STUDYING THE EFFECT OF MIXING MISCIBLE HYDROCARBON COMPONENTS ON THE MULTI-STAGE DISTILLATION OPERATION COMPARED WITH SINGLE COMPONENT DISTILLATION

MOHD NOR FIRDAUS BIN MOHD SALLEH

A thesis submitted in fulfilment of the
Requirement for the award of the degree of
Bachelor of Chemical Engineering
(Gas Technology)

Faculty of Chemical and Natural Resources Engineering
University Malaysia Pahang (UMP)

APRIL 2008
I declare that this thesis entitled ‘Effect of mixing miscible hydrocarbon component on the multi-stage distillation operation compared with single component’ is the results of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted candidature of any degree.

Signature : ..............................................
Name : MOHD NOR FIRDAUS BIN MOHD SALLEH
Date : 30th APRIL 2008
Special dedicated to my beloved father and mother and my whole family members
ACKNOWLEDGEMENT

Alhamdulillah all praises be to almighty Allah who made it possible for me to done this thesis by time.

First of all, I would like to express my appreciation especially to my loving caring parent, Mr. Mohd Salleh bin Daud and Madam Rahah binti Md Salleh and rest of my family members who are very supportive morally to whatever good things that I have involve and done all these years.

Secondly I am greatly indebted to final year project supervisor Doctor Hayder A. Abdul Bari who was very kind to accept me as his supervise student and allowed me to work with him until this project is done. He greatly influenced, guidance, encouragement, comments and motivated me to explore distillation process in depth. I am grateful to my co-supervisor Mr. Arman Bin Abdullah for the advices, motivation and helps in finishing my project. Also not to forget the lecturers especially at the Faculty of Chemical and Natural Resources Engineering who have been teaching me all this while.

Lastly, thousand of thank you to my undergraduate fellows and to all my colleagues who are helpful especially ideas, valuable and opinion during the progress of the project. Thank you.
ABSTRACT

Distillation is the oldest and the most universal process of chemical technology and other branches of industry incorporating separation of mixture. Distillation is used to separate mixtures components in term of boiling point. Distillation has substantial advantage over other process applied in order to separate mixtures. In the present work, three different components are tested to know the differences in comparison between the distillate mixtures with a single distillate compound with the effect of distillation time on distillation composition, the effect of mixing percentage on distillation composition and the effect of time. The experimental work was carried in a batch distillation column and than the distillate being test using ultraviolet-visible spectrophotometer to determine the concentration. The result showed some of the mixture distillate is same to a single component in term of graph shape and the behaviour. The result of the concentration of the mixtures also showed the unstable graph shape for all the mixtures.
ABSTRAK

Penyulingan adalah satu proses yang tertua dan merupakan proses universal dalam teknologi kimia dan pelbagai cabang industri berkaitan dengan pengasingan campuran bahan. Penyulingan digunakan untuk memisahkan campuran dua atau lebih bahan berdasarkan takat didih bahan tersebut. Penyulingan mempunyai keistimewaan didalam proses pengasingan berbanding dengan proses-proses pengasingan yang lain. Dalam projek saujana muda ini, tiga bahan yang berlainan digunakan untuk mengkaji perbezaan perbandingan antara hasil sulingan campuran dengan hasil sulingan satu bahan dengan kesan masa penyulingan terhadap kandungan penyulingan bahan, kesan peratusan campuran terhadap kandungan penyulingan bahan dan kesan terhadap masa. Eksperimen ini dijalankan menggunakan alat batch distillation column sebagai alat untuk memisahkan campuran bahan dan seterusnya menggunakan alat ultraviolet-visible spectrophotometer untuk mendapatkan bacaan kepekatan. Keputusan eksperimen menunjukkan, sesetengah hasil penyulingan bahan campuran adalah sama dengan hasil sulingan satu bahan berdasarkan bentuk graf dan sifat. Keputusan terhadap kepekataan bahan sama ada campuran ataupun satu bahan menunjukkan graf yang tidak stabil untuk semua jenis campuran.
TABLE OF CONTENTS

CHAPTER | TITLE | PAGE
---|---|---
TITLE PAGE | | i
DECLARATION OF ORIGINALITY AND EXCLUSIVENESS | | ii
DEDICATION | | iii
ACKNOWLEDGEMENT | | iv
ABSTRACT | | v
ABSTRAK | | vi
TABLE OF CONTENT | | vii
LIST OF FIGURE | | x
LIST OF TABLE | | xi

1 INTRODUCTION

1.1 Separation | | 1
1.2 Distillation | | 2
1.3 Problem Statement | | 2
1.4 Objective of the Research | | 3
1.5 Scope of the Research | | 3

2 LITERATURE REVIEW

2.1 Introduction | | 4
2.2 Historical Background | | 4
2.3 Separation Process | | 6
2.3.1 Adsorption 7
2.3.2 Crystallization 7
2.3.3 Drying 8
2.3.4 Evaporation 8
2.3.5 Absorption 8
2.3.6 Liquid-liquid Extraction 9
2.3.7 Leaching 9
2.3.8 Membranes Processing 9
2.3.9 Ion Exchange 10
2.3.10 Distillation 10

2.4 Distillation 11

2.5 Types of Distillation 12
2.5.1 Simple Distillation 13
2.5.2 Fraction Distillation 13
2.5.3 Vacuum Distillation 14
2.5.4 Steam Distillation 14
2.5.5 Azeotropic Distillation 14
2.5.6 Batch Distillation 15
2.5.7 Distillation in industry 16

2.6 Multicomponent Distillation 17
2.6.1 Characteristic of Multicomponent Separation 18
2.6.2 Factor Effecting Separation 18

3 METHODOLOGY

3.1 Introduction 19
3.2 Experimental Rig 20
3.2.1 Batch Distillation (Laboratory Scale) 20
3.2.2 Ultraviolet-visible spectroscopy 21
3.3 Material Used 21
3.3.1 Dichloromethane (CH2) 22
3.3.1.1 Properties  22
3.3.1.2 Toxicity  23
3.3.2 Cyclohexane (C₆)  23
  3.3.2.1 Properties  24
3.3.3 Tetrachloroethylene (C₂)  24
  3.3.3.1 Properties  25
  3.3.3.2 Health and Safety  25
3.4 Experimental Work  26
  3.4.1 Samples preparation  26
  3.4.2 Procedures  26
3.5 Block Diagram of experiment procedures  29

4 RESULT
  4.1 Result  30
  4.2 Effect of distillation time on distillation composition  31
  4.3 Effect of mixing percentage on distillation composition  41
  4.4 Effect of time  51

5 CONCLUSION AND RECOMMENDATION
  5.1 Conclusion  61
  5.2 Recommendation  62
    5.2.1 Using pipette not syringe  62
    5.2.2 Cover up mouth of condenser  63
    5.2.3 Pipette before time  63

REFERENCES  64

APPENDIX  66
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2(a)</td>
<td>Distillation by retort</td>
<td>5</td>
</tr>
<tr>
<td>2.5(a)</td>
<td>Fractional distillation apparatus</td>
<td>13</td>
</tr>
<tr>
<td>2.5(b)</td>
<td>A batch still showing the separation of A and B</td>
<td>15</td>
</tr>
<tr>
<td>2.5(c)</td>
<td>Typical industrial distillation tower 1</td>
<td>16</td>
</tr>
<tr>
<td>2.5(d)</td>
<td>Typical industrial distillation tower 2</td>
<td>17</td>
</tr>
<tr>
<td>3.2(a)</td>
<td>Batch distillation with reflux ratio</td>
<td>20</td>
</tr>
<tr>
<td>3.2(b)</td>
<td>Ultraviolet-visible spectrophotometer</td>
<td>21</td>
</tr>
<tr>
<td>3.3(a)</td>
<td>Dichloromethane</td>
<td>22</td>
</tr>
<tr>
<td>3.3(b)</td>
<td>Cyclohexane</td>
<td>23</td>
</tr>
<tr>
<td>3.3(c)</td>
<td>Tetrachloroethylene</td>
<td>24</td>
</tr>
<tr>
<td>4.2(a)</td>
<td>Time (min) versus Distillate composition (g) for Single component</td>
<td>31</td>
</tr>
<tr>
<td>4.2(b)</td>
<td>Time (min) versus Distillate composition (g) for Task B with C2</td>
<td>32</td>
</tr>
<tr>
<td>4.2(c)</td>
<td>Time (min) versus Distillate composition (g) for Task B with C6</td>
<td>33</td>
</tr>
<tr>
<td>4.2(d)</td>
<td>Time (min) versus Distillate composition (g) for Task C with C6</td>
<td>34</td>
</tr>
</tbody>
</table>
4.2(e)  Time (min) versus Distillate composition (g) for Task C with CH2

4.2(f)  Time (min) versus Distillate composition (g) for Task D with C2

4.2(g)  Time (min) versus Distillate composition (g) for Task D with CH2

4.2(h)  Time (min) versus Distillate composition (g) for Task E with C2

4.2(i)  Time (min) versus Distillate composition (g) for Task E with C6

4.2(j)  Time (min) versus Distillate composition (g) for Task E with CH2

4.3(a)  Time (min) versus Distillate composition (g) for 100% components

4.3(b)  Time (min) versus Distillate composition (g) for mixture of 30%+70% with C2

4.3(c)  Time (min) versus Distillate composition (g) for mixture of 30%+70% with C6

4.3(d)  Time (min) versus Distillate composition (g) for mixture of 30%+70% with CH2

4.3(e)  Time (min) versus Distillate composition (g) for mixture of 50%+50% with C2
<table>
<thead>
<tr>
<th>4.3(f)</th>
<th>Time (min) versus Distillate composition (g) for mixture of 50%+50% with C6</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3(g)</td>
<td>Time (min) versus Distillate composition (g) for mixture of 50%+50% with CH2</td>
</tr>
<tr>
<td>4.3(h)</td>
<td>Time (min) versus Distillate composition (g) for mixture of 70%+30% with C2</td>
</tr>
<tr>
<td>4.3(i)</td>
<td>Time (min) versus Distillate composition (g) for mixture of 70%+30% with C6</td>
</tr>
<tr>
<td>4.3(j)</td>
<td>Time (min) versus Distillate composition (g) for mixture of 70%+30% with CH2</td>
</tr>
<tr>
<td>4.4(a)</td>
<td>Time (min) versus concentration (mg/L) for single component</td>
</tr>
<tr>
<td>4.4(b)</td>
<td>Time (min) versus concentration (mg/L) for Task B With C2</td>
</tr>
<tr>
<td>4.4(c)</td>
<td>Time (min) versus concentration (mg/L) for Task B With C6</td>
</tr>
<tr>
<td>4.4(d)</td>
<td>Time (min) versus concentration (mg/L) for Task B With CH2</td>
</tr>
<tr>
<td>4.4(e)</td>
<td>Time (min) versus concentration (mg/L) for Task C With C2</td>
</tr>
<tr>
<td>4.4(f)</td>
<td>Time (min) versus concentration (mg/L) for Task C With C6</td>
</tr>
<tr>
<td>4.4(g)</td>
<td>Time (min) versus concentration (mg/L) for Task C With CH2</td>
</tr>
<tr>
<td>4.4(h)</td>
<td>Time (min) versus concentration (mg/L) for Task D With C2</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------</td>
</tr>
<tr>
<td>4.4(i)</td>
<td>Time (min) versus concentration (mg/L) for Task D With C6</td>
</tr>
<tr>
<td>4.4(j)</td>
<td>Time (min) versus concentration (mg/L) for Task D With CH2</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3(a)</td>
<td>Properties of Dichloromethane (CH2)</td>
<td>22</td>
</tr>
<tr>
<td>3.3(b)</td>
<td>Properties of Cyclohexane (C₆)</td>
<td>24</td>
</tr>
<tr>
<td>3.3(c)</td>
<td>Properties of Tetrachloroethylene (C₂)</td>
<td>25</td>
</tr>
<tr>
<td>3.4(a)</td>
<td>The different mixing volume percentages</td>
<td>27</td>
</tr>
<tr>
<td>3.4(b)</td>
<td>Materials percentage for Task E</td>
<td>28</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 SEPARATION

In chemistry and chemical engineering, a separation process is used to transform a mixture of substances into two or more compositionally-distinct products. Many chemical process materials and biological substances occur as mixtures of difference components in the gas, liquid, or solid phase. In order to separate or remove one or more of the components from its original mixture, it must be contacted with another phase. The two phases are brought into more or less intimate contact with each other so that a solute or solutes can diffuse from one to other. The two bulk phases are usually only somewhat miscible in each other. Almost every element or compound is found naturally in an impure state such as a mixture of two or more substances. During the contact of two phases the components of the original mixture redistribute themselves between the two phases. The phases are then separated by simple physical methods. By choosing the proper conditions and phases, one phase is enriched while the other is depleted in one or more components. Separation applications in the field of chemical engineering are very important. A good example is that of crude oil. Crude oil is a mixture of various hydrocarbons and is valuable in this natural form. Demand is greater, however, for the purified various hydrocarbons such as natural gases, gasoline, diesel, jet fuel, lubricating oils, asphalt, etc. There several types of separation are considered under separation processes which are adsorption, absorption, crystallization, drying, evaporation, liquid-liquid extraction, leaching, membrane processing, and ion exchange. [2] [6]
1.2 DISTILLATION

Distillation is by far the most common method of separation in the petroleum, and petrochemical industries. The distillation can be term as a method for separating homogeneous mixtures based upon equilibration of liquid and vapor phases. Substances that differ in volatility appear in different proportions in vapor and liquid phases at equilibrium with one another. Thus, vaporizing part of a volatile liquid produces vapor and liquid products that differ in composition. This outcome constitutes a separation among the components in the original liquid. The basic requirement for the separation of component by distillation is that the composition of the vapor be different from composition of the liquid which it is equilibrium at the boiling point of the liquid. Distillation is concerned with solutions where all components are appreciably volatile, such as ammonia-water, or ethanol-water solution, where both components will be in the vapor phase. The mixture of substances is placed in the flask and heated. Ideally, the substance with the lowest boiling point vaporizes first, the temperature remaining constant until that substance has completely distilled. The vapor is led into the condenser where, on being cooled, it reverts to the liquid in the overhead condenser and runs off into a receiving vessel. Those substances having a higher boiling point remain in the flask and constitute the residue. Generally there are two types of distillation, first is laboratory scale distillation which are simple distillation, fractional distillation, vacuum distillation, steam distillation, and azeotropic distillation and second is large scale which are industrial distillation and batch distillation.\[2\] and [6]

1.3 PROBLEM STATEMENT

In the industry, crude oil consists of hundreds of components as mixtures and to separate them, we have to use separation process which is distillation. In this research, the distillation will carry on with multistage distillation to distil heavy component and light component. The behavior of heavy hydrocarbon will be compare with light hydrocarbon in a various condition using a graph.
1.4 OBJECTIVES OF THE RESEARCH

The objectives of this thesis; effect of mixing two miscible hydrocarbon components on the distillation operation compared with single component distillation are:

i) To study the effect of mixing multicomponent miscible hydrocarbon on the multi-stage distillation operation compared with single component distillation.

ii) To study the behavior of heavy hydrocarbon with the light hydrocarbon.

iii) To study the effect of heavy hydrocarbon and light hydrocarbon in a different volume.

1.5 SCOPE OF THE RESEARCH

This thesis will be run on multi-stage distillation in a batch distillation with a multicomponent with a differences volume percentage.
CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Separation operations achieve their objective by the creation of two or more components which differ in temperature, pressure, composition, and/or phase state. Each molecular species in the mixture to be separate reacts in unique way. Consequently, as the system moves toward equilibrium, each species establish a different concentration and these movements result in a separation between the species.

The separation operation called distillation utilizes vapor and liquid phases at essentially the same temperature and pressure. Various kinds of devices such as random or structured packing and plates or trays are used to bring the two phases into close contact.

2.2 HISTORICAL BACKGROUND

Distillation was an invention of Greek alchemists in the first century AD and the later development of large-scale distillation apparatus occurred in response to demands for spirits. Hypathia of Alexandria is credited with having invented the distillation apparatus and the first exact description of apparatus for distillation is given by Zosimus of Alexandria, in the fourth century.
Distillation was developed further by Islamic alchemist Jabir ibn Hayyan in around 800 AD. He is credited with the invention of numerous chemical apparatus and processes that are still in use today. The design of the alembic (alembic means apparatus formerly used in distilling, or in refining or extracting) has served as inspiration for some modern micro-scale distillation apparatus such as the Hickman stillhead.[2]

As alchemy evolved into the science of chemistry, vessels called retorts became used for distillations. Both alembics and retorts are forms of glassware with long necks pointing to the side at a downward angle which acted as air-cooled condensers to condense the distillate and let it drip downward for collection. Figure 2.2 (a) shows the first apparatus that being used for distillation.

![Figure 2.2(a) Distillation by retort](image)

Later, copper alembics were invented. Riveted joints were often kept tight by using various mixtures, for instance dough made of rye flour. These alembics often featured a cooling system around the beak, using cold water for instance, which made the condensation of alcohol more efficient. These were called pot stills.

Today, the retorts and pot stills have been largely supplanted by more efficient distillation methods in most industrial processes. However, the pot still [2] is still widely used for the elaboration of some fine alcohols, such as cognac and Scotch whisky. Small pot stills are also sold for the domestic production of flower water or essential oils.
2.3 SEPARATION PROCESSES

Separation process is defined as a process that transforms a mixture of substances into two or more compositionally-distinct products. It is also defined as any set of operation that separate of two or more components into two or more products that differ in composition. [3]

Separation process is used to transform a mixture of substances into two or more compositionally-distinct products. Almost every element or compound is found naturally in an impure state such as a mixture of two or more substances. Separation applications in the field of chemical engineering are very important. A good example is that of crude oil. Crude oil is a mixture of various hydrocarbons and is valuable in this natural form.

Separation processes can essentially be termed as mass transfer processes. The classification can be based on the means of separation, mechanical or chemical. Mechanical separations are usually favored if possible due to the lower cost of the operations as compared to chemical separations [2]. These mechanical separation force include gravitational and centrifugal, actual mechanical, and kinetic arising from flow. Particles or fluid stream are separated because of the different effects produced on them by these forces. These separation processes are considered under the following classification:

i) Filtration.
ii) Settling and sedimentation.
iii) Centrifugal settling and sedimentation.
iv) Centrifugal filtration
v) Mechanical size reduction and separation
Systems that can not be separated by purely mechanical means (e.g. crude oil), chemical separation is the remaining solution. The mixture at hand could exist as a combination of any two or more states: solid-solid, solid-liquid, solid-gas, liquid-liquid, liquid-gas, gas-gas, solid-liquid-gas mixture, etc.

Depending on the raw mixture, various processes can be done to separate the mixtures. More of these processes have to be used in combination to obtain the desired separation. In addition to chemical processes, mechanical processes can also be applied where possible. In the example of crude oil, one upstream distillation operation will feed its two or more product streams into multiple downstream distillation operations to further separate the crude, and so on until final products are purified.

In chemistry process, there are several types of separation process that are usually used which are:

2.3.1 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or, a liquid (adsorbent), forming a molecular or atomic film. Examples include removal of organic compounds from polluted water, separation of paraffin from aromatic, and removal of solvent from air \cite{6}.

2.3.2 Crystallization

Solute constituents soluble in solution can be removed from a solution by adjusting a condition, such as temperature or concentration, so that the solubility of one or more of the constituents is exceeded and they crystallize out as a solid phase. Example of this separation process is crystallization of sugar from solution. In commercial crystallization not only are the yield and purity of the
crystals important but also the sizes and shapes of the crystals. Sometimes large crystals are requested by the purchaser, even though smaller crystals are just useful. Also, crystals of a certain shape are sometimes required, such as needles rather than cubes.\[6\]

2.3.3 Drying

Drying is a mass transfer process resulting in the removal of water moisture or moisture from another solvent, by evaporation from a solid, semi-solid or liquid to end in a solid state. To achieve this, there must be a source of heat, and a sink of the vapor thus produced.\[3\]

2.3.4 Evaporation

In evaporation the vapor from a boiling liquid solution is removed and a more concentrated solution remains. In other hand, evaporation refers to the removal of water from an aqueous solution.\[6\]

2.3.5 Absorption

Gas absorption is a process in which soluble components of gas mixture are dissolved in a liquid phase. This is the process where taking of molecules of one substance directly into another substance. Absorption, in chemistry, is a physical or chemical phenomenon or a process in which atoms, molecules, or ions enter some bulk phase like gas, liquid or solid material. It is contrasted with adsorption, in which the molecules adhere only to the surface of the second substance. Absorption may be either a physical or a chemical process, physical absorption involving such factors as solubility and vapor-pressure relationships and chemical absorption involving chemical reactions between the absorbed substance and the absorbing medium.
2.3.6 Liquid-liquid Extraction

Liquid-liquid extraction, also known as solvent extraction and partitioning, is a method to separate compounds based on their solution preferences for two different immiscible liquids, usually water and an organic solvent. \[3\]

2.3.7 Leaching

In the chemical processing industry, leaching is known as extraction. Leaching has a variety of commercial applications, including separation of metal from ore using acid. In an ideal leaching equilibrium stage, all the solute is dissolved by the solvent; none of the carrier is dissolved. The mass ratio of the solid to liquid in the underflow is dependent on the type of equipment used and properties of the two phases. \[3\]. Examples are leaching copper from solid ore by sulfuric acid.

2.3.8 Membrane Processing

Membrane processing is a technique that permits concentration and separation without the use of heat. Particles are separated on the basis of their molecular size and shape with the use of pressure and specially designed semi-permeable membranes. Separation of molecules by the use of membranes is a relatively new separation process \[2\]. The relatively thin, solid membrane controls the rate of movement of molecules between two phases. It is used to remove salt from water, to purify gases, in food processing and so on. \[6\]
2.3.9 Ion Exchange

In an ion-exchange process, certain ions are removed by an ion-exchange solid. This separation process closely resembles adsorption. A reversible chemical reaction between an insoluble solid and a solution during which ions may be interchanged, used in water softening and in the separation of radioactive isotopes. Ion-exchange also can be defined as reversible exchange of ions of the same charge between a solution and an insoluble solid in contact with it. Ions are atoms or molecules containing charge-bearing groups. Their interactions are dominated by the electrostatic forces between charge centers. These interactions are attractive when the ions are of opposite charge, or repulsive when the ions have the same charge. Ion exchange has numerous applications for industry and for laboratory research. By the quantity of materials used, water conditioning is the most important. Ion exchange is one of the primary analytical methods used to identify and quantify the concentration of ions in a wide range of environmental, biological, and industrial samples. [6]

2.3.10 Distillation

The process of purifying and concentrating a liquid through separating its components by heating it to the point of vaporization and collecting the cooled condensate (vapor that reverts to liquid through condensation). The apparatus used for distillation is a still of which there are two types-pots still and continuous still distillation. Distilled spirits are typically based on fermented fruit or cereal grains. After distillation, many are flavored in some way, either with added ingredients or by barrel aging, or both.
2.4 DISTILLATION

Distillation is the process of separating a liquid's components by heating it to the point of vaporization and collecting the cooled condensate (vapor that reverts to liquid through condensation) in order to obtain a purified and/or concentrated form.\[^3\]. Distillation, process of heating a liquid until its more volatile components pass into the vapor phase, and then cooling the vapor to recover such components in liquid form by condensation. The main purpose of distillation is to separate a mixture of several components by taking advantage of their different volatilities, or the separation of volatile materials from nonvolatile materials. In distillation, the principal object of the operation is to obtain the more volatile component in pure form. If the difference in volatility (and hence in boiling point) between the two components is great, the complete separation may be easily achieved by a single distillation.\[^4\]

For example the two simplest mixture of two miscible soluble liquids, the volatility of each is undisturbed by the presence of the other. In such a case, the boiling point of a mixture would be different between each other, and the degree of separation produced by a single distillation would depend only on the vapor pressure, or the volatility, of the separate components at this temperature. This simple relationship was first stated by the French chemist Franaeois Marie Raoult (1830-1901)\[^8\] and is called Raoult's law. Raoult's law applies only to mixtures of liquids that are very similar in chemical structure, such as benzene and toluene. Raoult's law assumes that a component contributes to the total vapor pressure of the mixture in proportion to its percentage of the mixture and its vapor pressure when pure. If one component changes another component's vapor pressure, or if the volatility of a component is dependent on its percentage in the mixture, the law will fail.

Another law that been use is Dalton's law\[^8\] Dalton’s law states that the total vapor pressure is the sum of the vapor pressures of each individual component in the mixture. When a multi-component system is heated, the vapor pressure of each component will rise, thus causing the total vapor pressure to rise. When the total vapor
pressure reaches the ambient pressure, boiling occurs and liquid turns to gas throughout the bulk of the solution. Note that a given mixture has one boiling point, when the components are mutually soluble.

2.5 TYPES OF DISTILLATION

The application of distillation can roughly be divided in four groups: laboratory scale, industrial distillation, distillation of herbs distillate and food processing. The former distillation is laboratory scale distillation and industrial distillation. Under laboratory scale there are several types of distillation such as simple distillation, fractional distillation, steam distillation, vacuum distillation, azeotropic distillation and etc.

The main difference between laboratory scale distillation and industrial distillation is that laboratory scale distillation is often performed batch-wise, the industrial distillation often perform continuously. In batch distillation, the composition of the material, the vapors of the distilling compounds and the distillate change during the distillation. In batch distillation, a still is charged (supplied) with a batch of feed mixture, which is then separated into its component fractions which are collected from most volatile to less volatile, with the bottoms (remaining least or non-volatile fraction) removed at the end. The still can then be recharged and the process repeated [4].

In continuous distillation, the materials, vapors and distillate are kept at a constant composition by carefully renewed the source material and removing fractions from both vapor and liquid in the system. This results in a better control of the separation process.
2.5.1 Simple Distillation

The simple distillation is usually run as batch distillation. In the simple distillation liquid is first charged to the heated kettle. The liquid is boiled slowly and the vapors are withdrawn as rapidly as they reached to a condenser. A condenser in which the heated vapor is cooled back to the liquid state, and a receiver in which the concentrated or purified liquid, called the distillate, is collected. This simple distillation also can be classified as batch distillation \[^4\][^6].

2.5.2 Fractional distillation

The fractionating column is a device for increasing the efficiency of this distillation process. It consists of a vertical column packed with some inert material, such as glass beads or glass helices for increasing the surface upon which the vapor may condense. As the hot vapors rise through the column, they condense and flow back down the column. The condensate, as it hits the lower, hotter portions of the column, is revaporized, and the more volatile components proceed up the column once again. This fractional distillation can be classified as batch distillation \[^2\][^7].

![Fractional distillation apparatus](image)
2.5.3 Vacuum Distillation

Some of chemical compounds have very high boiling points. To boil such compounds, it is often better to lower the pressure at which such compounds are boiled instead of increasing the temperature. Once the pressure is lowered to the vapor pressure of the compound (at the given temperature), boiling and the rest of the distillation process can commence. This technique is referred to as vacuum distillation and it is commonly found in the laboratory in the form of the rotary evaporator\(^4\).

2.5.4 Steam Distillation

Like vacuum distillation, steam distillation is a method for distilling compounds which are heat-sensitive. This process involves using bubbling steam through a heated mixture of the raw material. By Raoult's law, some of the target compound will vaporize (in accordance with its partial pressure). The vapor mixture is cooled and condensed, usually yielding a layer of oil and a layer of water. The used of steam distillation usually on production of essential oil such as perfume and aromatherapy\(^4\).

2.5.5 Azeotropic Distillation

An azeotrope is a mixture of two or more solvents in such a ratio that its composition cannot be changed by simple distillation. Interactions between the components of the solution create properties unique to the solution, as most processes entail nonideal. An azeotrope as a liquid mixture that is characterized by a constant maximum or minimum boiling point which is lower or higher than that of any of the components and that distils without change in composition. At an azeotrope, the solution contains the given component in the same proportion as the vapor, so that evaporation does not change the purity, and distillation does not effect separation\(^4\).
If the azeotrope is not considered sufficiently pure for use, there exist some techniques to break the azeotrope to give a pure distillate. This set of techniques is known as azeotropic distillation. Some techniques achieve this by "jumping" over the azeotropic composition by adding an additional component to create a new azeotrope, or by varying the pressure.

2.5.6 Batch Distillation

The mixture of two miscible volatile A and B heated by a reboiler; with A having the higher volatility, or lower boiling point in a batch distillation setup (figure 2.5.1) until the mixture is boiling results in a vapor above the liquid which contains a mixture of A and B. The ratio between A and B in the vapor will be different from the ratio in the liquid: the ratio in the liquid will be determined by how the original mixture was prepared, while the ratio in the vapor will be enriched in the more volatile compound, A. The vapor goes through the condenser and is removed from the system. This in turn means that the ratio of compounds in the remaining liquid is now different from the initial ratio (i.e. more enriched in B than the starting liquid).

![Figure 2.5(b) A batch still showing the separation of A and B](image)
2.5.7 Distillation in industry

Large scale industrial distillation applications include both batch and continuous fractional, vacuum, azeotropic, extractive, and steam distillation. The most widely used industrial applications of continuous, steady-state fractional distillation are in petroleum refineries, petrochemical and chemical plants and natural gas processing plants. The figure 2.5.2 shows the typical industrial distillation tower.

![Typical industrial distillation towers](image)

Industrial distillation applications include both batch and continuous fractional, vacuum, azeotropic, extractive, and steam distillation. The most widely used industrial applications of continuous, steady-state fractional distillation are in petroleum refineries, petrochemical and chemical plants and natural gas processing plants.

Industrial distillation is typically performed in large, vertical cylindrical columns known as distillation towers or distillation columns with diameters ranging from about 65 centimeters to 6 meters and heights ranging from about 6 meters to 60 meters or more. When the process feed has a diverse composition, as in distilling crude oil, liquid outlets at intervals up the column allow for the
withdrawal of different fractions or products having different boiling points or boiling ranges. The "lightest" products (those with the lowest boiling point) exit from the top of the columns and the "heaviest" products (those with the highest boiling point) exit from the bottom of the column and are often called the bottoms.

![Typical industrial distillation tower 2](image)

**Figure 2.5(d) Typical industrial distillation tower 2**

### 2.6 MULTICOMPONENT DISTILLATION

In this section it will be concerned with the fractional distillation of multicomponent mixture, i.e., those with three or more constituents. The simple word distillation will be used in place of more accurate phase fractional distillation. The multicomponent distillation will be from petroleum and chemical process industries, both of which use distillation as matter of course. Multicomponent distillation is more difficult than binary distillation. [14]
2.6.1 Characteristics of multicomponent separation

A multicomponent mixture is separate in fractionation column into an overhead or distillate product that is enriched in the lighter components and a bottoms product is enriched in the heavier components. The product compositions depend on the extent of fractionation (or separation) taking place inside the column and the product rates. [15]

2.6.2 Factor affecting separation

The separation into lighter and heavier products in a multistage column is accomplished as a result of a composition gradient that develops along the column. The upper stage has higher concentrations of lighter constituents and lower stages have higher concentrations of heavier constituents. In conventional distillation columns, the liquid and vapor streams within the column are generated internally by condensing vapor in the condenser and reboiling liquid in the reboiler. [14]

In column section where the liquid composition is considerably different from the vapor composition, the composition change in each phase from one stage to the next is not only the result of the temperature variation. In this type of process the temperature variation along the column is influenced less by phase equilibrium relations by latent heat or enthalpy balance. In this column, no temperature gradient is necessary to generate the compositional gradient along the column; the composition gradient is brought about by stream with distinct compositions entering the column at different location. [14]
CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

Batch distillation is widely used in chemical, biochemical, and food industries for the production of small amounts of products with high added value. The batch processing is a very attractive separation operation mainly for the following reasons:

i) A single batch column can separate a multicomponent feed mixture into several products within a single operation,

ii) The flexibility of a batch process is such that the frequent change of market demands and strict product purity requirements can be accommodated.

iii) The production amounts in a batch process are usually small with minimum raw material inventories; this often results in an economic incentive.

So, in these experimental procedures, it used batch distillation unit and tested using Ultraviolet-visible spectroscopy. This experiment is to investigate the behavior of heavy hydrocarbon component compare with light hydrocarbon component. In material
used section, there are three chemical constituents will be discuss which are cyclopentadiene, cyclohexane and tetrachloroethylene.

3.2 EXPERIMENTAL RIG

The methods are prepare in a laboratory scale with batch distillation and to the equipment for sample testing is Ultraviolet-visible spectroscopy.

3.2.1 Batch Distillation (Laboratory Scale)

Batch distillation is very important because it has received extensive attention over the past few years, partly due to the fact that it is frequently used in the production of small quantities of chemical and biochemical products of high value. Its main advantage in this context is its versatility. However, it is precisely this flexibility and the inherent unsteady nature of the process that pose challenging design and operation problems.

Figure 3.2(a) Batch distillations with reflux ratio
3.2.2 Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV/ VIS) involves the spectroscopy of photons and spectrophotometry. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of energy space molecules undergo electronic transitions. UV/Vis spectroscopy is routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds. Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for these determinations are often water for water soluble compounds, or ethanol for organic-soluble compounds. \cite{2}

![Ultraviolet-visible spectrophotometer](image)

Figure 3.2(b) Ultraviolet-visible spectrophotometer

3.3 MATERIALS USED

There are three chemicals component carry out in this experiment which are dichloromethane, cyclohexane and tetrachloroethylene. The general properties will be discussed in this section.
3.3.1 Dichloromethane (CH\textsubscript{2}Cl\textsubscript{2})

Dichloromethane (DCM) or methylene chloride is the chemical compound with the formula CH\textsubscript{2}Cl\textsubscript{2}. It is a colorless, volatile liquid with a moderately sweet aroma. It is widely used as a solvent, the general view being that it is one of the less harmful of the chlorocarbons, and it is miscible with most organic solvents.

Dichloromethane was first prepared in 1840 by the French chemist Henri Victor Regnault, who isolated it from a mixture of chloromethane and chlorine that had been exposed to sunlight.

![Figure 3.3 (a) Dichloromethane](image)

**Figure 3.3 (a) Dichloromethane**

3.3.1.1 Properties

<table>
<thead>
<tr>
<th><strong>Table 3.3(a) Properties of Dichloromethane (CH\textsubscript{2}Cl\textsubscript{2})</strong>\textsuperscript{[2][12][13]}</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Molecular formula</strong></td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
</tr>
<tr>
<td><strong>Molar mass</strong></td>
<td>84.93 g/mol</td>
</tr>
<tr>
<td><strong>Density and phase</strong></td>
<td>1.3255 g/cm\textsuperscript{3}, liquid</td>
</tr>
<tr>
<td><strong>Solubility</strong></td>
<td>- most organic solvent</td>
</tr>
<tr>
<td><strong>Melting point</strong></td>
<td>-96.7 °C (175.7 K)</td>
</tr>
<tr>
<td><strong>Boiling point</strong></td>
<td>39 °C (312.8 K)</td>
</tr>
<tr>
<td><strong>EU classification</strong></td>
<td>Harmful</td>
</tr>
</tbody>
</table>
3.3.1.2 Toxicity

Dichloromethane is the least toxic of the simple chlorohydrocarbons, but it is not without its health risks as its high volatility makes it an acute inhalation hazard. Dichloromethane is also metabolised by the body to carbon monoxide potentially leading to carbon monoxide poisoning. Prolonged skin contact can result in the dichloromethane dissolving some of the fatty tissues in skin, resulting in skin irritation or chemical burns.

It may be carcinogenic, as it has been linked to cancer of the lungs, liver, and pancreas in laboratory animals. Dichloromethane crosses the placenta. Fetal toxicity in women who are exposed to it during pregnancy however has not been proven. In animal experiments it was fetotoxic at doses that were maternally toxic but no teratogenic effects were seen. In many countries products containing dichloromethane must carry labels warning of its health risks.

3.3.2 Cyclohexane (C₆)

Cyclohexane \(^\text{[2]}\) is a cycloalkane with the molecular formula C₆H₁₂. Cyclohexane is used as a nonpolar solvent for the chemical industry, and also as a raw material for the industrial production of acidic acid and caprolactam, both of which are intermediates used in the production of nylon. On an industrial scale, cyclohexane is produced by reacting benzene with hydrogen. Due to its unique chemical and conformational properties, cyclohexane is also used in labs in analysis and as a standard.

![Figure 3.3(b) Cyclohexane](image)
3.3.2.1 Properties

Table 3.3(b) Properties of Cyclohexane (C$_6$) $^{[2]}$

<table>
<thead>
<tr>
<th>Property</th>
<th>Cyclohexane (C$_6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C$<em>6$H$</em>{12}$</td>
</tr>
<tr>
<td>Molar mass</td>
<td>84.16 g/mol</td>
</tr>
<tr>
<td>Density and phase</td>
<td>0.779 g/mL, liquid</td>
</tr>
</tbody>
</table>
| Solubility                    | - in water (immiscible) 
- ethanol, (miscible)       |
| Melting point                 | 6.55 °C (279.55 K)  |
| Boiling point                 | 80.74 °C (353.74 K) |
| EU classification             | Flammable, harmful, dangerous for the environment, Severe eye irritant, may cause corneal clouding |

3.3.3 Tetrachloroethylene (C$_2$)

Tetrachloroethylene $^{[2]}$ Cl$_2$C=CCl$_2$ is a manufactured chemical compound that is widely used for the dry cleaning of fabrics and for metal-degreasing. It is also used to make other chemicals and is used in some consumer products.

Other names for tetrachloroethylene include perchloroethylene, perc, PCE, and tetrachloroethene. It is a nonflammable liquid at room temperature. It evaporates easily into the air and has a sharp, sweet odor. Most people can smell tetrachloroethylene when it is present in the air at a concentration of 1 part per million (1 ppm), although some can smell it at even lower levels. Michael Faraday first synthesized tetrachloroethylene in 1821 by heating hexachloroethane until it decomposed into tetrachloroethylene and chlorine.

![Image of Tetrachloroethylene]

Figure 3.3(c) Tetrachloroethylene