Azeotropic separation of certain paraffins and naphthenes
by Stanford Vaughn Buckland

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:
The objective of this project was to study the application of azeotropic distillation to the separation of close-boiling paraffinic compounds from naphthenic compounds. This study was based on the improvement in relative volatility at a 50% composition for the hydrocarbon pairs: neohexane-cyclopentane, 2,4-dimethylpentane- cyclohexane, and isooctane-methylcyclohexane. The relative volatilities for these pairs are 1.006, 1.006, and 1.047 respectively.

The major items of equipment employed were two packed batch distillation columns (22 and 25 theoretical plates), a refractometer, and a gas chromatograph.

Various compounds, generally alcohols, amines, and acids, boiling within 20°C. of the hydrocarbon pairs, were evaluated for minimum boiling azeotropes. This was done by mixing the compound with the more volatile hydrocarbon to ascertain if the mixture boiled at a temperature lower than either of the two pure components. Once an azeotrope had been established, its composition was found by adjusting the charge to the overhead composition until the two agreed to within five percent of one another.

The effect on relative volatility was determined by adding the other hydrocarbon to give a 50% hydrocarbon mixture and by sampling overhead and bottoms after equilibrium had been established at total reflux. Relative volatilities were calculated by use of the Fenske equation.

The five entrainers tested for the cyclopentane-neohexane pair showed little effect on relative volatility.

Of the twelve entrainers tested with 2, 4-dimethylpentane-cyclohexane, five had no effect on relative volatility while the remainder showed some increase, the maximum being 1,026 using acetone.

The fifteen entrainers tested with isooctane-methylcyclohexane gave seven that increased the relative volatility, six that had no effect, and two that decreased it. The highest values were 1.083, using ethanol and 1, 4-dioxane No apparent coorelation was evident between the structure, boiling point, azeotropic composition, or functional character and their effect on relative volatility.

AZEOTROPIC SEPARATION OF CERTAIN PARAFFINS AND NAPHTHENES

by

STANFORD VAUGHN BUCKLAND

A thesis submitted to the Graduate Faculty in partial
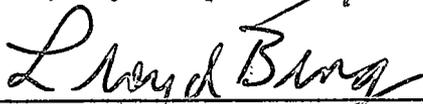fulfillment of the requirements for the degree
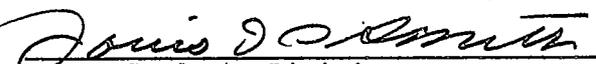
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Dean, Graduate Division

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ABSTRACT

The objective of this project was to study the application of azeotropic distillation to the separation of close-boiling paraffinic compounds from naphthenic compounds. This study was based on the improvement in relative volatility at a 50% composition for the hydrocarbon pairs: neohexane-cyclopentane, 2,4-dimethylpentane-cyclohexane, and isooctane-methylcyclohexane. The relative volatilities for these pairs are 1.006, 1.006, and 1.047 respectively.

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No apparent coorelation was evident between the structure, boiling point, azeotropic composition, or functional character and their effect on relative volatility.

INTRODUCTION AND THEORY

The objective of this project was to study the application of azeotropic distillation to the separation of certain paraffins from close boiling naphthenes. The paraffin-naphthene pairs studied were: neohexane-cyclopentane, 2,4-dimethylpentane-cyclohexane, and isooctane-methylcyclohexane.

A. Background

The separation of close-boiling paraffinic and naphthenic constituents of complex crude petroleum is a difficult problem. Since these compounds are valuable materials in the oil and petro-chemical industries, an easy and inexpensive method of separation is desirable.

The method now employed to obtain these materials in their desired purity is to apply fractional crystallization or to synthesize them. Since the use of refrigeration and tall distillation columns involves considerable expense, methods of avoiding this are of considerable interest.

The use of azeotropic distillation has scarcely been considered as a possible method of reducing the number of theoretical plates necessary to separate the components and possibly to avoid the refrigeration step. Mair (7) studied the separation of isooctane-methylcyclohexane using azeotropic distillation and found that one of the perfluorocyclic ethers, such as $CF_2CF_2CF_2CF_2CF_2CFOCF_2CF_3$, gave good separation, using compositions as determined by refractive index. This

compound is not produced in commercial quantities and is thus likely
to be more expensive than using refrigeration methods.

B. Theory

Separation by distillation depends upon the relative tendencies
of the components to vaporize. The lowest boiling, or most volatile,
component will vaporize more readily and thus cause the vapors leaving
the liquid to be richer in the more volatile constituent.

A distillation column employs plates or packing that give a
better degree of separation. As the vapors pass up through a column,
they are continually condensed and revaporized, each time the vapors
being enriched in the more volatile constituent while the liquid is
becoming enriched in the least volatile compound. In general, the
height of the packed column, the geometry, and the packing determine
the number of plates which determines the degree of separation.

The simplest measure of the tendency to vaporize is its boiling
point. Compounds such as those selected for separation in this pro-
ject have boiling points differing by only a few tenths of a degree,
making it virtually impossible to separate them by straight distilla-
tion.

Another measure is 'relative volatility', which is defined as
the ratio of the compositions of the liquid and vapor phases in equil-
ibrium in a single stage.

$$\alpha_{AB} = \frac{\left(\dfrac{y_A}{x_A}\right)}{\left(\dfrac{y_B}{x_B}\right)} = \frac{y_A \; x_B}{y_B \; x_A}$$

where α_{AB} = the volatility of component A
relative to component B

y_A, y_B = mole (or weight) fraction of components
A and B in the vapor phase

x_A, x_B = mole (or weight) fraction of components
A and B in the liquid phase

Note that for a binary system, weight fraction can be used
instead of mole fraction since the molecular weights and total number
of moles in either the liquid or vapor phases would cancel each other.

Fenske (4) developed an equation defining the relationship
between the number of theoretical plates, n, the relative volatil-
ity, and the purity of the products:

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

Although this derivation has limitations of constant relative
volatility, total reflux, and incomplete separation, it can be con-
sidered good for the purposes of comparing the effect of various factors
on it. It should be emphasized that the relative volatility is not
necessarily constant for all compositions and that it also differs
with pressure changes (2).

C. Azeotropic Distillation

When certain compounds are mixed together, a constant boiling mixture of a certain binary or ternary composition occurs, i.e. the liquid and vapor equilibrium lines at this composition are identical. This mixture is referred to as an azeotrope, or constant boiling mixture. Thus the overall mixture would contain the azeotrope plus the component in excess. Only binary azeotropes were considered in this investigation.

Azeotropes are of several types: homogeneous or heterogeneous and maximum or minimum boiling azeotropes (1). Homogenous azeotropes occur in miscible compounds while heterogeneous azeotropes occur in immiscible liquids. Minimum boiling azeotropes boil at a temperature lower than either pure component and are the type considered in this investigation as they are more common and are generally more useful. Maximum boiling azeotropes occur when the mixture boils at a temperature higher than either of the two pure components. It might be mentioned that all heterogeneous, or two-phase, systems at the boiling point form minimum boiling azeotropes.

The minimum boiling azeotrope can then be separated from the other compounds, provided the boiling point is sufficiently different and the column is efficient enough. Distillation that involves the formation of constant boiling mixtures is defined as azeotropic distillation.

Thus, in a commercial operation, a third component called an entrainer is added to the two components to be separated. The entrainer will azeotrope with one, or both, of the constituents, depending on its selectivity. Compounds have been classified by Berg, Ewell, and Harrison (1) according to their azeotrope-forming capabilities. Since paraffinic and naphthenic compounds tend to form azeotropes with the same entrainers, it is likely that few selective entrainers exist.

Another factor that must be considered in this study is that azeotrope formation is dependent on pressure. Changes in pressure affect the azeotropic composition by changing the vapor-liquid equilibrium line, even to the point where an azeotrope no longer exists. No method is available for predicting this effect.

Horsley (6) presents the azeotropic compositions for over 14,000 binary systems at 760 mm. pressure. Since the atmospheric pressure is somewhat different (635 mm.) at this laboratory, compositions were determined at the existing pressure.

D. Analysis

In order to calculate the relative volatility, the compositions of the hydrocarbons in the overhead and bottoms samples were necessary. Analysis was done with the aid of a gas chromatograph. For a brief description of how this instrument operates, the reader is referred to Wilkinson (9).

Fortunately, relative peak heights could be used as a quantitative measure of the amount of each hydrocarbon present. Noebels (8) states that the relative magnitude of peak heights or areas is not affected by the presence of other components; the entrainer need not be removed from the hydrocarbon mixture before analysis except, of course, when the entrainer peak coincides with the hydrocarbon peak.

RESEARCH OBJECTIVES

The objective of this project was to study the application of azeotropic distillation to the separation of certain paraffinic compounds from close-boiling naphthenic compounds. This study was based on the improvement in relative volatility at a certain composition between the hydrocarbons using azeotropic distillation over that using straight distillation.

EQUIPMENT

The major equipment employed in this project consisted of a Valentine refractometer, two four-foot packed distillation columns, and a gas chromatagraph.

A refractometer with a constant temperature water bath maintained at 20°C. was used to determine refractive indices.

Weights were determined by a triple-beam balance.

Two identical distillation columns were used throughout the project, one with 22 theoretical plates and the other with 25 theoretical plates. Both were one-inch diameter columns packed to a bed height of 48 inches with 1/8-in. stainless steel Fenske rings. Cold-finger condenser heads were used since the columns were run at total reflux. Adiabatic conditions were maintained by a nichrome wire wrapping. Figure 1, page 9 gives a detailed schematic drawing of the apparatus.

Sample analysis was done using an Aerograph gas chromatograph equipped with a Minneapolis-Honeywell recorder. The 1/4-inch, 5-foot chromatograph column was an Aerograph Silicone GE-SF (high methyl) column.
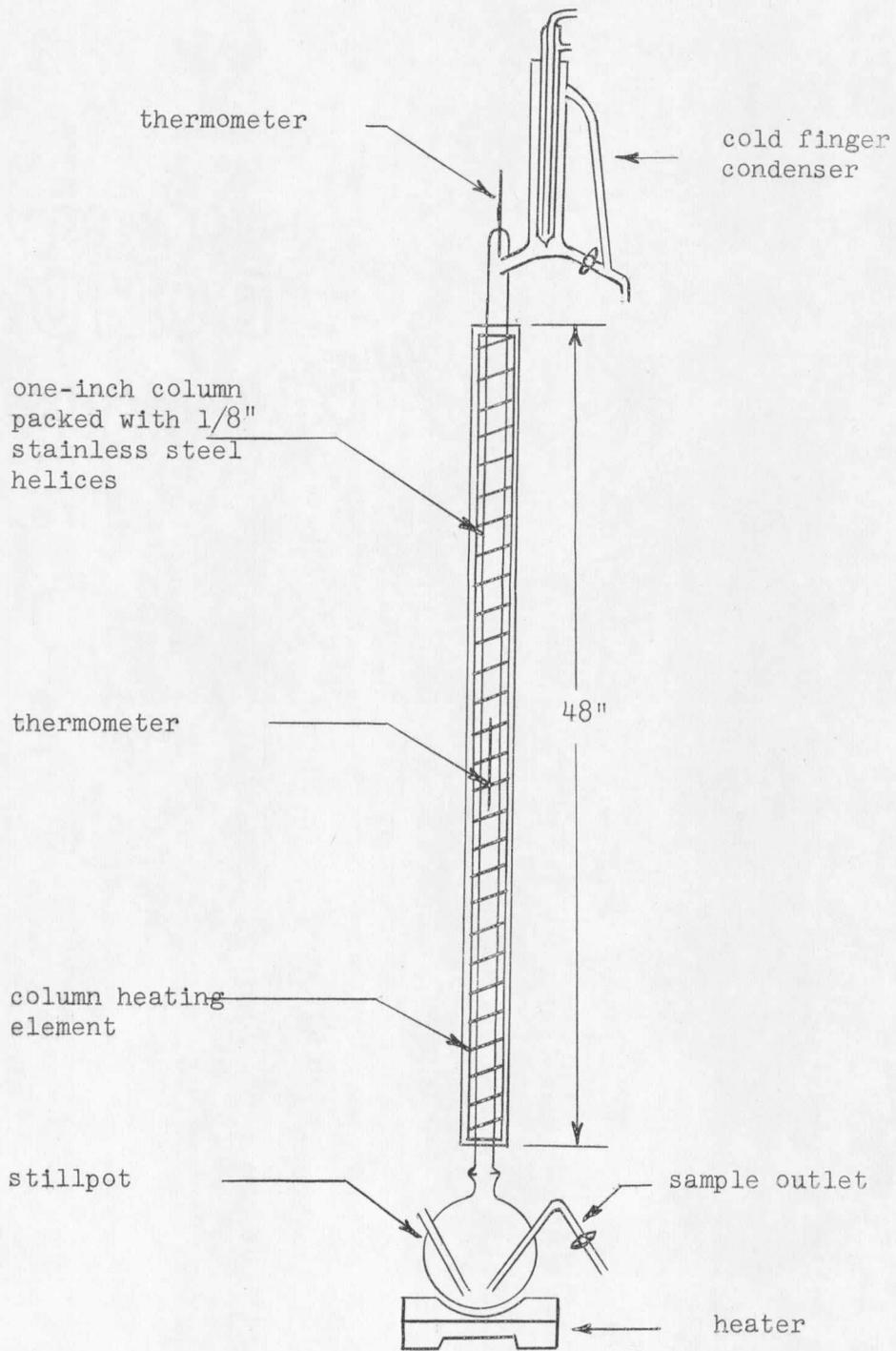
thermometer

cold finger
condenser

one-inch column
packed with 1/8"
stainless steel
helices

thermometer

48"

column heating
element

stillpot

sample outlet

heater

Figure 1: Schematic diagram of distillation apparatus

EXPERIMENTAL PROCEDURE

The overall experimental procedure consisted of three main parts: initial entrainer evaluation, composition determination, and relative volatility tests.

Close-boiling paraffins and naphthenes were selected from Doss (3) as the compounds to be separated. Three pairs of hydrocarbons were selected representing three different boiling-point ranges (760 mm):

(1)	cyclopentane	49.5°C
	2,2-dimethylbutane (neohexane)	49.7
(2)	2,4-dimethylpentane (2,4-DMP)	80.5°C
	cyclohexane	81.4
(3)	isooctane (2,2,4-trimethyl pentane)	99.3°C
	methylcyclohexane (MCH)	100.3

The Aerograph gas chromatograph was then calibrated with the synthetic hydrocarbon mixtures. Weight percents used were 20, 40, 50, 60, and 80 weight percent of the more volatile constituent.

Two methods of using chromatogram peaks quantitatively are comparing relative peak areas and relative peak heights (8). Both methods were tried with the relative peak height method showing the most promise since the peaks were sharp with little area. Calibration curves comparing relative peak height percent were plotted for all three pairs, in the absence of any entrainer (Figures 3-5).

The conditions used for the calibrations and all subsequent runs for each pair were: (1) cyclopentane-neohexane - helium rate, 50 ml/min; temperature, 39°C. (2) 2,4-dimethylpentane-cyclohexane-helium rate, 50 ml/min; temperature 71°C. and (3) isooctane-methylcyclohexane - helium rate, 126 ml/min; temperature 71°C. Figure 2 illustrates the type of resolution obtained with these conditions.

A. Initial Entrainer Evaluation

Various possible entrainers of the type described by Berg, et al (1) were selected from among commercially produced compounds. These were generally alcohols, amines, and acids boiling within 20°C. of the hydrocarbon pair (Refer to Table I-III).

Horsley (6) gives the compositions and boiling points of over 14,000 binary systems. This source was first checked to see if any selective entrainers could be found from the available data. Since the information available for the most volatile hydrocarbon constituent of each pair was limited, this proved to be of little value.

The compounds were initially evaluated by boiling point depression. If the more volatile hydrocarbon-entrainer mixture boiled lower than either of the two pure components, an azeotrope had been formed. The entrainer was distilled in the column until a constant overhead temperature was attained and the more volatile of the hydrocarbon pair added. If the boiling point of the resulting mixture was lower, the column was