this column. The middle column was 120 cm. long with an inside diameter of 45 mm. This column served as a support for 32 feet of Nichrome resistance heating wire. The outermost column served as an insulating jacket. This outer column was 120 cm. in length with an inside diameter of 63 mm. The base of the innermost column was a ground glass ball joint to allow attachment of a stillpot.

The stillpots used had the corresponding ground glass joint and were equipped with thermowell and sampling tube for obtaining stillpot temperature and composition data. Stillpots with the capacities of one and two liters were used. The sampling tube opening was located about one quarter of an inch above the stillpot bottom to allow sampling with

a minimum amount of liquid in the stillpot. Heat was supplied to the stillpot by an electric laboratory resistance heater. Stillpot and column heaters were controlled with 120 volt Powerstats. A diagram of the type of distillation apparatus constructed and used may be seen in Figure 1.

Equipment used in the analysis of compositions included a precision chain balance for preparation of refractive index samples and a constant temperature refractometer. A constant temperature bath was employed to keep the refractometer prisms at $20^{\circ}\text{C} \pm .5^{\circ}$.

Preparation of distillation charges of known composition was accomplished with the use of a laboratory triple beam balance with a capacity of 2100 grams.

Composition of the distillate and stillpot mixtures of the various relative volatility runs were determined by use of an Aerograph 660 Series chromatograph. This chromatograph was equipped with a flame ionization detector unit. The chromatograph column used was a 10 foot stainless steel column with an outside diameter of one-eighth inch. The column was packed with 10% di-n-octyl phthalate on 90-100 mesh Anakrom ABS.

A Model SR Sargent recorder was used to record the output signal from the chromatograph.

Data analysis was done using the method of relative peak areas as outlined in the Procedure section of this thesis. A compensating polar planimeter was used to determine areas under the recorded peaks.

CHEMICAL MATERIALS

The chemical compounds investigated for use as entrainers in the azeotropic separation of the cresols were chosen on the basis of 1, commercial availability, and 2, being within the boiling point limits (at 760 mm. Hg) of 180-220°C.

Commercial availability was chosen as a criteria in entrainer selection since commercial application of thesis results might prove possible. The boiling point limits of approximately ± 20 C° of the meta and para cresol boiling points were chosen because of the higher probability of azeotrope formation within these limits than over a more indefinite temperature range.

The commercial grade 2° meta-para cresol mixture used in initial entrainer evaluation was obtained from Pitt-Consol Co. Meta cresol of 96.5% (minimum) was obtained from Koppers Co., while para cresol of 99⁺% was obtained from Hercules Co.

The majority of the compounds evaluated as entrainers were obtained from Union Carbide, Dow, Pennsalt, Eastman, and Hooker. Single sample contributions were made by Miles Laboratories, Celanese, Ethyl Corp., Reilly Tar and Chemical Co. and Commercial Solvents Corp. A number of compounds listed as available in commercial quantities (8) but not listed in Chemical Materials Catalog were obtained from Fisher Scientific Company.

A complete listing of all compounds evaluated as entrainers and results of initial evaluations may be found in Table I of this work.

PROCEDURE

The procedure used in this thesis may be divided into three parts. These are: 1, initial entrainer evaluations; 2, azeotropic composition determinations; and 3, determinations of relative volatilities.

Initial Entrainer Evaluation.

The purpose of the initial entrainer evaluations was to determine if the proposed entrainer under study would form an azeotrope with either or both of the cresol isomers.

The proposed entrainer was charged to the stillpot and heat was then applied to stillpot and column. Once refluxing had begun, small increments of the proposed entrainer were drawn off until the temperature stabilized. This procedure allowed the "cutting" of light end impurities which might be present in the entrainer. Once the vapor temperature had become stable, the stillpot heat was lowered and cresols were added so that the composition became approximately 50 wt% entrainer. The column was once again brought to refluxing conditions. An hour was allowed for the column to come to equilibrium. The temperatures were noted. If the refluxing mixture had an overhead vapor temperature below the boiling point of the lowest boiling component in the mixture a minimum boiling azeotrope was indicated. If the refluxing temperature was not indicative of a minimum boiling azeotrope small increments were drawn from the column at intervals until (1) the temperature stabilized at a point higher than the highest boiling isomer, (2) the temperature

remained at the temperature of the lower boiling component and suddenly rose to the boiling point of the higher boiling component, or (3) the temperature gradually climbed to the boiling point of the higher boiling component. If the first condition was noticed, the presence of a maximum-boiling azeotrope was indicated. If the second condition was the case it was deduced that the column was effectively separating the proposed entrainer and the cresol with a sudden jump in temperature indicating that all of the lower boiling component had been drawn off and the higher boiling component was beginning to appear in the overhead. With some entrainer evaluations the temperature varied as stated in the third condition. In these instances it is felt that the pattern of variation of the temperature indicated that the column was not effective enough to separate completely the proposed entrainer and the cresols because of a relative volatility of very near unity existing between these compounds. The gradually increasing vapor temperature indicated that the overhead composition was shifting and becoming richer in the less volatile component of the system as samples were taken from the overhead.

The main indication of azeotrope formation was the overhead vapor temperature. Proposed entrainers which did not give a boiling point depression or elevation were classed as nonazeotroping compounds with respect to meta and para cresol.

When a boiling point elevation or depression was noticed, samples

of the overhead were taken so that by use of refractive index the azeotropic composition could be determined.

Azeotropic Composition Determination.

If initial entrainer evaluations as outlined above indicated formation of an azeotrope the following procedure was used.

Refractive index versus composition plots were prepared by plotting refractive indices of known composition samples against the weight percent cresol isomer present. The samples were prepared using a precision balance. The refractive indices of these samples were determined using a constant temperature refractometer.

Using the plotted refractive index curve and the sample saved from the initial evaluation studies, the approximate composition of the azeotrope could be determined. This composition was duplicated and charged to the distillation column. Portions of the condensate were drawn off until the temperature became stable. An hour distillation at total reflux was allowed for conditions to come to equilibrium. Samples of the distillate and bottoms product were then taken. The refractive indices of these samples were used to determine their composition. If these compositions were in close agreement (within 5 wt %) the azeotropic composition was taken as the condensate composition for minimum-boiling azeotropes or as the bottoms composition for maximum-boiling azeotropes. If agreement of condensate and stillpot samples was not

within the 5 wt % limits, the charge to the column was adjusted to bring the total column composition nearer the condensate or stillpot compositions for minimum or maximum boiling azeotropes respectively. The amount of deficient component needed to produce the desired total column composition was calculated on the basis of the size of the initial charge allowing a column holdup during operation of 50 ml. This procedure was followed until the condensate and stillpot compositions were within the prescribed limits.

Relative Volatility Determination.

The relative volatility of the two cresol isomers when distilled in the presence of the azeotroping agent could be determined once the compositions had been determined for each entrainer-isomer azeotrope. Determination of the relative volatilities of the cresols in the presence of entrainers causing minimum boiling azeotropes was done by the method outlined by Wilkinson (20). This method consisted of charging to the column a 50-50 wt % mixture of the meta and para isomers and enough of the entrainer as determined by the composition of the azeotrope to insure formation of an azeotrope with all of the lower boiling isomer. This mixture was then distilled at total reflux for a period of three hours. At the end of this time period, samples were taken of the condensate and stillpot mixture and saved for analysis.

The procedure for the relative volatility runs made with entrainers causing maximum-boiling azeotropes varied somewhat from

that used for minimum boiling azeotropes. In order that a separation might be effected if the relative volatility was enhanced by the presence of the maximum-azeotrope producing entrainer, the ratio of the cresol isomers in the charge was adjusted so that the lower-boiling maximum azeotrope could be contained in the column hold-up volume during distillation. It was noted that the lower boiling maximum azeotrope did not always occur with the para-entrainer combination. The charges to the columns for these determinations were made in the following manner. Taking the volume of the column holdup as 50 ml., the weights of the cresol isomer and entrainer causing the lower boiling maximum azeotrope needed to occupy this volume were calculated. The weight of entrainer needed to form an azeotrope with 200 grams of the remaining isomer was then calculated. The resulting stillpot charge was 200 grams of cresol isomer causing the higher boiling maximum azeotrope, the calculated weight of the other cresol isomer and five grams more than the stoichiometrically required amount of entrainer to form azeotropes with both isomers. This charge was then heated and condensate samples were drawn off until the condenser temperature stabilized at the boiling point of the lower boiling maximum azeotrope. The column was then operated at total reflux for a period of three hours. At the end of this time period, samples of condensate and stillpot compositions were taken and saved for analysis.

Analysis of the samples was done by gas chromatography. Since increased peak resolution could be obtained by using smaller sample

injections, the samples were diluted with carbon disulfide in the ratio of 100:1. Carbon disulfide was used as the diluent as this solvent does not cause a peak with flame ionization detector units. The gas chromatograph was operated at the following conditions:

Detector temperature	(°C):	165
Injector temperature	(°C):	250
Column temperature	(°C):	140
Flame range		10 ²
Nitrogen flow rate	(ml/min):	30
Hydrogen flow rate	(ml/min):	30
Attenuation		2 -8
Sample size, diluted, (μ l):		1

DISCUSSION OF RESULTS

The methods of initial entrainer evaluation and of azeotropic composition determination were found to be accurate means of determining existence and compositions of azeotropes. Agreement with the literature (9) was very good with respect to formation of minimum, maximum or non-azeotropic mixtures. The variations in azeotropic composition noted between this work and that data reported in Horsley can be, at least in part, explained by the differences in pressure due to elevation between locations where the data was gathered. It is possible that there exist more azeotropes than the fourteen reported in the investigation of the sixty-five compounds studied as entrainers in this thesis. However, if any do exist their boiling points are within $.2^{\circ}\text{C}$ of the lowest or highest boiling compound in the mixture being distilled, depending on their being either minimum or maximum azeotropes respectively. Because of the very slight difference in boiling points these azeotropes, if existing, would be of little commercial interest.

The determination of azeotropic composition by use of the refractive index was a fast accurate method. Each of the refractive index curves was drawn with at least seven data points. It is of interest to note that one refractive index curve could be used in determining the azeotropic composition of the entrainer with each of the two cresol isomers being investigated. This was possible because the refractive indices of the isomers were 1.5398 and 1.5395 for meta and para isomers respectively. The accuracy of these curves was tested with known

compositions and found to be reproducible to within 2 % by weight.

In the discussion of theory of this thesis it was pointed out that the validity of the Fenske Equation was dependent upon the fulfillment of a number of restrictions. One of these was that the relative volatility should be approximately constant over the range of concentrations and temperatures involved. To check on the fulfillment of this restriction, the relative volatility of the meta and para isomers was checked at three different concentration levels. Figure 3 is a relative volatility versus composition diagram. The relative volatility of the cresols varied .004 between mixtures of 90% meta, 10 % para, and 10 % meta, 90 % para. Because of this variation in the relative volatility with composition, the fulfillment of this restriction may be questionable. However, to reduce error as much as possible, the theoretical plate ratios of azeotropic distillation to straight rectification given in Table VI are determined using the relative volatility of the cresol composition corresponding most closely with the cresol isomer ratio used in the relative volatility runs for each entrainer. As an example, the cresol relative volatility used in the separation ratio with the Carbitol data was the value found by straight rectification of a 90% meta, 10% para isomer mixture. This cresol relative volatility was used because the percentages of total cresols in the Carbitol charge was 90% meta, 10% para. In every case the cresol relative volatility used for comparison with the azeotrope may be found at the top of the table (Tables III-V) where the azeotrope

relative volatility data is listed.

One of the most difficult parts of this thesis to complete was the final analysis of the relative volatility data. The difficulty encountered here was due to the fact that a column for use with the gas chromatograph which would give a suitable separation of the cresol isomers could not be found. Six columns were tried before one which gave a reproducible set of peaks with a reasonable retention time was found. Since the meta and para isomers were not totally separated in the column, the chromatogram showed two peaks which were not totally resolved. A calibration curve was drawn relating the area under each isomer peak to the actual weight percent of that isomer in the sample. The areas were divided by drawing a straight line perpendicular to the base line and passing through the minimum point between the two peaks. In the cases where one isomer was in great excess, there would appear only one peak with a definite shoulder indicating the presence of the second isomer. The isomer areas were separated here by drawing a line perpendicular to the base line and passing through the point of inflection between the shoulder and the peak. Since the samples were analyzed in exactly the same way the calibration was made, error was held to a minimum. The calibration curve was constructed with area ratios found in triplicate runs of ten solutions of known composition. The maximum deviation of any one sample of known composition from the calibration curve was 2% with the average deviation from the curve being of the

order of .4%. This was felt to be well within the limits of accuracy to be expected as a polar planimeter was used in determination of the areas under the curves and duplicate determinations with this instrument could easily vary as much as .6-1%. Figure 2 is a chromatographic trace obtained in this analysis work. The shaded area under the first peak is the area calibrated as representing the amount of para cresol in the total sample, the combined area of both curves being the total sample.

Calculations based on the Fenske Equation and data from the steam distillation runs show that an error of 3% in the estimation of peak areas causes a deviation of only .002 in the relative volatility. An error in the number of plates in the column of 10% causes an error of .001 in the relative volatility. Noting that the manufacturer of the chromatographic column guaranteed the reproducibility of analysis to only $\pm 2\%$ it is felt that the average deviation of .0027 in the relative volatility determinations is sufficiently explained.

In the determination of the azeotropic compositions it was noted that the lowest boiling isomer-entrainer pair was not always the para isomer-entrainer combination. Therefore the relative volatility data are reported in three groups, (1) minimum boiling azeotropes, (2) maximum boiling azeotropes where the para isomer entrainer azeotrope is lower boiling, and (3) maximum boiling azeotropes where the meta isomer-entrainer azeotrope is lower boiling. These values may be

seen in Tables III-V.

An inspection of Table V will show that a relative volatility of the cresols in the presence of diethylene glycol ethyl ether of .989. This indicates that the volatility of the cresol isomers has been reversed and the least volatile component has become the most volatile. These data are reported without a duplicate determination as there was not enough of the entrainer to permit a second run.

Inspection of Tables III-VI will show that none of the minimum boiling azeotropic systems gave an appreciable increase in the relative volatility while nine of the eleven maximum azeotropes gave increases in this quantity.

The number of theoretical plates needed to effect a 95% separation of the cresol isomers by straight rectification has been calculated to be 1053. Duplicate determinations for three maximum boiling azeotropes reduce this number to about 407 theoretical plates. Although this is a reduction in the number of theoretical plates of about 60% it must be emphasized that separation of meta and para cresol by azeotropic distillation involving any of the systems studied in this thesis work would probably not be commercially feasible.

CONCLUSIONS

The conclusion of this thesis study is that the number of theoretical plates needed to effect a 95% separation of the meta and para isomers of the cresols can be reduced as much as 60% with the addition of certain azeotrope-forming compounds.

SAMPLE CALCULATIONS

I. DETERMINATION OF RELATIVE VOLATILITY OF META AND PARA CRESOL:

Sample calculation based on data of trial 1 of steam distillation.

DATA:		Mol % para cresol	Mol % meta cresol
	overhead	52.0	48.0
	bottoms	48.2	51.8

Application of the Fenske Equation, Eqn. 10;

$$\alpha_{PM}^{n+1} = \frac{y_P x_M}{x_P y_M}$$

- where:
- α = Relative volatility (Para to Meta)
 - n = number of theoretical plates in column (26)
 - y_P = mol % of more volatile component in overhead (52% para)
 - y_M = mol % of less volatile component in overhead (48% meta)
 - x_P = mol % of more volatile component in bottoms (48.2% para)
 - x_M = mol % of less volatile component in bottoms (51.8% meta)

yields:

$$\alpha_{PM}^{26+1} = \frac{(52)(51.8)}{(48)(48.2)} = 1.163$$

$$\log \alpha_{PM} = \frac{\log 1.163}{27} = \frac{.06558}{27} = .00243$$

$$\alpha_{PM} = 1.006$$

II. DETERMINATION OF THEORETICAL PLATE RATIO OF AZEOTROPES TO STRAIGHT DISTILLATION FOR 95% SEPARATION OF ISOMERS

α_c = Average relative volatility of para to meta cresol

$$\alpha_c = 1.0056$$

Application of Fenske Equation to a 95 % separation gives;

$$1.0056^{n+1} = \frac{(95)(95)}{(5)(5)} = 361$$

$$n = \frac{\log 361}{\log 1.0056} - 1$$

$$n = 1054 - 1$$

Number of theo. plates needed for a 95% separation of para and meta cresol by straight rectification = n_s

$$n_s = 1053$$

Data from Carbitol investigation gives an average relative volatility of = 1.0145

$$1.0145^{n+1} = \frac{(95)(95)}{(5)(5)} = 361$$

$$n = \frac{\log 361}{\log 1.0145} - 1$$

$$n = 408 - 1$$

Number of theo. plates needed for a 95% separation of para and meta cresol by azeotropic distillation with Carbitol as the entrainer = $n_a = 407$

Therefore the ratio of theoretical plates needed in each case is;

$$\frac{\text{Azeotrope}}{\text{Straight Rectification}} = \frac{n_a}{n_s} = \frac{407}{1053} = .386 \approx .39$$

APPENDIX

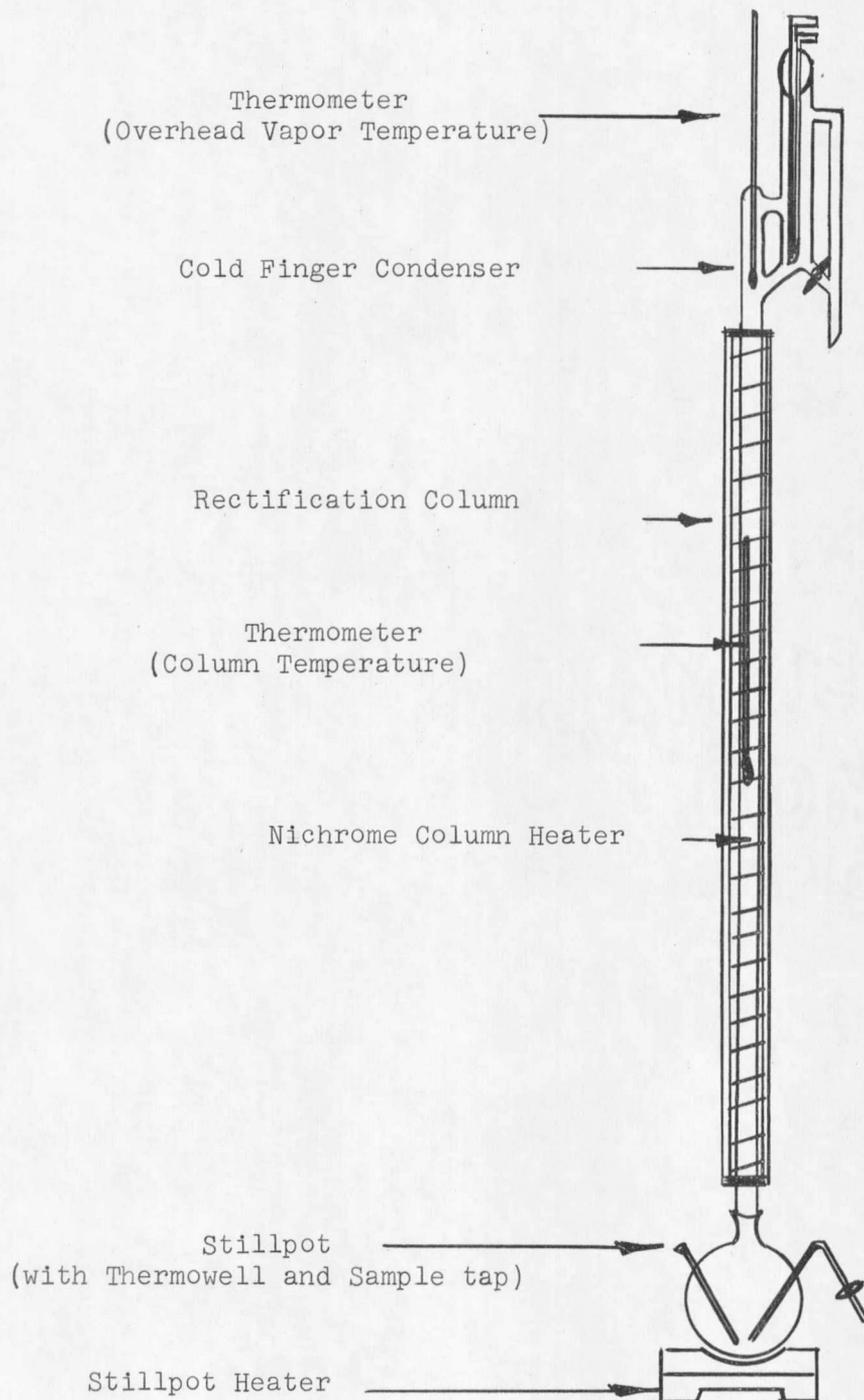
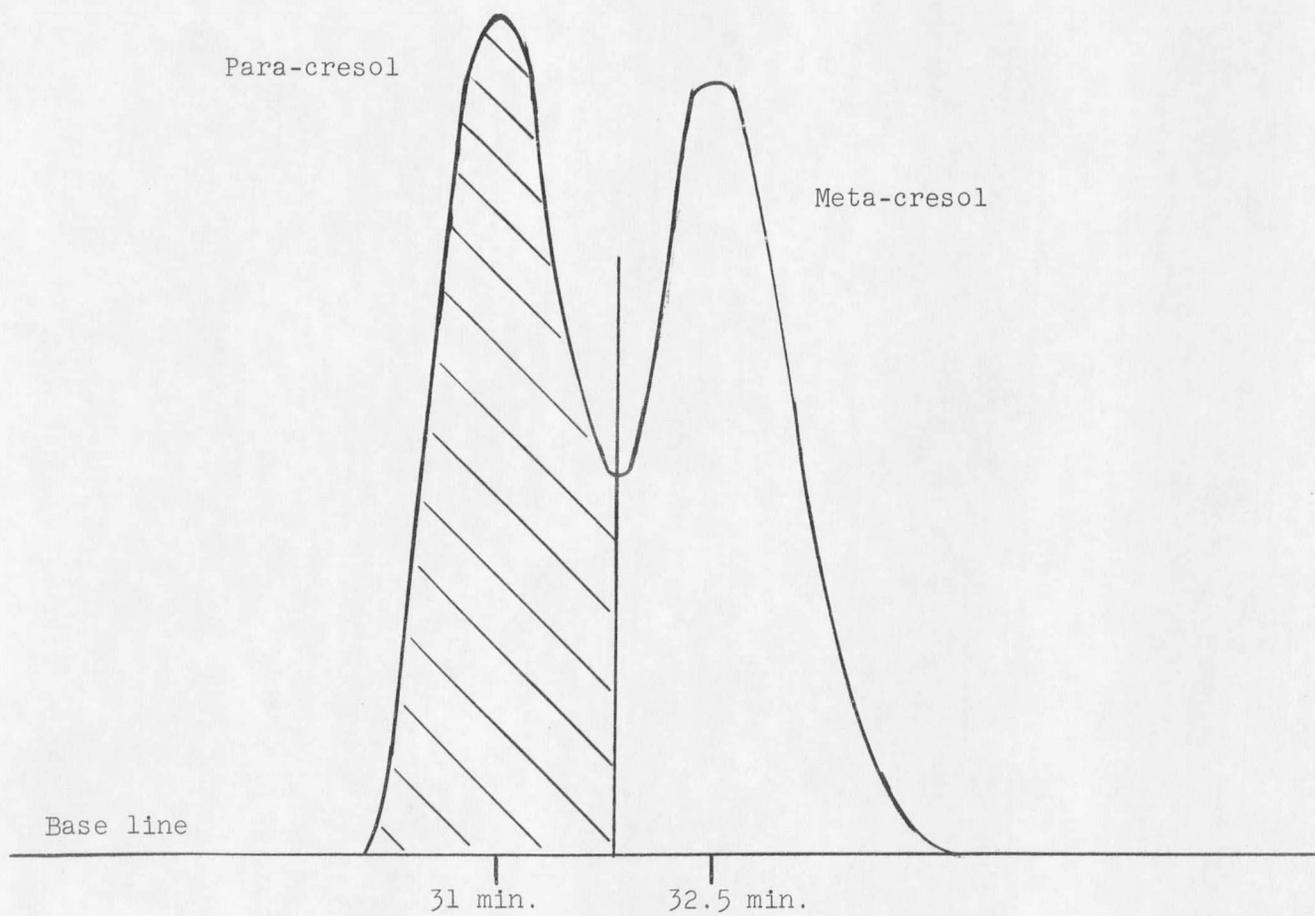


Figure 1
Diagram of Distillation Apparatus



Shaded area represents area calibrated as para-cresol.

Figure 2

Chromatograph Separation Using Di-n-octyl phthalate Column

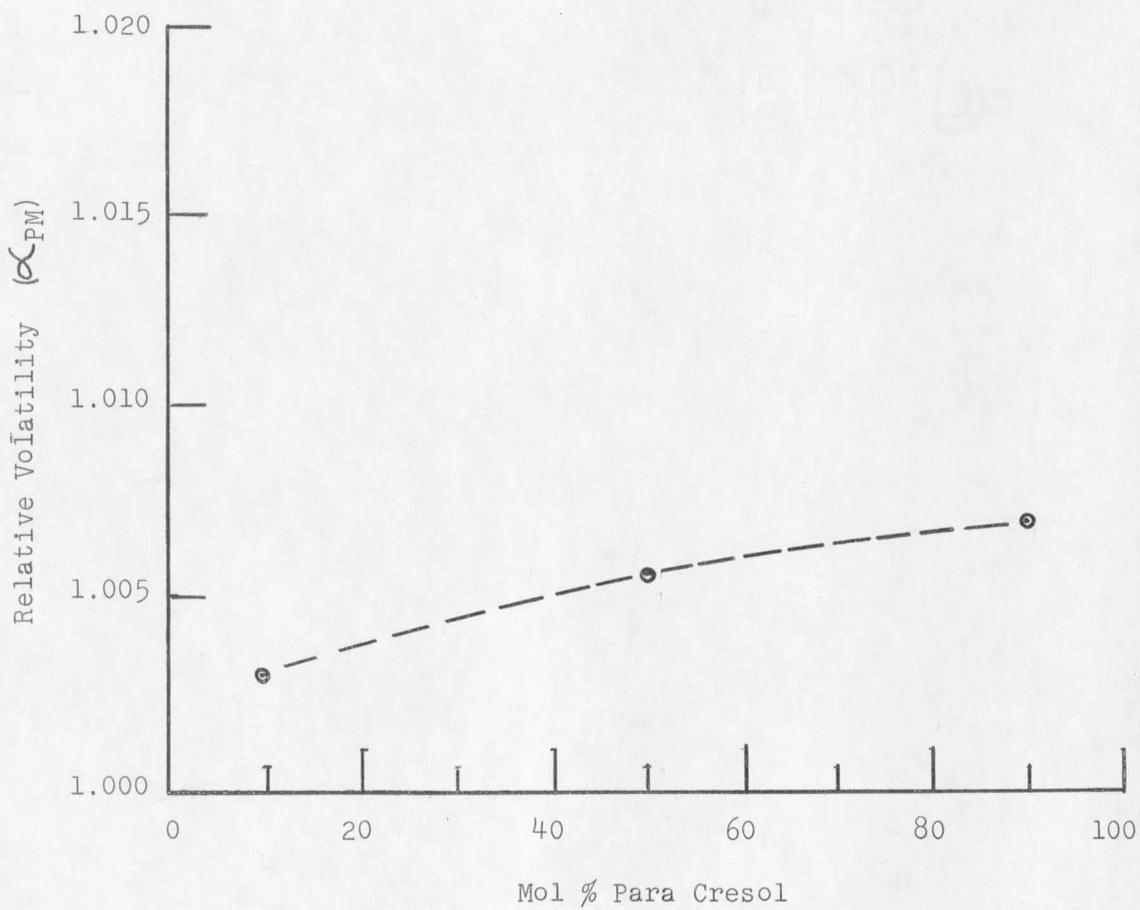


Figure 3

Relative Volatility of Para and Meta Cresol
versus
Mol % Para Cresol

TABLE I

COMPOUNDS EVALUATED AS ENTRAINERS WITH CRESOLS

COMPOUND	STRUCTURE	B.P. at 760 mm Hg	RESULTS OF INITIAL EVALUATION
1-2-4-5 TETRAMETHYL BENZENE	$(\text{CH}_3)_4\text{C}_6\text{H}_2$	195	NONAZEOTROPE
DIETHYLENE GLYCOL METHYL ETHER	$\text{CH}_3(\text{OC}_2\text{H}_4)_2\text{OH}$	194.2	NONAZEOTROPE
DIPROPYLENE GLYCOL METHYL ETHER	$\text{CH}_3(\text{OC}_3\text{H}_6)_2\text{OH}$	188.3	NONAZEOTROPE
DIETHYLENE GLYCOL ETHYL ETHER	$\text{C}_2\text{H}_5(\text{OC}_2\text{H}_4)_2\text{OH}$	202	MAXIMUM AZEOTROPE
PROPYLENE GLYCOL	$\text{CH}_3\text{.CHOH.CH}_2\text{OH}$	187.2	NONAZEOTROPE
CHLOROACETIC ACID	$\text{C}_2\text{H}_3\text{O}_2\text{Cl}$	188.8	NONAZEOTROPE (HIGHLY CORROSIVE TO PACKING)
ETHYLENE GLYCOL	$\text{HOCH}_2\text{CH}_2\text{OH}$	197.3	MINIMUM AZEOTROPE
DIETHYL BENZENE	$(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_4$	181	NONAZEOTROPE
DIISOPROPYL BENZENE (ISOMER MIXTURE)	$(\text{C}_3\text{H}_7)_2\text{C}_6\text{H}_4$	206 (IBP)	ISOMER FRACTIONS DISTILL OFF
O-DICHLOROBENZENE	$\text{C}_6\text{H}_4\text{Cl}_2$	180.4	NONAZEOTROPE
1-2-4 TRICHLOROBENZENE	$\text{C}_6\text{H}_3\text{Cl}_3$	214	NONAZEOTROPE
DICHLOROETHYL ETHER	$\text{C}_4\text{H}_8\text{OCl}_2$	178	NONAZEOTROPE

TABLE I (continued)

<u>COMPOUND</u>	<u>STRUCTURE</u>	B.P. at <u>760. mm Hg</u>	<u>RESULTS OF INITIAL EVALUATION</u>
SALICYALDEHYDE	$\text{HO}C_6H_4\text{CHO}$	195.5	DECOMPOSITION ON REFLUX- ING WITH CRESOLS
α -PINENE	$C_{10}H_{16}$	154	NONAZEOTROPE
DIPENTENE	$C_{10}H_{16}$	176	NONAZEOTROPE
2-ETHYL HEXANOL	$C_4H_9CH(C_2H_5)-CH_2OH$	185	NONAZEOTROPE
MONOETHANOL AMINE	$NH_2-CH_2CH_2OH$	171	NONAZEOTROPE
TETRAHYDROPYRAN-2-METHANOL	$\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_2\text{OH}$	187.2	NONAZEOTROPE
HEXYLENE GLYCOL	$CH_3CH(OH)CH_2C(OH)(CH_3)_2$	197.1	NONAZEOTROPE
DICHLOROISOPROPYL ETHER	$[ClCH_2(CH_3)CH]_2O$	187	NONAZEOTROPE
BUTYL CELLOSOLVE ACETATE	$CH_3COOC_2H_4OC_4H_9$	192.2	NONAZEOTROPE
n-HEXYL CELLOSOLVE	$C_6H_{13}OCH_2CH_2OH$	208.1	NONAZEOTROPE
ISOBUTYL HEPTYL KETONE	$(CH_3)_2CH-CH_2COCH_2CH(CH_3)CH_2CH(CH_3)_2$ 218.2	218.2	NONAZEOTROPE
ACETOPHENONE	$CH_3COC_6H_5$	201.6	MAXIMUM AZEOTROPE
N-N DIISOPROPYLETHANOL AMINE	$[(CH_3)_2CH]_2NC_2H_4OH$	190.9	NONAZEOTROPE
BENZYL AMINE	C_7H_9N	184.5	NONAZEOTROPE

TABLE I (continued)

<u>COMPOUND</u>	<u>STRUCTURE</u>	<u>B.P. at 760 mm Hg</u>	<u>RESULTS OF INITIAL EVALUATION</u>
HYDROQUINONE-DIMETHYL ETHER	$\text{CH}_3\text{OC}_6\text{H}_4\text{OCH}_3$	213	NONAZEOTROPE
PHENYL METHYL CARBINOL	$\text{C}_6\text{H}_5\text{CHOHCH}_3$	203.4	NONAZEOTROPE
DIETHYLENE TRIAMINE	$(\text{NH}_2\text{C}_2\text{H}_4)_2\text{NH}$	206.7	NONAZEOTROPE
n-OCTYL MERCAPTAN	$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{SH}$	205	MINIMUM AZEOTROPE
BENZYL MERCAPTAN	$\text{C}_6\text{H}_5\text{CH}_2\text{SH}$	194	ENTRAINER DECOMPOSITION ON REFLUXING
METHYL CARBITOL	$\text{CH}_3\text{O}[\text{C}_2\text{H}_4\text{O}]_2\text{H}$	193.6	MAXIMUM AZEOTROPE
2-METHYL-5-ETHYL PYRIDINE	$(\text{C}_2\text{H}_5)(\text{CH}_3)\text{C}_5\text{H}_3\text{N}$	178.3	NONAZEOTROPE
2-ETHYL HEXYL ACETATE	$\text{CH}_3\text{COOCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$	198.4	MAXIMUM AZEOTROPE
1-3 BUTYLENE LYCOL	$\text{CH}_3\text{CHOHCH}_2\text{CH}_2\text{OH}$	204	NONAZEOTROPE
DIETHYL CARBITOL	$(\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2)_2\text{O}$	188.4	MAXIMUM AZEOTROPE
CARBITOL ACETATE	$\text{CH}_3\text{COO}(\text{C}_2\text{H}_4\text{O})_2\text{C}_2\text{H}_5$	217.4	NONAZEOTROPE
GLYCOL DIACETATE	$(\text{CH}_2\text{OOCCH}_3)_2$	190.8	MAXIMUM AZEOTROPE
ETHYLTHIOETHANOL	$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}$	183	NONAZEOTROPE
TRIETHYL PHOSPHATE	$(\text{C}_2\text{H}_5)_3\text{PO}_4$	215	ENTRAINER DECOMPOSITION ON REFLUXING

TABLE I (continued)

<u>COMPOUND</u>	<u>STRUCTURE</u>	<u>B.P. at 760 mm Hg</u>	<u>RESULTS OF INITIAL EVALUATION</u>
DIGLYCOLAMINE	$\text{NH}_2\text{OH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	221	MAXIMUM AZEOTROPE
N-AMINO ETHYL PIPERAZINE	$\text{H}_2\text{NC}_2\text{H}_4\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2$	222	NONAZEOTROPE
BUTYL LACTATE	$\text{CH}_3\text{CHOHCOO}(\text{CH}_2)_3\text{CH}_3$	188	NONAZEOTROPE
DECYL ALCOHOL	$\text{C}_{10}\text{H}_{22}\text{O}$	210	NONAZEOTROPE
BENZOYL CHLORIDE	$\text{C}_6\text{H}_5\text{COCl}$	197.5	REACTION WITH CRESOLS
CARBITOL SOLVENT	$\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	195	MAXIMUM AZEOTROPE
CAPRYL CHLORIDE	$\text{CH}_3(\text{CH}_2)_6\text{COCl}$	195	REACTION WITH CRESOLS
DIAMYL AMINE	$(\text{C}_5\text{H}_{11})_2\text{NH}$	189	NONAZEOTROPE
BUTYLAMINOETHANOL	$\text{CH}_3(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{OH}$	201	NONAZEOTROPE
4-ISOPROPYL PYRIDINE	$(\text{CH}_3)_2\text{CHC}_5\text{H}_4\text{N}$	178	DECOMPOSITION OR REACTION WITH CRESOLS
N-BENZYL METHYL AMINE	$\text{C}_8\text{H}_{11}\text{N}$	184	NONAZEOTROPE
TETRA PROPYLENE	C_{12} OLEFIN ISOMER MIXTURE	187-197	SOLVENT FRACTIONS DISTILL OFF
ACETONYL ACETONE	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{COCH}_3$	192	MAXIMUM AZEOTROPE
ETHYLACETOACETATE	$\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$	181	REACTION WITH CRESOLS

TABLE I (continued)

<u>COMPOUND</u>	<u>STRUCTURE</u>	<u>B.P. at 760 mm Hg</u>	<u>RESULTS OF INITIAL EVALUATION</u>
1-6 HEXANEDIAMINE	$\text{NH}_2(\text{CH}_2)_6\text{NH}_2$	198	NONAZEOTROPE
3-3-5 TRIMETHYLCYCLOHEXANOL (LOW MELTING POINT)	$\text{C}_9\text{H}_{19}\text{O}$	197.6	NONAZEOTROPE
DI-n-BUTYL-d-TARTRATE	$\text{C}_{12}\text{H}_{22}\text{O}_2$	---	ENTRAINER DECOMPOSES
ISOPHORONE	$(\text{CH}_3)_2\text{CCH}_2\text{C}(\text{CH}_3):\text{CHCOCH}_2$	215.2	MAXIMUM AZEOTROPE
PROPIOPHENONE	$\text{CH}_3\text{CH}_2\text{COC}_6\text{H}_5$	218	MAXIMUM AZEOTROPE
TRIBUTYL AMINE	$[\text{CH}_3(\text{CH}_2)_3]_3\text{N}$	214	NONAZEOTROPE
TRIMETHYL PHOSPHATE	$(\text{CH}_3\text{O})_3\text{PO}$	193	NONAZEOTROPE
CAPROIC ACID	$\text{C}_6\text{H}_{12}\text{O}_2$	205	NONAZEOTROPE
2-ETHYL HEXYL ACRYLATE	$\text{CH}_2:\text{CHCOOCH}_2\text{CH}(\text{C}_2\text{H}_5)(\text{CH}_2)_3\text{CH}_3$	208	POSSIBLE POLYMERIZATION (DISTILLATION STOPPED)
UCAR SOLVENT 2LM	SOLVENT MIXTURE	187.2	SOLVENT FRACTIONS DISTILL OFF
DIVINYLBENZENE	$\text{CH}_2:\text{CHC}_6\text{H}_4\text{CH}:\text{CH}_2$	195	POLYMERIZATION ON HEATING

TABLE II

AZEOTROPIC COMPOSITION DATA OF EFFECTIVE ENTRAINERS

<u>COMPOUND</u>	B.P. (°C) <u>at 635 mm Hg</u>	Meta Cresol Azeotrope		Para Cresol Azeotrope	
		<u>BP Azeo</u>	<u>Wt% M-cresol</u>	<u>BP Azeo</u>	<u>Wt% P-cresol</u>
ETHYLENE GLYCOL	191	189.5	41.2	189.2	39.7
DIETHYLENE GLYCOL ETHYL ETHER	193	202.3	52.3	203	51.6
DIGLYCOLAMINE	206	217	41.8	219	41.1
2-ETHYL HEXYL ACETATE	191	197	52.7	194	51.0
PROPIOPHENONE	204	206.5	10.3	206.3	9.5
METHYL CARBITOL	186	203	62	202	61.3
CARBITOL SOLVENT	188	205	50.4	200	50
DIETHYL CARBITOL	183	201.5	60.8	200	63
ACETONYL ACETONE	195	201.5	67.2	201	63.63
ISOPHERONE	191	201	36	200	39
ACETOPHENONE	195	201.4	49	201	48
n-OCTYL MERCAPTAN	191	187	38.5	185	37
GLYCOL DIACETATE	178	194.8	69	194.5	71

TABLE III

RELATIVE VOLATILITIES OF INVESTIGATED MINIMUM AZEOTROPES

ENTRAINER		RELATIVE VOLATILITY		
		Trial 1	Trial 2	Average
NO ENTRAINER (3 trials) 50-50% by weight meta-para cresols	1.003	1.006	1.008	1.0056
WATER		1.006	1.009	1.0075
ETHYLENE GLYCOL		1.003	1.008	1.0055
n-OCTYL MERCAPTAN		1.005	1.007	1.006

TABLE IV

 RELATIVE VOLATILITIES OF INVESTIGATED MAXIMUM AZEOTROPES
 (LOWER BOILING PARA-ENTRAINER MAXIMUM AZEOTROPE)

ENTRAINER	RELATIVE VOLATILITY		
	Trial 1	Trial 2	Average
NO ENTRAINER 90% meta, 10% para cresol mixture	1.003	1.003	1.003
CARBITOL	1.014	1.015	1.0145
METHYL CARBITOL	1.016	1.013	1.0145
2-ETHYL HEXYL ACETATE	1.014	1.015	1.0145
DIETHYL CARBITOL	1.016	1.012	1.014
ISOPHORONE	1.010	1.016	1.013
ACETOPHEONONE	1.012	1.009	1.0105
GLYCOL DIACETATE	1.009	1.010	1.0095
ACETONYL ACETONE	1.012	1.007	1.0095
PROPIOPHENONE ¹	1.015	---	---

¹ Results of Propiophenone investigation are based on one relative volatility determination only.

TABLE V

RELATIVE VOLATILITIES OF INVESTIGATED MAXIMUM AZEOTROPES
(LOWER BOILING META-ENTRAINER MAXIMUM AZEOTROPE)

ENTRAINER	RELATIVE VOLATILITY		
	Trial 1	Trial 2	Average
NO ENRAINER 90% para, 10% meta cresol mixture	1.006	1.008	1.007
DIGLYCOL AMINE	1.006	1.008	1.007
DIETHYLENE GLYCOL ETHYL ETHER ¹	.989	--	--

¹ Results of Diethylene glycol ethyl ether investigation are based on one relative volatility determination only. See Discussion of results for discussion of this run.

TABLE VI

THEORETICAL PLATE RATIO
AZEOTROPIC DISTILLATION TO STRAIGHT RECTIFICATION¹

ENTRAINER:	RATIO
PROPIOPHENONE ²	.37
CARBITOL	.39
METHYL CARBITOL	.39
2-ETHYL HEXYL ACETATE	.39
DIETHYL CARBITOL	.40
ISOPHERONE	.43
ACETOPHENONE	.53
GLYCOL DIACETATE	.60
ACETONYL ACETONE	.60
WATER	.75
DIGLYCOL AMINE	.80

¹ Basis is 95% separation of cresol isomers, required number of plates by straight rectification is 1053.

² Results of Propiophenone investigation are based on one relative volatility determination only.

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