Application of azeotropic distillation to the separation of paraffins and olefins
by Walter Bruce Robinson

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemical Engineering
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Abstract:
The purpose of this Investigation was to study the possible application of azeotropic distillation to the separation of paraffins and olefins. An attempt was made to enhance the ease of separation of three pairs of compounds by using azeotropic distillation. These three pairs were 3-methylpentane and hexene-1, 3 methylpentane and 2-ethyl-l-butene, and 2-ethyl-l-butene and n-hexane. The degree to which a compound (called an entrainer) helped separation was measured by how much it increased the relative volatility between the particular pair of compounds being separated over the value obtained when the pure compounds were distilled alone.

Compounds picked as entrainers were those which contained oxygen, nitrogen, and halogen atoms and were for this reason likely to give large deviation from Raoult's Law in solution. The compounds were picked to boil within about ±20°C of the hydrocarbons being separated. Twenty-nine compounds satisfying these requirements were tried as possible entrainers.

Major pieces of equipment used included four identical distillation columns packed with Fenske rings and fitted with cold finger condensing heads, a gas chromatograph, and a refractometer.

The evaluation of an entrainer consisted of determining whether or not an azeotrope was formed, determining the azeotropic composition, and determining the relative volatility between the hydrocarbons using the entrainer. Relative volatilities were calculated from the Fenske equation after overhead and bottoms samples from the distillation runs had been analyzed with the chromatograph. Duplicate runs were made for each relative volatility determination and seemed to agree quite well.

For the 3-methylpentane-hexene-1 system, methyl acetate appeared to be the best entrainer as it increased the relative volatility from 1.009 to 1.104 and reduced the; theoretical plate requirement for 95% separation from 657 to 78. For the 3-methylpentane-2-ethyl-l-butene system ethyl formate was the best entrainer as it increased the relative volatility-from 1.037 to 1.103 and reduced the number of theoretical plates required for 95% separation from l6l to 40. For the 2-ethyl-1-butene-n-hexane system chloroform was the only entrainer found to make the relative volatility greater than the 1.056 value obtained for the pure components. Chloroform gave a Value of 1.094 and reduced the number of -theoretical plates needed for 95$ separation from 107 to 64.

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ABSTRACT

The purpose of this investigation was to study the possible application of azeotropic distillation to the separation of paraffins and olefins. An attempt was made to enhance the ease of separation of three pairs of compounds by using azeotropic distillation. These three pairs were 3-methylpentane and hexene-1, 3 methylpentane and 2-ethyl-1-butene, and 2-ethyl-1-butene and n-hexane. The degree to which a compound (called an entrainer) helped separation was measured by how much it increased the relative volatility between the particular pair of compounds being separated over the value obtained when the pure compounds were distilled alone.

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The evaluation of an entrainer consisted of determining whether or not an azeotrope was formed, determining the azeotropic composition, and determining the relative volatility between the hydrocarbons using the entrainer. Relative volatilities were calculated from the Fenske equation after overhead and bottoms samples from the distillation runs had been analyzed with the chromatograph. Duplicate runs were made for each relative volatility determination and seemed to agree quite well.

For the 3-methylpentane-hexene-1 system, methyl acetate appeared to be the best entrainer as it increased the relative volatility from 1.009 to 1.104 and reduced the theoretical plate requirement for 95% separation from 657 to 78. For the 3-methylpentane-2-ethyl-1-butene system ethyl formate was the best entrainer as it increased the relative volatility from 1.037 to 1.103 and reduced the number of theoretical plates required for 95% separation from 161 to 40. For the 2-ethyl-1-butene-n-hexane system chloroform was the only entrainer found to make the relative volatility greater than the 1.056 value obtained for the pure components. Chloroform gave a value of 1.094 and reduced the number of theoretical plates needed for 95% separation from 107 to 64.

INTRODUCTION AND THEORY

The purpose of this investigation was to study the possible application of azeotropic distillation to the separation of paraffins and olefins.

In recent years several investigations of the application of azeotropic distillation to various separation problems have been made at Montana State College. This investigation is a continuation of these studies and was not prompted by any specific separation problem. Difficult to separate paraffin and olefin mixtures are certainly not an unusual problem in the chemical and petroleum industries however. One need only look in a handbook for a moment and see the enormous number of paraffin and olefin hydrocarbons falling in the same boiling point ranges to realize that this is probably the case.

Straight distillation is used extensively to separate one compound from another if their boiling points are a large distance apart. When their boiling points are close together it many times becomes impossible to obtain one or the other of the compounds in any purity without building a very tall distillation column with a large number of theoretical plates. Frequently this is uneconomical or unfeasible to do and some other method must be used to effect the separation. Among these methods are fractional crystallization, use of a selective solvent, and azeotropic distillation.

A mixture of volatile liquids can be separated by distillation because generally the composition of the vapor coming from the liquid mixture is different from that of the liquid. The vapor is richer in the component which boils at the lower temperature. In most cases the lower the boiling point of a substance the greater is its volatility or tendency to vaporize. When the liquid and vapor are in equilibrium the greatest difference exists between the vapor and liquid compositions. If the vapor from the vaporizing liquid mixture is condensed and then partially revaporized the resulting vapor will be even richer in the more volatile component. If this process is continued the vapor will become increasingly richer in the more volatile component. A rectification column contains several stages which accomplish this. "A stage may be defined as a unit of equipment in which two dissimilar phases are brought into intimate contact with each other and then mechanically separated" (3). In a rectification column liquid and vapor are in intimate contact in a stage which may consist of a bubble plate or a quantity of some kind of packing. The vapor from a stage is condensed by the liquid on the next stage above it and this liquid is essentially revaporized. The process continues up the column. The overall result in the case of a binary mixture is that the more volatile compound becomes concentrated near the top of the column and the less volatile compound becomes concentrated near the bottom. In the case of a multicomponent mixture the different components distribute themselves according to boiling point throughout the column with the lowest boiling component at the top.

An equilibrium stage is one in which the liquid and vapor are in equilibrium. Because the largest difference between the vapor and liquid compositions exists at equilibrium the best possible separation is effected in an equilibrium stage. In practice the liquid and vapor in a column are usually not in contact long enough for equilibrium to occur. The separating power of a column is therefore measured in theoretical plates. A column is said to contain one theoretical plate if the same difference in composition between liquid and vapor is obtained as that which 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 being considered, and for any one mixture it varies with the composition (6).

In this investigation the following three pairs of compounds were being used: (1) 3-methylpentane and hexene-1, (2) 3-methylpentane and 2-ethyl-1-butene, (3) 2-ethyl-1-butene and n-hexane. The normal boiling points of 3-methylpentane, hexene-1, 2-ethyl-1-butene, and n-hexane are 63.2, 63.7, 66.2, and 68.8°C, respectively (2).

These compounds were chosen because they boil so close together that separation of the different pairs would require a very large number of theoretical plates if ordinary rectification were used.

It is not an unusual pheonomena for two or more liquids to form a mixture which when boiled gives a vapor of exactly the same composition as that of the liquid. The only other case in which liquid and vapor have the same composition is when a pure compound is boiling. Indeed, such a mixture acts as if it were a pure compound and is constant-boiling. A constant-boiling mixture is called an azeotrope and the composition of the liquid or vapor is the azeotropic composition. Azeotropes always boil either lower or higher than any of the components composing the azeotrope or any other mixture of the components if the azeotrope contains more than two components. An azeotrope that boils lower is called a minimum boiling azeotrope and one that boils higher is called a maximum boiling azeotrope. Minimum boiling azeotropes are by far the more common. If the liquids making up the constant boiling mixture are completely miscible the azeotrope is called a homogeneous azeotrope. If the liquid mixture has more than one phase the azeotrope is termed heterogeneous. It is worth mentioning that when any binary mixture having two liquid phases is distilled the vapor will be of constant composition and a minimum azeotrope will exist as long as the two liquid phases are present.

The exact azeotropic composition doesn't have to be present in the liquid mixture for the azeotrope to form. For instance ethyl acetate and methanol form a minimum boiling azeotrope containing 44 weight per cent methanol at atmospheric pressure (4). A mixture containing more than 44 weight per cent methanol can be separated into the azeotrope and the excess methanol. If the mixture were rectified the first vapor coming off would contain the azeotropic composition (provided enough plates were present). This azeotrope would continue to come off at its boiling point until all the ethyl acetate was gone. At this point the azeotrope would be gone and methanol, which would be the only thing left, would start distilling off. In other words, as was stated before, the azeotrope acts as a single compound with its own boiling point. As such it can be separated from other compounds or azeotropes by distillation if the boiling point spread is sufficient. This is the principle of azeotropic distillation.

If it were desired to obtain a better degree of separation between 3-methylpentane and hexene-1 than is possible by ordinary rectification, a third component could be added to the mixture which would form a minimum azeotrope with one or both of the compounds. The lower boiling azeotrope could then be distilled off. If the relative volatility between the azeotrope and the other compound or azeotrope was greater than the original relative volatility the separation by rectification would be easier and would require fewer theoretical plates. The third compound that is added is called an azeotropic entrainer. It is designated a selective entrainer if it forms an azeotrope with only one of the compounds. It is called a non-selective entrainer if it forms an azeotrope with both the compounds to be separated. An entrainer will most likely be non-selective if the compounds to be separated are of similar chemical structure. The paraffins and the olefins used in this investigation differed by little more than a double bond. As was expected, no selective entrainers were found and the study was confined to non-selective ones.

Also, azeotropic distillation introduces the problem of separating the entrainer from the other compound in the azeotrope once the azeotrope has been distilled over. This problem has several avenues of approach (7), but they will not be discussed here as the evaluation of entrainers regarding their ability to enhance separation of the compounds previously mentioned was the basic purpose of this investigation, The problem could not be overlookd in an industrial application, of course.

In determining the worth of an entrainer as an agent in separating the three pairs of compounds being used, a quantity known as the relative volatility was used. "The term volatility is commonly used in a broad sense to refer to ease or difficulty of evaporation or vaporization of substances," (6). For use in distillation the volatility of a substance in a liquid mixture is defined as its partil vapor pressure divided by the mole fraction in the liquid. The relative volatility of two compounds is simply the ratio of their volatilities. The larger volatility is usually put in the numerator so that the ratio is greater than one. If Dalton's law applies, the relative volatility may be written as

$$\alpha_{1-2} = \frac{y_1}{y_2}\frac{x_2}{x_1} \qquad (1)$$

where α_{1-2} = relative volatility

y_1, y_2 = mole fractions of compounds 1 and 2 in the vapor

x_1, x_2 = mole fractions of compounds 1 and 2 in the liquid.

When the relative volatility of the two compounds is equal to unity no separation is possible because both compounds have the same tendency to vaporize. If the relative volatility is extremely close to unity very little difference in composition between the liquid and the vapor will be present at equilibrium and the compounds will be very hard to separate. Thus, the larger the relative volatility of two compounds, the easier they are to separate by distillation. Entrainers in this study were evaluated by comparing the relative volatilities of the pure components to the relative volatilities with the entrainer added. In a rectification column, if the vapor-liquid equilibrium follows the relative volatility relation mentioned above and the relative volatility is approximately constant over each plate the following relationship can be derived, (6):

$$\alpha_{AB}^{n+1} = \frac{y_A}{y_B} \frac{x_B}{x_A} \qquad (2)$$

where n = the number of theoretical plates in the column

x_A, x_B = the mole fractions of A and B in the stillpot

y_A, y_B = the mole fractions of A and B in the overhead

The exponent $n + 1$ is used where separation equal to one theoretical plate is obtained between the stillpot and the base of the column. Equation (2) is known as the Fenske Equation.

Analysis of overhead and bottoms samples was accomplished using a gas chromatograph. Peak area per cents were used in the analysis as almost completely separate peaks were obtained for each compound with the chromatograph column being used. This method is explained in the Experimental Procedure section. A detailed discussion of chromatographic analysis and how the gas chromatograph operates is given in Wilkinson (7) and Nelson (5).

RESEARCH OBJECTIVES

The objective of this investigation was to look into the possibility of separating close-boiling paraffins and olefins by azeotropic distillation. A comparison of the relative volatility between the paraffin and olefin using azeotropic distillation to that using straight rectification was the basis for the evaluation of various compounds as azeotropic entrainers.

CHOICE OF ENTRAINERS

The formation of an azeotrope depends upon two factors: (a) the magnitude of the deviations from Raoult's Law in the mixture and (b) the difference in boiling point between the two pure components. The closer the boiling point of the two components, the smaller the deviations from Raoult's Law must be for an azeotrope to form. If an azeotrope is formed, positive deviations from Raoult's Law give a minimum boiling azeotrope and negative deviations give a maximum boiling azeotrope. The deviations from Raoult's Law in a mixture can be attributed to the effects of hydrogen bonds or internal pressures (1).

Berg (1) has classified liquids into five groups and has given a systematic summary of the type of deviations from Raoult's Law that can be expected when liquids from any two of these groups are mixed. Hydrocarbons such as those used in this study fall into a group which, unless an ideal solution is formed, always give positive deviations when mixed with liquids from their own or any other group. Compounds containing oxygen, nitrogen, or halogen atoms such as alcohols, acids, amines, esters, halogenated hydrocarbons and so forth are likely to form solutions with hydrocarbons which have large positive deviations from Raoult's Law.

Thus, compounds chosen as possible entrainers were those of the types just mentioned that boiled close to the hydrocarbons whose separation was being attempted. Compounds boiling within about ± 20°C of the hydrocarbons were selected. In some cases compounds fit the above two criteria but were not used because of unusual expense.

The compounds evaluated as azeotropic entrainers are as follows:

acetone	methyl ethyl ketone
methanol	propylene oxide
ethanol	vinyl acetate
methyl acetate	ethylene dichloride
chloroform	n-butyl chloride
ethyl formate	tert-butanol
2-methylfuran	dihydropyran
methylene chloride	methyl formate
1,1-dichloroethane	Freon 113*
tetrahydrofuran	ethyl ether
isopropanol	isopropyl ether
ethyl acetate	methylal
isopropyl acetate	furan
n-propyl formate	isopropyl amine
diethyl amine	

* 1,1,2-trichloro-1,2,2-trifluoroethane

EQUIPMENT

The main equipment used in this study is as follows:

1. four batch rectification columns

2. one #A-90C Aerograph gas chromatograph with thermal conductivity detector.

3. one Ohaus triple-beam balance

4. one #1013 Valentine refractometer

5. one #AB-2 Christian Becker Chainomatic balance

6. one #620005 Keuffel and Esser Compensating Polar Planimeter

The four rectification columns were equipped with cold finger condensing heads and electric stillpot heaters. The columns were identical, each made from three concentric glass cylinders which were 48 inches long. The cylinders had diameters of 1.0, 1.75, and 2.5 inches and the inside cylinder was packed with 46 inches of 1/8" stainless steel helices (Fenske rings). Stillpots were two-liter round-bottom flasks with thermowells and side-arms for taking samples. A diagram of such a column is shown in Figure 1. and a further description is given in Nelson (5). It should be noted that the condensers used were of the cold finger type which do not allow the setting of definite reflux ratios, but this was not needed as will be explained.

A Valentine refractometer was used for determining azeotropic compositions by means of graphs plotting weight per cent versus refractive index. A constant temperature bath maintained the

the refractometer prisms at 20 ± .3°C. The Christian Becker balance was used to weigh up known weight per cent solutions used to make the refractive index curves.

The Ohaus triple-beam balance was used for weighing the charges boiled up in the columns.

The Aerograph chromatograph was used to analyze overhead and bottoms samples from the rectification columns when relative volatilities were being determined. A Keuffel and Esser Compensating Polar Planimeter was used to measure peak areas in the analysis. Two chromatograph columns were used. The one used for determining relative volatilities was a 1/4-inch stainless steel tube, 7 feet in length containing 30-60 mesh C-22 firebrick as the solid support and oxydipropinitrile as the stationary phase. In a few cases where the refractive indices of the entrainer and one of the hydrocarbons were too close together, azeotropic compositions were determined using the chromatograph. In these cases an Aerograph GE, SF-96, silicone column was used. The chromatographic peaks were recorded on a Sargent recorder.

EXPERIMENTAL PROCEDURE

The first step in the evaluation of an entrainer was to determine whether it formed an azeotrope with a particular paraffin or olefin. This was done merely by noting the boiling point when a random mixture of the entrainer and hydrocarbon were boiled in one of the rectification columns. If the boiling point was less than that of either component an azeotrope was assumed to have been formed. When this was the case the charge was allowed to boil for an hour at total reflux and at this time the refractive indices of overhead and bottoms samples were taken for use in the next step.

The next step was determination of the azeotropic composition. If the refractive indices of the entrainer and the hydrocarbon were far enough apart, samples were weighed, refractive indices determined, and a plot made of composition versus refractive index. From its refractive index the composition of the overhead sample previously taken was determined and a charge of this composition was put in the stillpot and distilled for an hour at total reflux. Overhead and bottoms samples were then taken and their compositions determined to see if they were the same since the liquid and vapor compositions for an azeotrope are identical. If the per cent entrainer in the overhead was within four of the per cent entrainer in the bottoms the overhead composition was taken as the azeotropic composition. If this was not the case the still pot composition was adjusted to be the same as the overhead composition just determined and the procedure was then repeated as many times as was necessary to get the overhead and bottoms compositions to agree with each other.

In some cases the refractive indices of the entrainer and a particular paraffin or olefin were so close that it was impossible to make a refractive index versus composition plot. This was true in the case of tetrahydrofuran, isopropanol, and tert-butanol. Chromatographic analysis was used to determine the azeotropic compositions for these compounds. Plots were prepared of peak height per cent versus actual weight per cent entrainer by use of samples of known composition which had been weighed out. These plots were used with the chromatograph to analyze overhead and bottoms samples. The Aerograph GE,SF-96 silicone column was chosen because it gave short retention times and sharp peaks for the entrainers as well as the paraffins and olefins. The column was operated at 70°C with a helium flow rate of 62.5 ml/min and a chart speed of 2"/min.

Once the azeotropic compositions had been determind relative volatility runs could be made. A charge was made up by first weighing the correct amounts of material to give the azeotropic composition of the more volatile component with the entrainer. An amount of the less volatile component, equal by weight to the more volatile component, was then added. Every time a charge was made up enough material for two charges was weighed and then split into equal volumes. Duplicate runs were made for every relative volatility determination and the two charges were in this way assured of being of exactly the same composition. Each charge was boiled and after two or three milliliters of material was drawn off the top to get rid of trace impurities the charge was allowed to distill at total reflux for at least two and one half hours. Overhead and bottoms samples were then taken. Since a column was operated at total reflux except when a sample was being taken or material drawn off to stabilize the temperature the cold finger condensers used were adequate.

Overhead and bottoms samples were analyzed with the chromatograph using the oxydipropinitrile column. This column was chosen because (1) it gave short retention times for the hydrocarbons, (2) it gave almost complete resolution between the paraffin and olefin peaks, and (3) it gave long retention times for the compounds being evaluated as entrainers. There was never any trouble with an entrainer peak falling on top of the peak of one of the paraffins or olefins using this column. The column did not give complete resolution of the hydrocarbon peaks but it was so close that the tails of the peaks were merely drawn in for purposes of area measurement. A typical chromatogram is shown in Figure 2. The column was operated at 70°C with a helium flow rate of 12.5 ml/min and a chart speed of 1"/min. Analysis was performed by running samples of known composition through the chromatograph and measuring the areas of the peaks obtained. Plots were then prepared of the area per cent of a particular compound versus its actual weight per cent in the sample. The data for these plots is given in Table VIII. When an overhead or bottoms sample containing, say, 3-methylpentane, hexene-1, and some entrainer was shot into the chromatograph, the areas of the resulting 3-methylpentane and hexene-1 peaks were measured, and the per cent of the total area contained in the 3-methylpentane peak determined. The weight per cent 3-methylpentane in the sample could then be obtained from the plot previously prepared. Note that the entrainer would also give a peak but its area was not measured. Thus, the value obtained for the weight per cent 3-methylpentane would not be the actual weight per cent but only the amount of 3-methylpentane relative to the total amount of 3-methylpentane and hexene-1 on an entrainer free basis. This difficulty was of no consequence as will be explained.

After the overhead and bottoms samples were analyzed relative volatilities were determined using the Fenske equation. This equation can be written:

$$\alpha_{AB}^{n+1} = \frac{Y_A / Y_B}{X_A / X_B}$$

Upon examining the numerator of this equation it can be seen that it is a ratio of mole fractions. The same holds true for the denominator. The ratios are just expressions of the amount of compound A relative to compound B in the overhead and bottoms. These were the quantities found in the chromatographic analysis as stated above. The total moles in a sample did not have to be known because this term cancels when the ratio is taken. Likewise, the mole fractions could just as well be weight fractions because all units cancel when the numerator is divided by the denominator.

DISCUSSION OF RESULTS

The boiling points of 3-methylpentane, hexene-1, 2-ethyl-1-butene and n-hexane at 640 mm were found to be 56.8, 57.2, 59.0, and 62.8°C, respectively.

Of the twenty-nine chemicals tested as possible entrainers, thirteen formed azeotropes with the compounds being separated. All of these were non-selective entrainers. For all of these compounds except two the azeotropic compositions were determined for the entrainer with 3-methylpentane, hexene-1, and 2-ethyl-1-butene. A list of entrainers with their azeotropic compositions is given in Tables II, III, and IV. In the case of methylene chloride the azeotropic compositions were not determined exactly because of the difficulty of telling whether an azeotrope had formed or the mixture in the overhead was just the result of the inability of the column to separate the components completely. In the case of ethyl acetate the refractive indices of this chemical and the hydrocarbons were too close for analysis by refractive index and its retention time was too close to the hydrocarbons to make analysis using the chromatograph possible.

When furan, n-propyl formate, propylene oxide, and vinyl acetate were refluxed to determine their boiling point at the prevailing pressure it was found that the overhead temperatures did not stabilize but continued to rise steadily well past even the normal boiling points. This indicated that some kind of polymerization or break down was taking place and the compounds could not be evaluated further.

No literature values were available with which to compare the azeotropic compositions determined when using entrainers and 3-methylpentane, hexene-1, and 2-ethyl-1-butene. Two azeotropic compositions were determined between n-hexane and entrainers. The values of 23.3 and 54.5 wt. % n-hexane with chloroform and acetone, respectively, agree fairly well with the literature values (4) of 28% and 46.5% when the difference in pressure is taken into account (literature values were at 760 mm while experimental values were determined at 640 mm). It is unfortunate that an absolute comparison with literature values cannot be made. The calibration curves that were prepared for refractometer and chromatograph analysis were in all cases smooth curves requiring little judgement by the investigator in connecting the data points. For this reason it is felt that an error of no more than 1% is present in the azeotropic composition values.

In making up the chromatograph calibration curves of area per cent versus actual per cent for the anlysis of relative volatility runs it was found that the curves were almost straight lines. In fact the largest difference found between an area per cent and the actual weight per cent was 1.9 per cent (see Table VIII). Thus, very little error would have resulted even if the area per cents had been used directly. An error of about .003 in the value of α would be caused if both the overhead and bottoms compositions were one weight per cent in error.

The four columns used had 22, 25, 26, and 28 theoretical plates as calculated using the McCabe-Thiele method and a test mixture of methylcyclohexane and toluene. Several factors could change the number of theoretical plates in a column. A change of one theoretical plate would cause an error of about .001 in the value of the relative volatility. It was felt that in this particular investigation differences in boil-up rate may have been the largest single cause of error. This is because the compounds being worked with were very volatile and the boil-up rate could be varied quite a bit with a small change in the heat being supplied to the column. The high volatilities also made it hard to store samples without a change in composition.

In all cases duplicate relative volatility runs were made and these values are tabulated in Table V, VI, and VII. For all except two the duplicate runs were within .010 of each other. In the 3-methylpentane, hexene-1 system the values using tetrahydrofuran and 2-methylfuran differed by .013 and .014, respectively. Since it could be seen that these entrainers were not among the best possible entrainers used for this system no more runs were made to get better agreement.

Using the average of the duplicate runs an analysis can be made of how much the various entrainers enhance the separation of the three pairs of compounds. The relative volatility of 3-methylpentane to hexene-1 was found to be 1.009. Using the Fenske equation shows that to effect 95% separation of the two compounds would require 657 theoretical plates. Use of methyl acetate increased the relative volatility to an average 1.103 and reduced the theoretical plate requirement to 78. Use of acetone and ethyl formate gave average relative volatilities of 1.100 and 1.097. Thus, all three entrainers would give just about the same separation. Methylene chloride gave the most improvement in relative volatility at 1.159 and a theoretical plate requirement of 39. However, the azeotropic composition is only 10.3% 3-methylpentane which will undoubtedly make it of little commercial interest.

The relative volatility of 3-methylpentane to 2-ethyl-1-butene was found to be 1.037 which means 161 plates would be required to get 95% separation. In this case ethyl formate increased the relative volatility to 1.156 and reduced the theoretical plate requirement to 40. Acetone, chloroform, and methyl acetate gave values of 1.149, 1.141, and 1.142, respectively, for the relative volatility. Theoretical plates required for 95% separation would be 43, 44, and 44. In the case of methylene chloride the separation was so good that a peak was not even obtained for the 2-ethyl-1-butene when the overhead sample was analyzed. To obtain a value for the relative volatility a shorter sixteen plate column was tried. Even though a peak was obtained this time, it was so small that the analysis was impossible. Here again methylene chloride would probably be of no interest because the azeotropic composition is 89.7% methylene chloride (10.3% 3-methylpentane). For this reason building an even shorter column to get a value for the relative volatility was not considered.

The 2-ethyl-1-butene, n-hexane system was different from the other two because all the entrainers gave relative volatilities that were less than the 1.056 value obtained using no entrainer. Acetone, chloroform, 2-methylfuran, isopropanol and ethyl formate actually reversed the volatilities and made n-hexane the more volatile of the two as indicated by the relative volatility values of less than unity. For acetone and chloroform the runs were repeated with the stillpot charges containing the azeotropic compositions of entrainer with n-hexane. Values of 1.046 and 1.094 were obtained this time for acetone and chloroform, respectively. Chloroform and possibly ethyl formate which was not tried again because of lack of material were the only entrainers that looked like they would improve the relative volatility. Chloroform would reduce the theoretical plates required for 95% separation from 107 to 64. The chloroform, n-hexane azeotrope contains 76.5% chloroform which would make it of doubtful commercial interest.

It should be remembered that the Fenske equation is derived for a total reflux situation and the theoretical plate values given above are the minimum limit of what would be required at a finite reflux ratio.

It was thought that perhaps there was a correlation between the azeotropic composition and the particular hydrocarbon being used. For instance, maybe the per cent 3-methylpentane in an azeotrope with a given entrainer would always be greater than the per cent hexene-1 in an azeotrope with the same entrainer. Examination of Tables II, III, and IV shows no such correlation.

As already noted by Wilkinson (7) and Nelson (5) there appears to be no correlation of relative volatility with the boiling points of entrainers.

CONCLUSIONS

It is possible to separate 3-methylpentane from hexene-1, 3-methylpentane from 2-ethyl-1-butene, and 2-ethyl-1-butene from n-hexane by azeotropic distillation using fewer theoretical plates than is required using straight distillation. Economic factors would determine which entrainers would be best in a particular case and whether azeotropic distillation would be commercially feasible.

SAMPLE CALCULATIONS

Relative volatility calculation-

For 2-ethyl-1-butene, n-hexane, tert-butanol system; run 1:

$$\alpha_{AB}^{n+1} = \frac{y_A \; x_B}{y_B \; x_A}$$

y_A & y_B = mole per cent* 2-ethyl-1-butene and n-hexane in overhead

x_A & x_B = mole per cent 2-ethyl-1butene and n-hexane in bottoms

n = number of theoretical plates

$y_A = 69.1$

$y_B = 30.9$

$x_A = 45.5$

$x_B = 54.5$

$n + 1 = 25$

$$\alpha_{AB}^{n+1} = \frac{(69.1)(54.5)}{(30.9)(45.5)} = 2.68$$

$25 \log \alpha = .42813$

$\log \alpha = .0171$

$\alpha = 1.040$

*weight % can be used instead of mole % as explained in Experimental Procedure

Sample Calculations (continued)

Calculation of the number of theoretical plates required to give 95% separation of 2-ethyl-1-butene and n-hexane:

using no entrainer-

$$1.056^{\,n+1} = \frac{(95)(95)}{(5)(5)} = 361$$

$$n + 1 = \frac{\log 361}{\log 1.056} = 108$$

$$n = 107$$

using chloroform as an entrainer-

$$1.094^{\,n+1} = 361$$

$$n + 1 = 65$$

$$n = 64$$

APPENDIX

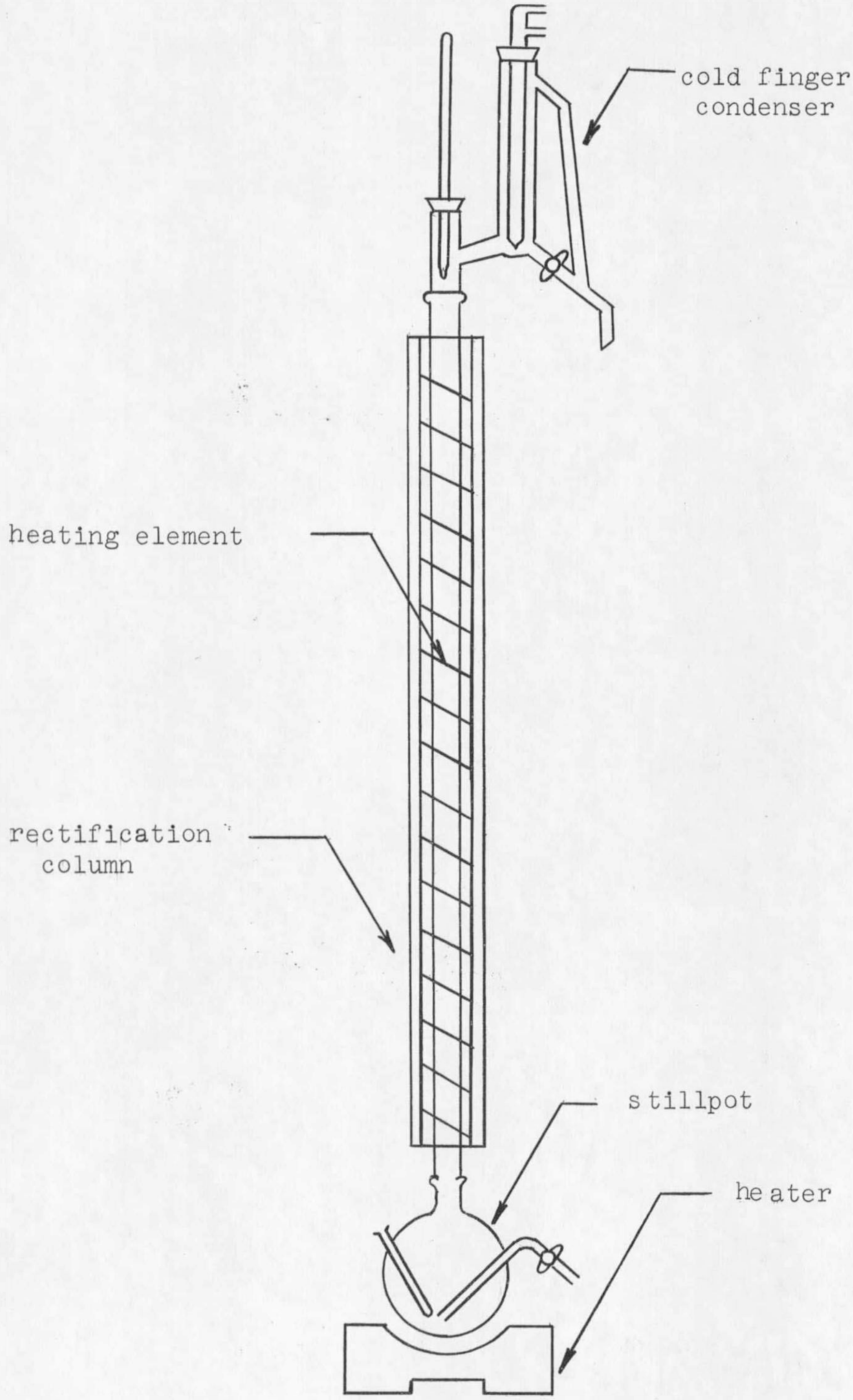

Figure 1 - Rectification Apparatus

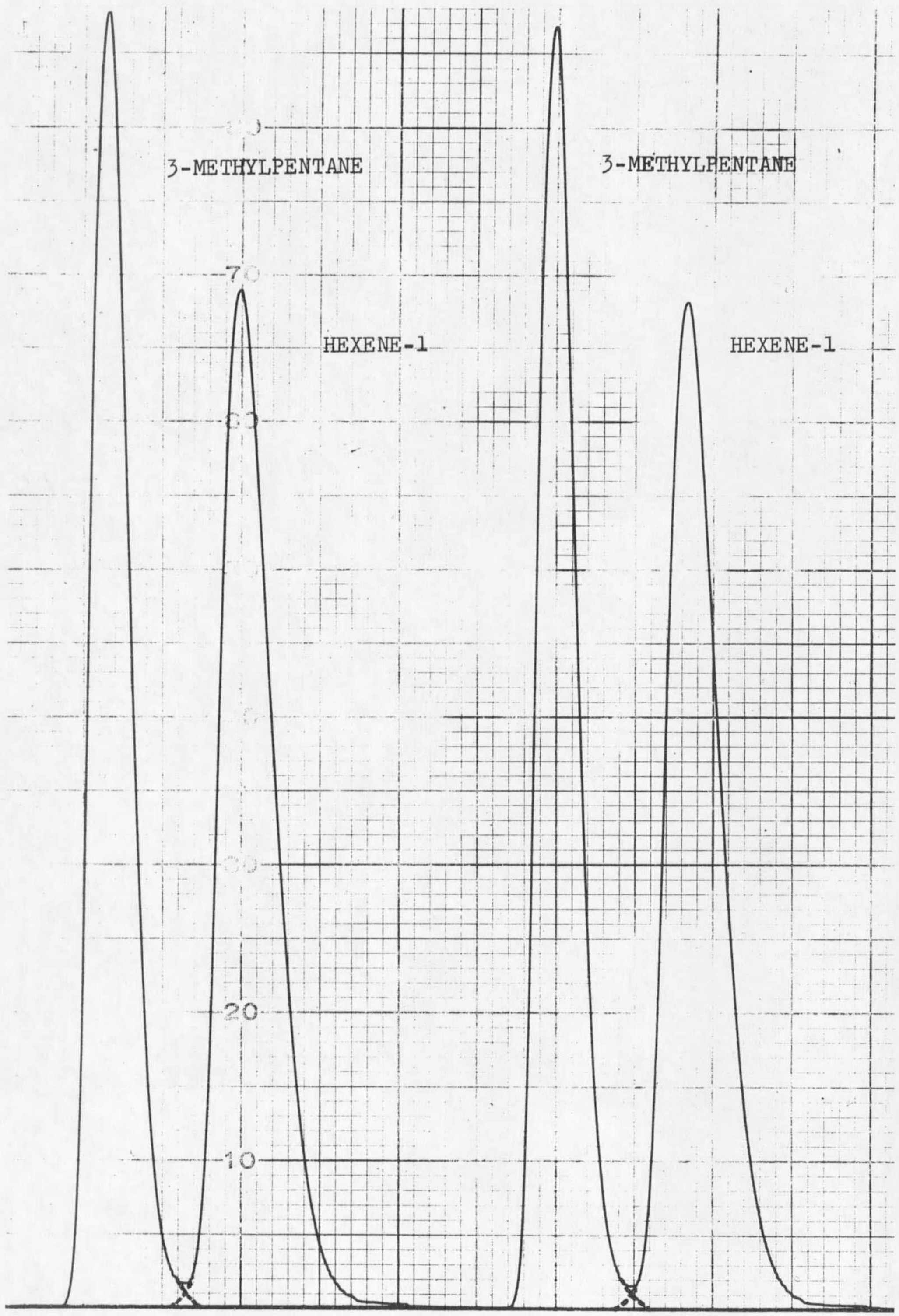

FIGURE 2- TYPICAL CHROMATOGRAM FOR DETERMINING
RELATIVE VOLATILITIES

TABLE I

STRUCTURES AND BOILING POINTS OF ENTRAINERS

ENTRAINER	STRUCTURE	BOILING POINT (635-640 mm Hg)
acetone	CH_3COCH_3	50.8 °C
methanol	CH_3OH	60.5
ethanol	CH_3CH_2OH	73.1
methyl acetate	CH_3COOCH_3	51.4
chloroform	$CHCl_3$	55.4
ethyl formate	$HCOOC_2H_5$	48.1
2-methylfuran	$\underline{CH:CHCH:C(CH_3)O}$	58.7
methylene chloride	CH_2Cl_2	35.4
1,1-dichloroethane	CH_3CHCl_2	51.9
tetrahydrofuran	$\underline{OCH_2CH_2CH_2CH_2}$	59.5
isopropyl alcohol	$CH_3CHOHCH_3$	76.6
ethyl acetate	$CH_3COOC_2H_5$	71.1
methylal	$CH_2(OCH_3)_2$	37.4
ethyl ether	$C_2H_5OC_2H_5$	29.3
isopropyl ether	$(CH_3)_2CHOCH(CH_3)_2$	63.2
isopropyl acetate	$CH_3COOCH(CH_3)_2$	82.5
isopropyl amine	$(CH_3)_2CHNH_2$	28.0
diethyl amine	$(C_2H_5)_2NH$	50.8
methyl ethyl ketone	$CH_3COC_2H_5$	75.5
ethylene dichloride	CH_2ClCH_2Cl	77.7

TABLE I. (continued)

ENTRAINER	STRUCTURE	BOILING POINT (635-640 mm Hg)
n-butyl chloride	$CH_3(CH_2)_2CH_2Cl$	71.7 °C
tert-butanol	$(CH_3)_3COH$	54.4
Freon 113*	CCl_2FCClF_2	42.2
dihydropyran	$OCH_2CH_2CH_2CHCH$	79.0
furan**	$OCH{:}CHCH{:}CH$	---
n-propyl formate**	$HCOOCH(CH_3)_2$	---
propylene oxide**	OCH_2CHCH_3	---
vinyl acetate**	$CH_3COOCHCH_2$	---

*1,1,2-trichloro-1,2,2-trifluoroethane

**boiling point not determined, see Discussion of Results

TABLE II

AZEOTROPIC COMPOSITIONS
(ENTRAINER WITH 3-METHYLPENTANE)

ENTRAINER	AZEOTROPIC B.P.	COMPOSITION (wt.% 3-methylpentane)
acetone	42.0 °C	55.0
methanol	42.7	75.7
ethanol	49.4	82.0
methyl acetate	44.7	57.8
chloroform	53.0	33.2
ethyl formate	42.8	40.5
2-methylfuran	54.1	54.5
methylene chloride	35.1	10.3
1,1-dichloroethane	50.4	27.3
tetrahydrofuran	53.8	55.1
isopropanol	53.0	84.1
tert-butanol	54.4	85.5

TABLE III

AZEOTROPIC COMPOSITIONS
(ENTRAINER WITH HEXENE-1)

ENTRAINER	AZEOTROPIC B.P.	COMPOSITION (wt.% hexene-1)
acetone	43.5°C	49.25
methanol	43.0	79.3
ethanol	50.6	80.9
methyl acetate	47.1	45.5
chloroform	55.4	21.7
ethyl formate	44.4	36.0
2-methyl furan	56.3	49.9
methylene chloride	less than 10% hexene-1	
1,1-dichloroethane	50.5	20.3
tetrahydrofuran	56.8	39.3
isopropanol	53.4	84.5
tert-butanol	55.8	81.5

TABLE IV

AZEOTROPIC COMPOSITIONS
(ENTRAINER WITH 2-ETHYL-1-BUTENE)

ENTRAINER	AZEOTROPIC B.P.	COMPOSITION (wt.% 2-ethyl-1-butene)
acetone	55.4°C	46.2
methanol	44.1	79.3
ethanol	51.7	80.25
methyl acetate	47.9	40.0
chloroform	55.2	15.8
ethyl formate	45.3	34.5
2-methylfuran	56.4	51.5
methylene chloride	less than 10% 2-ethyl-1-butene	
1,1-dichloroethane	51.2	19.3
tetrahydrofuran	57.1	62.5
isopropanol	54.9	84.2
tert-butanol	57.1	85.2

TABLE V

RELATIVE VOLATILITIES, α_{AB}
(A) = 3-METHYLPENTANE, (B) = HEXENE-1

ENTRAINER	RELATIVE VOLATILITY	
	RUN 1	RUN 2
none	1.009	1.009
acetone	1.095	1.099
methanol	1.047	1.043
methyl acetate	1.102	1.104
1,1-dichloroethane	1.072	1.070
chloroform	1.083	1.086
2-methylfuran	1.042	1.056
methylene chloride	1.155	1.163
tetrahydrofuran	1.047	1.060
isopropanol	1.023	1.023
tert-butanol	1.018	1.018
ethyl formate	1.096	1.104
ethanol	1.033	1.033

TABLE VI

RELATIVE VOLATILITIES, α_{AB}

(A) = 3-METHYLPENTANE, (B) = 2-ETHYL-1-BUTENE

ENTRAINER	RELATIVE VOLATILITY	
	RUN 1	RUN 2
none	1.034	1.040
acetone	1.144	1.153
methanol	1.072	1.080
methyl acetate	1.144	1.139
1,1-dichloroethane	1.125	1.133
chloroform	1.141	1.140
2-methylfuran	1.086	1.079
methylene chloride*	--	--
tetrahydrofuran	1.083	1.076
isopropanol	1.068	1.059
tert-butanol	1.049	1.052
ethyl formate	1.159	1.153
ethanol	1.059	1.062

*could not analyze

TABLE VII

RELATIVE VOLATILITIES, α_{AB}, α_{BA}

(A) = 2-ETHYL-1-BUTENE, (B) = N-HEXANE

ENTRAINER	RELATIVE VOLATILITY RUN 1	RUN 2
α_{AB}		
none	1.054	1.058
acetone	.954	.957
methanol	1.017	1.017
methyl acetate	1.047	1.049
1,1-dichloroethane	.948	.953
chloroform	.923	.916
2-methylfuran	1.0004	1.0005
tetrahydrofuran	1.009	1.019
isopropanol	.968	.967
tert-butanol	1.040	1.036
ethanol	1.030	1.037
ethyl formate	.945	.935
methylene chloride	--	--
α_{BA}		
acetone*	1.045	1.046
chloroform*	1.094	1.094

*reruns using a still pot charge containing the azeotropic composition of entrainer with n-hexane; azeotropic compositions were 54.5 wt% n-hexane with acetone and 23.5 wt% n-hexane with chloroform; the azeotropic boiling points were 43.8 and 53.4°C, respectively, at 635-640 mm.

TABLE VIII

DATA FOR AREA PER CENT VERSUS ACTUAL WEIGHT PER CENT CURVES USED IN CHROMATOGRAPHIC ANALYSIS

AREA PER CENT 3-METHYLPENTANE WITH HEXENE-1	ACTUAL WEIGHT PER CENT 3-METHYLPENTANE
19.0	19.6
38.3	39.2
57.6	58.8
79.6	80.7
AREA PER CENT 3-METHYLPENTANE WITH 2-ETHYL-1-BUTENE	**ACTUAL WEIGHT PER CENT 3-METHYLPENTANE**
11.7	9.8
22.3	19.9
40.2	39.9
60.3	60.6
89.3	89.8
AREA PER CENT 2-ETHYL-1-BUTENE WITH N-HEXANE	**ACTUAL WEIGHT PER CENT 2-ETHYL-1-BUTENE**
20.0	20.7
38.1	39.4
58.2	59.4
75.1	76.3

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