MONTANA STATE UNIVERSITY

Effect of composition on recovery in the azeo-tropic system methly cyclohexane-toluene-n-propyl alcohol
by James Daly

A THESIS Submitted to the Graduate Committee in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University
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Abstract:
The purpose of this paper is to show the effect upon recovery both in quantity and purity, of varying percentage composition of charge in the separation of a binary mixture by means of azectropic distillation The binary methylcyclohexane-toluene with n-propyl alchohol as the entrainer was chosen as the system to use in making this study.

Non-azeotropic distillations were made upon the system in order to obtain data with which to compare the results obtained by azeotropic means.

The distillations were carried out using a labor-atory rectification column that calibrated 32 theoretical plates.

The following conclusions may be drawn from data ob-tained: 1. Azeotropic distillation is superior to non-azeotropic distillation in the percentage recovery of a given purity of both the components of the binary.

2. In azeotropic distillation? the recovery of the least volatile component in the charge is indepen-dent of its relative quantity in the charge. In non-azeotropic distillation the recovery of the least vola-tile component in the charge is dependent on its rela-tive quantity in the charge.

3. The recovery of the most volatile component is dependent upon the amount of that component charged both in azeotropic and non-azeotropic distillation. The greater its proportion In the charge the greater will he the recovery of a given purity.

4. The purity obtainable in azeotropic distillation of the most volatile component is higher than in non-azeo-tropic distillation.

EFFECT OF COMPOSITION ON RECOVERY IN THE
AZEOTROPIC SYSTEM METHYLCYCLOHEXANE-
TOLUENE-n-PROPYL ALCOHOL

by

JAMES DALY

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ABSTRACT

The purpose of this paper is to show the effect upon recovery both in quantity and purity, of varying percentage composition of charge in the separation of a binary mixture by means of azeotropic distillation.

The binary methylcyclohexane-toluene with n-propyl alcohol as the entrainer was chosen as the system to use in making this study.

Non-azeotropic distillations were made upon the system in order to obtain data with which to compare the results obtained by azeotropic means.

The distillations were carried out using a laboratory rectification column that calibrated 32 theoretical plates.

The following conclusions may be drawn from data obtained:

1. Azeotropic distillation is superior to non-azeotropic distillation in the percentage recovery of a given purity of both the components of the binary.

2. In azeotropic distillation, the recovery of the least volatile component in the charge is independent of its relative quantity in the charge. In non-azeotropic distillation the recovery of the least volatile component in the charge is dependent on its relative quantity in the charge.

3. The recovery of the most volatile component is dependent upon the amount of that component charged both in azeotropic and non-azeotropic distillation. The greater its proportion in the charge the greater will be the recovery of a given purity.

4. The purity obtainable in azeotropic distillation of the most volatile component is higher than in non-azeotropic distillation.

I   INTRODUCTION

The purpose of this paper is to show the effect upon re-
covery, both in quantity and purity, of varying percentage com-
position of charge in the separation of a binary mixture by
means of azeotropic distillation.

The system toluene-methylcyclohexane, with n-propyl alco-
hol as the entrainer, was chosen because this system shows
certain desirable characteristics for a study of this sort.
The hydrocarbons and the alcohol are easily obtained in a high
grade of purity and the break in the distillaion curve of this
system is sharp. The refractive indices of the two hydrocarbons
are far enough apart to permit analysis of fractional cuts by
use of a refractometer, and the constituents of the azeotrope,
methylcyclohexane-n-propyl alcohol, are easily separated by
water washing.

In the separation by distillation of binary systems, it is
often found that the components of the system have boiling
points so nearly the same that separation is exceedingly dif-
ficult without resorting to a column with a great number of
plates and/or a very high reflux ratio. One means that has
been suggested to make such a separation in columns of normal
size at moderate reflux ratios is the use of an entrainer to
form an azeotrope with one or both of the components (3,4,7).

An azeotropic mixture may be defined as one that yields,
upon mixing, either a vapor pressure greater than that of the

lowest boiling component, or yields a vapor pressure less than the vapor pressure of the highest boiling component. The former is called a minimum boiling azeotrope; the latter a maximum boiling azeotrope (7). In making separations by means of distillation of azeotropic mixtures, the minimum boiling azeotrope is more satisfactory.

An entrainer may be defined as the agent that is added to the binary system to form an azeotrope with one or both of the components. There is available in the literature a moderate amount of data from which azeotropic compositions may be ascertained (5,6). There is also available in the literature a method of selecting a suitable entrainer for a given separation (1).

The separation, by azeotropic distillation, of a 40 weight percent methylcyclohexane, 60 weight percent toluene mixture has been reported by Berg and Harrison (1). No attempt was made to study the effect upon recovery of varying the percentage composition of the hydrocarbon charge.

Because no data were available from the literature of the actual percent recovery possible by straight rectification of the system methylcyclohexane - toluene, it was necessary to make several such runs, during this study, to provide the necessary data for comparison purposes. These data are tabulated in this report.

Boiling temperatures of cuts listed in this paper were not

corrected to standard pressure since no good method is available to convert the boiling point of azeotropic mixtures from one pressure to another. The average barometer reading at the station where this work was done is 635 mm.

II EQUIPMENT, METHODS, AND COMPOUNDS

A. EQUIPMENT

The equipment used in this work consisted of a precision rectification column, a Corad constant reflux ratio condenser, a graduated water-cooled receiver, a Harvard type triple beam balance, a mercury filled "U" type manometer, round bottom glass distilling flasks with side arm, a Valentine refractometer, a ceramic heater, two autotransformers and two glass stem mercury thermometers.

The column was constructed of three concentric glass tubes. The innermost tube was 33 mm. in diameter, packed with Fenske one-eighth inch stainless steel helices. A thermometer was fastened to the outside surface of the inner tube about halfway between top and bottom. The second or middle tube was wrapped with Nichrome wire which was connected to a small 110 volt auto-transformer to provide heat to the column. The third or outer tube served as a protector and insulator. The column was forty-eight inches high. At total reflux the column calibrated 32 theoretical plates. The Corad head is so designed as to give constant reflux ratios of 5:1, 10:1, 20:1, and 30:1.

The manometer used was a "U" shaped tube about twelve inches in height with one end opened to the atmosphere and the other leading through a stopcock to a ball joint connecting to a side arm of the distilling flask. This device was used to measure pressure drop in the column.

The distilling flasks used were of two sizes, one liter and two liter, with a side arm ball joint that fitted into the manometer and another ball joint at the top that fitted into the bottom of the column.

The heater used had a ceramic base with a concave depression in which were Nichrome coils. The flasks fitted approximately into the concave depression. The current input to the heater was controlled by another small 110 volt autotransformer.

The refractometer was a Valentine of the glass prism type capable of reading to six significant figures. All refractive indices were read at 20 degrees Centigrade plus or minus 0.1 degrees Centigrade.

The autotransformers were Superior Electric Company Powerstats of seven and one-half ampere maximum input at 110 volts A.C. The output, or secondary, was fused at six amperes with a voltage range of 0 to 135 volts.

B. METHODS

1. Determining the Azeotropic Composition:

The composition of the methylcyclohexane-n-propyl alcohol azeotrope was obtained from the literature (1). This value was checked by the use of an Othmer vapor-liquid equilibrium still and was found to be in agreement with our experimentally determined value even though the literature value had been obtained at a pressure of 760 mm. and our experimental value at a pressure of 640 mm. The value found in the literature, and experimentally checked by us, was 65 weight percent methylcyclohexane and 35 weight percent n-propyl alcohol.

To obtain a further check upon this value two charges were made up; one containing 63 weight percent methylcyclohexane and 37 weight percent n-propyl alcohol, and the other 67 weight percent methylcyclohexane and 33 weight percent n-propyl alcohol. Each charge was then refluxed in the column for an hour and a small overhead cut obtained. The refractive indices of the two overhead cuts were measured and the deviation of these refractive indices from the refractive index of the original charge plotted against percent composition. Since the charges selected straddled the correct azeotropic composition, one deviation was positive and the other negative. The intersection of a line connecting the two points with the zero deviation line indicated the percent composition of the azeotrope. This was found to be 65.7 weight percent methylcyclohexane and 34.3 weight

percent n-propyl alcohol. This value was used throughout in making up the charges for the azeotropic distillations.

2. Making up Charges for Azeotropic Runs:

Charges were made up on a weight percent basis using a Harvard type triple-beam balance. Due to the operational holdup of the column it was found necessary to make up the charge so that there was at least 150 grams of the least volatile component. The smallest charge used was 300 grams total of hydrocarbons. The amount of entrainer added was dependent upon amount of methylcyclohexane present. (See sample calculations). In all cases a two gram excess of n-propyl alcohol was added to insure complete removal of all the methylcyclohexane.

3. Making the Azeotropic Runs:

Each charge was placed in the distilling flask and heat flow adjusted by means of the autotransformers. The column was allowed to flood and then to run at total reflux for one hour. Vapor velocity through the column was kept at a constant value by adjusting the heat flow to the still pot and the column by control of the autotransformers. The vapor velocity which is directly proportional to the pressure drop across the entire column was measured by means of the manometer. A vapor velocity of 80 percent of the priming or flooding velocity corresponding to a pressure drop across the column of 15 mm. plus or minus 1 mm. was maintained throughout all the runs.

After the column had been allowed to come to equilibrium,

the reflux ratio was set and overhead cuts were taken. The vapor temperature and weight of each cut was noted and these data used in making up the plots. The size of the cuts taken depended upon the rate of increase of the vapor temperature. When the break or mid-fraction cut was reached, smaller cuts were taken in order to define properly the distillation curve. Runs were made from compositions of 10 percent toluene and 90 percent methylcyclohexane to 80 percent toluene and 20 percent methylcyclohexane, each composition being run at four different reflux ratios: 5:1, 10:1, 20:1 and 30:1.

The refractive index of each cut was determined and then the cut was washed with distilled water to remove the n-propyl alcohol. The water washed cuts were then dried over calcium chloride and the refractive index of each was measured again.

In the runs of 10 percent toluene and 90 percent methyl-cyclohexane composition, the size of the charge, which included 150 grams of toluene and 1350 grams of methylcyclohexane plus entrainer, became too large for the still pots available. Since 150 grams of toluene represented the minimum amount necessary to take care of column holdup and completely drive off the azeotrope, a chaser was introduced. The use of a chaser permitted cutting the charge to a size suitable for proper handling. Cumene was the chaser used because it forms no azeotrope with toluene, methylcyclohexane, or n-propyl alcohol and the break in the distillation curve between cumene and toluene is very sharp.

The size of the charge, using a chaser, could be cut to 50 grams of toluene, 450 grams of methylcyclohexane, 150 grams of cumene plus entrainer. This method of cutting down on the quantity of charge also eliminated the poor accuracy resulting from slight leaks during the extended period of time necessary to run off the larger charge.

4. Plotting the Data of Azeotropic Runs:

The data were plotted as weight percent distilled, versus vapor temperature, and also weight percent distilled versus midpoints of each refractive index step. Figure 1 is a sample plot for an azeotropic run containing a charge of 60 weight percent toluene, 40 weight percent methylcyclohexane at a reflux ratio of 20:1, Run Number 11, Table I. The percent recovery of methylcyclohexane and toluene was obtained from these curves. (See sample calculations and Figure Number 1.)

5. Non-azeotropic Runs:

In order to obtain data with which to compare the efficiency of recovery by azeotropic distillation, a series of control runs were made. The runs were made using the same reagents as those that were used in the azeotropic runs, in the same column, and the same charges minus the entrainer. The control runs were carried out at only one reflux ratio, 20:1. A chaser, cumene, was used for the 10 percent toluene, 90 percent methylcyclohexane, and the 20 percent toluene, 80 percent methylcyclohexane charges. These data are tabulated in Table II.