EFFECTS OF TEMPERATURE ON VAPOR LIQUID EQUILIBRIUM OF MTBE-METHANOL MIXTURES

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A thesis submitted in fulfillment of requirement for
the award of the degree of Bachelor of Chemical Engineering

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DECEMBER 2010

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering

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I declared that this thesis entitled “Vapor Liquid Equilibrium Diagram of MTBE Methanol Binary Mixture at Various Temperature and Constant Pressure” is the result of my own researched excepted as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidate in candidature of any other degree.

Signature:
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To my beloved Mother and Father…

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ABSTRACT

In separation process of binary mixture the vapor liquid equilibrium diagram is integral to design the separation apparatus. This research objective is to construct the vapor liquid equilibrium diagram for MTBE-Methanol binary mixture system at various temperatures and at constant pressure. Other objective is also to find the Azeotropic point which the MTBE-Methanol binary mixture formed at certain point that posed problems in separation processes. The separation process encountered problems during the Azeotropic point which vapor and liquid fraction is equal. The equipment used is Vapor Liquid Equilibrium Unit Equipment in the Unit Operation Laboratory. Initially the steps taken are to find the calibration curve for MTBE-Methanol mixture. The experiment started with MTBE volume set at constant and gradually increase the Methanol volume. The mixture in the equipment will be heated at four different temperatures which will give enough data to construct the diagram. Record the RI index and the temperature. The experiment was conducted at four different temperatures. The result, MTBE fraction of x vapor fraction and y liquid fraction formed Azeotropic point at $0.6 \sim 0.7 = x = y$.

ABSTRAK

Dalam proses penapisan bahan kimia diagram untuk Wap dan Cecair diagram amat penting untuk membantu jurutera mereka alat penapisan. MTBE dan Methanol ialah produk yang terhasil daripada reaksi kimia Isobutylene. MTBE ialah bahan kimia yang digunakan sebagai bahan penambah yang boleh membantu pembakaran didalam minak Petrol. Salah satu masalah yang dihadapi dalam pemisahan antara MTBE dan Methanol ialah fenomena Azeotrope. Fenomena ini menyebabkan pecahan wap dan pecahan cecair mempunyai suhu didih yang sama. Pemisahan yang sedia ada adalah pemisahan yang memanipulasi suhu. Jika pecahan cecair dan pecahan wap mempunyai suhu didih yang sama, alat pemisahan tersebut tidak dapat memanipulasi suhu untuk memisahkan MTBE dan Methanol. Campuran binary ini mempunyai titik Azetrope pada 0.7 . Prosedure eksperimen ialah dengan melakukan ekperimen yang memvariasikan komposisi Methanol dan menetapkan isipadu MTBE didalam alat. Alat yang digunakan dalam eksperiman in ialah Vapor Liquid Equilibrium Unit yang terdapat di Makmal Unit Operasi.Konklusi yang boleh dibuat berdasarkan kajian ini ialah campuran binary MTBE-Methanol mampu menghasilkan titik Azeotrope dan Polyethylene Glycol tidak mampu memecahkan titik Azeotrope.

TABLE OF CONTENTS

1 INTRODUCTION

2 LITERATURE REVIEW

3 METHODOLOGY

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

NOMENCLATURE

y - Vapor fraction
x - Liquid fraction
P - Total Pressure
P_a - Partial pressure A
P_b Partial pressure B
α_{AB} - Volatility A-B
$C_5H_{12}O$ - *tert*-Butyl Methyl Ether

$wt\%$ - Weight percent
x_b - Liquid Mole fraction B
x_a - Liquid Mole fraction A
y_a - Vapor mole fraction A
y_b - Vapor mole fraction B
cc - Cubic centimeter cm^3
CH_4O - Methanol

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The separation process depends heavily on both chemical and physical properties of the material needed to be separated. These properties determined the type of separation process. Separation process in the bigger picture used to transform a mixture of substances into two or more distinct product. Because the fundamental part of separation process is manipulating both chemical and physical properties of the elements aimed to be separated and the separated product could differ in chemical properties or physical properties such as size, boiling point and other properties. Bearing in minds almost every element or compound is found to be naturally in an impure state such as mixture of two or more components. Separation applications in the fields of chemical engineering are very important.

Separation processes can be essentially be defined as mass transfer, mass transfer occurs in distillation, absorption, drying, liquid-liquid extraction, adsorption, ion-exchange, crystallization, and membrane processes (Geankoplis, 2003) .Mass transfer is important in many areas of science and engineering it occurred when a component in mixture migrates in the same phase or from phase to phase because of difference in certain properties such as boiling point, concentration or component size this justify why separation process manipulate either chemical or physical properties as mentioned above (Geankoplis, 2003)The classification can be based on the mean of separation, mechanical or chemical. The choice of separation depends on the pros and cons of each. Mechanical separations are usually favoured if possible due to the lower cost of the operations as compared to chemical separations. Systems that cannot 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.

Distillation is a unit operation or a physical separation process and not a chemical reaction. Commercially distillation has a number of applications. It used to separate crude oil into more fractions, other example is the distillation process used to distillate water to remove its impurities. Distillation process can be divided into two main types of distillation which is batch distillation and continuous distillation. Batch distillation refers to the use of distillation in batches, meaning that a mixture is distilled to separate it into its component fractions before the distillation still is again charged with more mixture and the process is repeated. This is in contrast with continuous distillation where the feedstock is added and the distillate drawn off without interruption. Batch distillation has always been an important part of the production of seasonal or low capacity and high-purity chemicals. It is a very frequent separation process in the pharmaceutical industry and in wastewater treatment units. And continuous distillation is an ongoing separation in which a mixture is continuously (without interruption) fed into the process and separated fractions are removed continuously as output streams as time passes during the operation (Juntao Zhanga, 2010).

The distillation process operated by manipulating the physical properties based on the volatility of the component in the mixture, the boiling point differences of the components in the mixture, using the boiling point is a way to separate the components from mixture is through heating process, by heating the mixture it will evaporate the components that have lower boiling point in comparison with the other components. This will leave behind the component that have higher boiling point that is still in liquid form. And to recover the evaporated components the condenser will be used condense the vapour back into liquid form. This is roughly the basic ideas behind distillation process. In much more complex system of distillation column the vapour liquid equilibrium principles were used as guidelines in the distillation process. In industrial level each of the binary or ternary mixture contains a set vapour liquid equilibrium data that helps engineer to perform separation process. Vapour Liquid Equilibrium data are the reason this study is conducted.

The applications of distillations can be roughly divided in few groups, laboratory scale, and industrial distillation. The main difference between laboratory scale distillation and industrial is that laboratory scale is often performed batch-wise, whereas industrial distillation often occurs continuously.

However azeotropic phenomena limit the separation achievable by ordinary distillation. Complete separation of azeotropic mixtures requires either the coupling the distillation columns with other separation methods such as adsorption, membranes, and extraction or the use of more complex distillation schemes based on a modification of the equilibrium to effect the complete separation. Although many new separation techniques are being developed, distillation will remain the method of choice for large-scale separation of nonideal mixtures including azeotropic mixtures. Separation of such mixtures is achieved by use of one of the enhanced distillation methods. These include extractive distillation, salt distillation, pressure-swing distillation, reactive distillation, and azeotropic distillation. The latter method involves the use of entrainers to alter the relative volatility of the components and break the azeotrope. The choice of separation method depends on the specific system and economics (Silva, 2006).

1.2 Problem Statement

Binary mixture of MTBE-Methanol have been subject of numerous investigations in recent years because of their anti knock properties. However azeotropic phenomena limit the separation of this mixture achievable by ordinary distillation. Complete separation of azeotropic mixtures requires either the coupling the distillation columns with other separation methods such as adsorption, membranes, and extraction or the use of more complex distillation schemes based on a modification of the equilibrium to effect the complete separation. Although many new separation techniques are being developed, distillation will remain the method of choice for large-scale separation of nonideal mixtures including azeotropic mixtures. Separation of such mixtures is achieved by use of one of the enhanced distillation methods. These include extractive distillation, salt distillation, pressure-swing distillation, reactive distillation, and azeotropic distillation. The latter method involves the use of entrainers to alter the relative volatility of the components and break the azeotrope. The choice of separation method depends on the specific system and economics (Silva, 2006).

The final steps in the synthesis process of MTBE are the separations of the compound from the methanol via azeotropic distillations. The study of Vapour Liquid of the mixture is of great interest to supplement the design of the distillation processes, because the mixture showed deviations from Raoult`s Law that is positive azeotropic (Coto, 1997), positive or negative azeotrope will influence separations in terms of its efficiencies. Initial step in studying azeotropes is study on Vapour Liquid Equilibrium Diagram.

1.3 Objective

The objective of study is to investigate the effect of different temperature on Vapour Liquid Equilibrium of MTBE-Methanol binary mixture at constant atmospheric pressure 1atm.

1.4 Scope of Study

I. To obtain Vapour Liquid Equilibrium diagram for MTBE-Methanol binary mixture at various temperature at constant pressure.
II. To construct *x*-*y* and *T*-*xy* diagram for MTBE-Methanol at different temperature.
III. Determine azeotropic point of MTBE-Methanol mixture.

1.5 Rationale and Significance

Azeotrope has limits the separation achievable by ordinary distillation. It is possible to shift or break the azeotropic point by applying entrainer in separation process. To research on what type of entrainer that would work in enhancing separation process, the research on the Vapour Liquid Equilibrium of the mixture must be completed first. The significant of study into the Vapour Liquid Equilibrium is that it can provide data such as temperature, pressure and vapour/liquid fraction compositions that can be simplified in a diagram that could help the study of finding the entrainer (Al-Amer, 2000).

CHAPTER 2

LITERATURE REVIEW

2.1 Distillation

Distillation is the oldest and the most universal process of chemical technology and other branches of industry incorporating separation mixtures. Distillation, which is the most widely, used separation technique in the chemical process industries, accounts for about 3% of the world energy consumption. Although mature and well optimized, distillation remains an energy-intensive operation (Juntao Zhang, 2010). Distillation has substantial advantages over the other processes applied in order to separate a mixture, such extraction, crystallization, semi permeable membranes etc. As a rule, it is the most cost effective process, so it may be used for mixtures with diverse properties. This process is based on the fact that the composition of the boiling liquid and that of the vapour over it differ. Thus, if the boiling temperature is low (e.g., air separation), it is necessary to use low temperature refrigerants and conduct the process at a higher pressure. If it is high (e.g., in separation of heavy oil fractions or metals), high temperature heat carries or fire preheating have to be used and the process is run under vacuum. If the composition of the boiling point of the liquid and that of vapour over it are quite close, there is substantial energy consumption, which results in high capital costs. It is impossible to conduct the distillation process in the case of azeotropic composition (Petlyuk, 2004).

2.2 Batch Distillation

Batch distillation has always been an important part of the production of seasonal or low capacity and high-purity chemicals. It is a very frequent separation process in the pharmaceutical industry and in wastewater treatment units. In differential distillation, liquid is first charged to a heated kettle .The liquid charge is boiled slowly and the vapour are withdrawn as rapidly as they form to a condenser, where the condensed vapour or also known as distillate is collected. The first portion of vapour condensed will be richest in more volatile component. Heating an ideal mixture of two volatile substances A and B with A having the higher volatility, or lower boiling point in a batch distillation setup such as in Figure 2.1 until the mixture is boiling results in a vapour above the liquid which contains a mixture of A and B. Due to the higher volatility of A it will form vapour quickly and will rise up the upper section of the container. The vapour A 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).The result is that the ratio in the liquid mixture is changing, becoming richer in component B. This causes the boiling point of the mixture to rise. If the difference in vapour pressure between the two components A and B is large (generally expressed as the difference in boiling points), the mixture in the beginning of the distillation is highly enriched in component A, and when component A has distilled off, the boiling liquid is enriched in component B (Geankoplis, 2003).

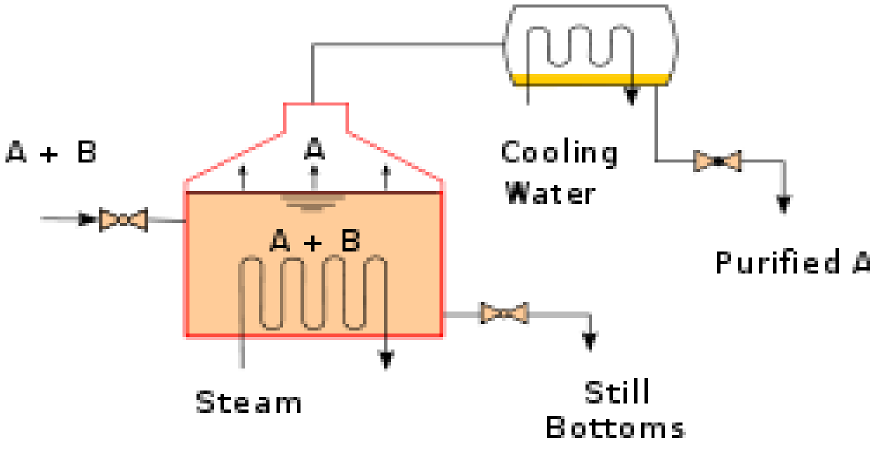


Figure 2.1: Batch Distillation

2.3 Continuous Distillation

Continuous distillation is an ongoing distillation in which a liquid mixture is continuously (without interruption) fed into the process and separated fractions are removed continuously as output streams as time passes during the operation. Continuous distillation produces at least two output fractions, including at least one volatile distillate fraction, which has boiled and been separately captured as a vapour condensed to a liquid. There is always a bottoms (or residue) fraction, which is the least volatile residue that has not been separately captured as a condensed vapour. Continuous distillation differs from batch distillation in the respect that concentrations should not change over time. Continuous distillation can be run at a steady state for an arbitrary amount of time. Given a feed of in a specified composition, the main variables that affect the purity of products in continuous distillation are the reflux ratio and the number of theoretical equilibrium stages (practically, the number of trays or the height of packing). Reflux is a flow from the condenser back to the column, which generates a recycle that allows a better separation with a given number of trays. Equilibrium stages are ideal steps where compositions achieve vapour-liquid equilibrium, repeating the separation process and allowing better separation given a reflux ratio. A column with a high reflux ratio may have fewer stages, but it refluxes a large amount of liquid, giving a wide column with a large holdup. Conversely, a column with a low reflux ratio must have a large number of stages, thus requiring a taller column. Continuous distillation requires building and configuring dedicated equipment. The resulting high investment cost restricts its use to the large scale. Figure 2.2 shows the process of continuous distillation (Geankoplis, 2003).

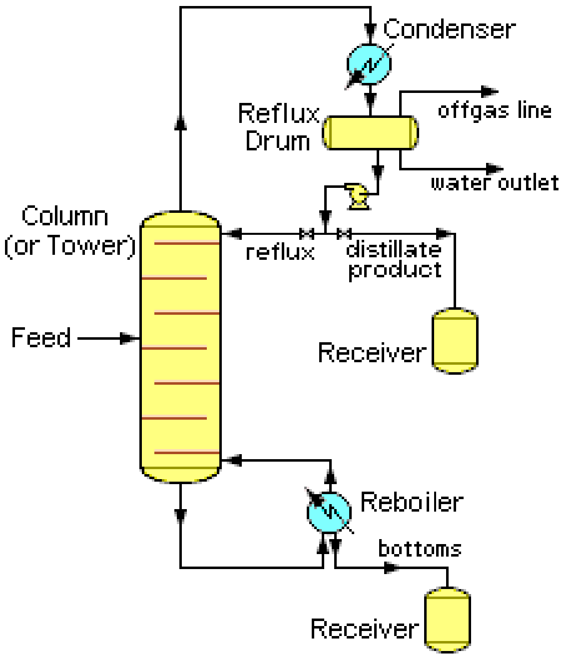


Figure 2.2: Continuous Distillation

2.4 Binary Mixture MTBE-Methanol

MTBE also known as methyl tertiary butyl ether and MTBE is a chemical compound with molecular formula $C_5H_{12}O$ .MTBE is a volatile, flammable and colourless liquid that is immiscible with water. MTBE has a minty odour vaguely reminiscent of diethyl ether, leading to unpleasant taste and odour in water. MTBE is a gasoline additive, used as oxygenate and to rise the octane number, although its use has declined in the United States in response to environmental and health concerns. The production of MTBE is from the chemical reaction of Isobutylene and Methanol but in this reaction not all the reactants turn to MTBE, Methanol still exist in the final product of this reaction which the Methanol is the undesired product so it is important to separate the undesired and the desired product.

2.4.1 Conventional production of MTBE

Methyl tertiary butyl ether is a high octane fuel additive and non-toxic as well as none polluting in contrast to lead alkyl additives. The high number of process licensors and plant under operation underline the economical importance of MTBE. The demand is predicted to increase from 8 to 32 million tons in the year 2000 making it worthwhile to improve existing production facilities. (Uwe Hommerich, 1998)

Figure 2.3 shows a schematic subdivision into three parts. In the reactor cascade, i-butene, which is available in $C_4 -$Raffinate from a steamcracking or catalytic cracking processes. Therefore, the effluent from the cascade consists mainly of MTBE, linear butenes (n-butenes) and excess methanol. Particularly the azeotrope formation of methanol with both MTBE and –C_4 poses difficulties on the subsequent product purification. In column 1 operated at 6 bar, the reactor effluent is separated into and n$-C_4$ /methanol distillate with azeotropic composition and a bottom product containing approximation of 97 wt% MTBE and 3 wt% methanol. The distillate is fed to third process part where high selectivity of the etherification is used for producing pure n-C_4 hydrocarbons. The MTBE /methanol stream of column 1 is fed to third process part where high selectivity of the etherification is used for producing pure n-C_4 hydrocarbons. The MTBE/methanol stream of column 1 is fed to a second distillation at 12 bars in order to achieve the final product quality of over 99 wt% for MTBE. The MTBE/methanol azeotrope at the top of column 2 has to be recycled into the reaction zone, since an economical separation is not feasible because of the small amount (approx. 4% of the reactor effluent) (Uwe Hommerich, 1998).

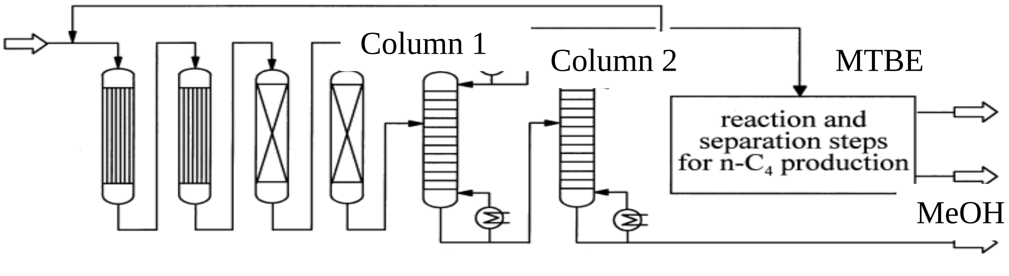


Figure 2.3: Production of MTBE schematic diagram (Uwe Hommerich, 1998)

2.5 Importance of Vapour-Liquid Equilibrium Diagram

VLE is a set of data necessary especially for engineer in separation process. This data is importance in chemical industries. Most industries handle two type of distillation which is continuous and batch distillation, and VLE is at the heart of the process as it provides guidance at how to design of the distillation equipments itself.VLE is especially important to continuous distillation or fractional distillation. In distillation it is importance to have a boiling diagram of the binary mixture. The diagram provide the information of the mixture in terms of which components is more volatile(boiling point) and which is less volatile(higher boiling point).In the boiling point diagram it also show the fraction of the mixture at different temperature and pressure. This information is paramount to conduct any distillation process. Once the data acquired this will provide the engineer at what temperature and at what pressure should the distillation process be proceeds and provide how much distillate will be resulted from distillation and how much condensate will be obtained. And this much more importance particularly for the continuous distillation process A mathematical and graphical method for determining the numbers of theoretical trays or stages in distillation column needed for a distillation process have been developed by McCabe Thiele method in 1925. McCabe-Thiele method is considered the simplest and perhaps most instructive method for analysis of binary distillation. This method uses the fact that the composition at each theoretical tray (or equilibrium stage) is completely determined by the mole fraction of one of the two components (Geankoplis, 2003).

2.6 Theory of Vapour Liquid Equilibrium

As in gas-liquid systems the equilibrium in vapour liquid system is restricted by the phase rule. For two components system and two phases there are four variables which are temperature, pressure and compositions of y_a which is the fraction mixture in vapour condition and x_a which is in liquid conditions. In the mixture of two components let say MTBE and Methanol the mixture is in two phase vapour and liquid. .VLE is a set of data obtained experimentally to provide ways for engineer to separate the mixture effectively. VLE is a condition where a liquid and its vapour (gas phase) are in equilibrium with each other, a condition or state where the rate of evaporation (liquid changing to vapour) equals the rate of condensation (vapour changing to liquid) on a molecular level such that there is no net (overall) vapour-liquid interconversion. Although in theory equilibrium takes forever to reach, such an equilibrium is practically reached in a relatively closed location if a liquid and its vapour are allowed to stand in contact with each other long enough with no interference or only gradual interference from the outside. There are many types of VLE. VLE can be of one component and or more than one.VLE that comprise more than one component were called binary mixture (two components) of ternary for three components. It said that the more components we have in VLE the more complicated it will be (Geankoplis, 2003)

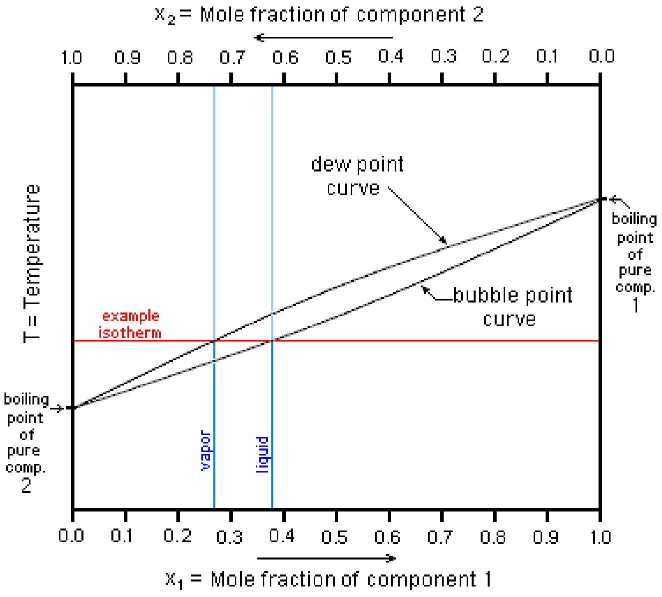


Figure 2.4: VLE Diagram of Binary Mixture

Figure 2.4 the binary mixture of two components. Often the VLE relations for a binary mixture let say A(MTBE) and B(Methanol) are given as a boiling point diagram as shown above. The upper line is the saturated vapour line (or the dew point line) and the lower line is the saturated liquid line (the bubble point line).The region between those lines is the area which vapour and liquid are in mixture. In other word the mixture is between those line is a two phase region. The concentration of a vapour in contact with its liquid, especially at equilibrium, is often given in terms of vapour pressure, which could be a partial pressure (part of the total gas pressure) if any other gas are present with the vapour. The equilibrium vapour pressure of a liquid is usually very dependent on temperature. At vapour-liquid equilibrium, a liquid with individual components (compounds) in certain concentrations will have an equilibrium vapour in which the concentrations or partial pressures of the vapour components will have certain set values depending on all of the liquid component concentrations and the temperature. It also means that if a vapour with components at certain concentrations or partial pressures is in vapour-liquid equilibrium with its liquid, then the component concentrations in the liquid will be set dependent on the vapour concentrations, again also depending on the temperature. The equilibrium concentration of each component in the liquid phase is often different from its concentration (or vapour pressure) in the vapour phase, but there is a correlation. Such VLE concentration data is often known or can be determined experimentally for vapour-liquid mixtures with various components. In certain cases such VLE data can be determined or approximated with the help of certain theories such as Raoult's Law, Dalton's Law, and/or Henry's Law (Geankoplis, 2003).

2.6.1 Raoult`s Law

The law was established by by François-Marie Raoult`s. Raoult's law states the vapour pressure of an ideal solution is dependent on the vapour pressure of each chemical component and the mole fraction of the component present in the solution which in mathematical is expressed as:

$$\mathrm{P_a} + P_b = P \quad \textbf{(2.1)}$$

$$x_a + x_b = 1 \quad \textbf{(2.2)}$$

$$P_a x_a + P_b x_b = \mathrm{P} \quad \textbf{(2.3)}$$

P is the total pressure vapour pressure of all the components exist in the mixture consequently, as the number of components in solution increases, the individual vapour pressures decrease, since the mole fraction of each component decreases with each additional component. If a pure solute which has zero vapour pressure (it will not evaporate) is dissolved in a solvent, the vapour pressure of the final solution will be lower than that of the pure solvent. This law is strictly valid only under the assumption that the chemical interactions between the two liquid is equal to the bonding within the liquids: the conditions of an ideal solution. The vapour pressure and composition in equilibrium with a solution can yield valuable information regarding the thermodynamic properties of the liquids involved. Raoult's law relates the vapour pressure of components to the composition of the solution. The law assumes ideal behaviour. It gives a simple picture of the situation just as the ideal gas law does. The ideal gas law is very useful as a limiting law. As the interactive forces between molecules and the volume of the molecules approaches zero, so the behaviour of gases approach the behaviour of the ideal gas (Geankoplis, 2003)

2.6.2 Relative Volatility

Relative volatility is a measure comparing the vapour pressures of the components in a liquid mixture of chemicals. This quantity is widely used in designing large industrial distillation processes. In effect, it indicates the ease or difficulty of using distillation to separate the more volatile components from the less volatile components in a mixture. By convention, relative volatility is usually denoted as α. Relative volatilities are used in the design of all types of distillation processes as well as other separation or absorption processes that involve the contacting of vapour and liquid phases in a series of equilibrium stages. In order to separate a binary mixture using distillation process, there must be differences in volatilities of the components. A numerical measure of this separation is the relativity α_{AB} .This is defined as the ratio of the concentration of A in the vapor to the concentration of A in the liquid divided by the ratio of the concentration of B in the vapour to the concentration of B in the liquid (Geankoplis, 2003)

$$\alpha_{AB} = \frac{Y_A/X_A}{Y_B/X_B} = \frac{Y_A/X_A}{1-Y_A/1-X_A} \qquad \textbf{(2.4)}$$

Where α_{AB} is the relativity of volatility of A with respect to B in the binary system if the system obeys the Raoult`s Law as does the benzene- toluene system.

$$y_A = \frac{P_A x_A}{P} \qquad y_B = \frac{P_B x_B}{P} \tag{2.5}$$

$$\alpha_{AB} = \frac{P_A}{P_B} \tag{2.6}$$

2.7 Azeotrope

Departures of the Raoult`s Law frequently manifest themselves in the formation of azeotropes particularly mixtures of close boiling species of different chemical types whose liquid solutions are non ideal. azeotropes are formed by liquid mixtures exhibiting maximum and minimum boiling point. These represent, respectively negative or positive deviations from Raoult`s Law. Vapour and liquid compositions are identical at the azeotropic compositions thus all the K values are 1 and no separation can take place. There are types of azeotropes that are commonly encountered with the binary mixture. The most common type by far is the minimum boiling homogenous azeotrope. Heterogeneous azeotrope is always minimum boiling point mixture because activity coefficient must be significantly greater than 1 to cause the splitting into two liquid phases. This is true for the MTBE –Methanol mixture which showed minimum azeotrope position. azeotropes limit the separation achievable by ordinary distillation. It is possible to shift the equilibrium by changing the pressure sufficiently to break azeotrope or move it away from the region where required separation must take place (j.d. seaders, 1998)

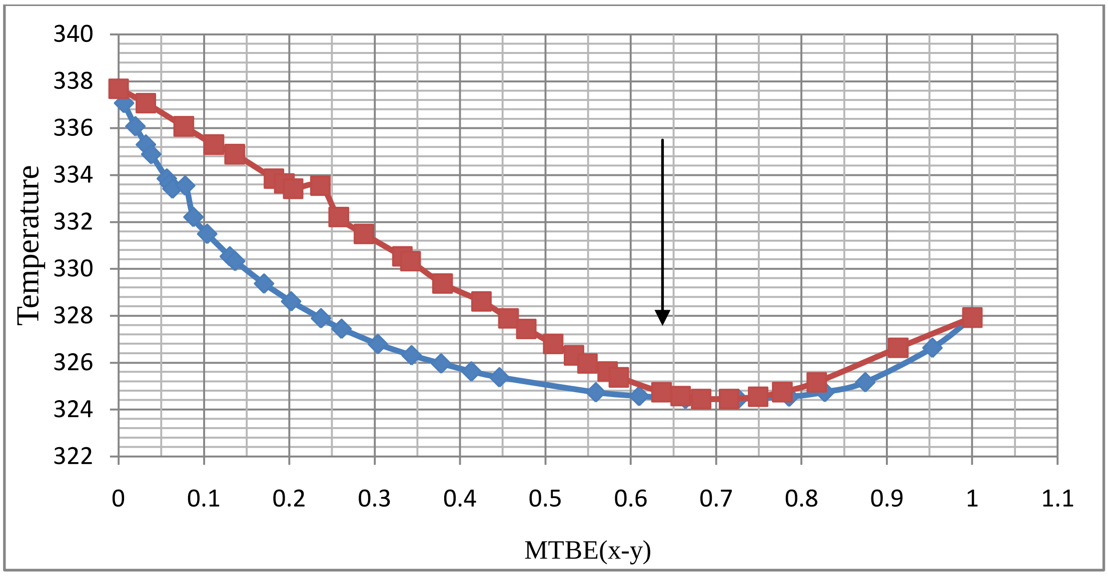


Figure 2.5: MTBE-Methanol VLE Diagram

The Figure 2.5 shows the T-*xy* diagram of MTBE-Methanol mixture. This is an example of minimum boiling point azeotrope. From figure it showed that MTBE-Methanol formed azeotropic point at 51 ℃ and at compositions of 0.7052 liquid(*x)* and also 0.7052 of vapour(*y)* (Gmehling, 2002). At this point the Azeotropic formed the minimum boiling point or positive azeotrope highlighting that this is the positive deviation of Raoult`s Law.

2.7.1 Azeotrope Distillation

Interactions between the components of the solution create properties unique to the solution, as most processes entail nonideal mixtures, where Raoult`s Law does not hold. Such interactions can result in a constant boiling azeotrope which behaves as if it were a pure component in the same proportion as the vapour, so the evaporation does not change the purity, and distillation does not affect separation. For example, ethyl alcohol and water form an azeotrope of 95.6% at 78. ℃ .

If the azeotrope is not considered sufficiently pure for use, there exist some techniques to break azeotrope to give 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. Others work by chemically or physically removing or sequestering impurity. For example to purify ethanol beyond 95% a drying agent or a desiccant such as potassium carbonate can be added to convert the soluble water insoluble water crystallization. Molecular sieves are often used for this purpose as well. Immiscible liquid, such as water and toluene are easily from azeotrope. Commonly these azeotropes are referred to as low boiling point of either pure component. The temperature and composition of the azeotrope is easily predicted from the vapour pressure of pure components, without use of Raoult`s Law. The azeotropes are easily broken in a distillation set-up by using a liquid-liquid separator (decanter) to separate the two liquid layers that are condensed overh Only one of the two liquid layers is refluxed to the distillation set-up.

CHAPTER 3

METHODOLOGY

3.1 Chemical and Apparatus

This experiment used Analytical Grade of tert-butyl methyl ethers (MTBE) and Methanol as chemical substances. The properties of the chemicals are as in Table 3.1.

Table 3.1: tert-Methyl Butyl Ethers and Methanol properties

Property	MTBE	Methanol
Boiling Point	55.2 C	64.7 C
Density @25 C	0.7404 g/cc	0.7918 g/cc
Molar Mass	88.15 g/mol	32.04 g/mol
Molecular Formula	$C_5H_{12}O$	CH_4O

The apparatus used in this experiment is Vapour Liquid Equilibrium Unit (Model: BP16) shown in Figure 3.1.This equipment was fabricated by Solution Engineering. Another apparatus is Refractometer by Atago. The equipment of Vapour Liquid Equilibrium Unit (Model: BP16) unit is capable of performing the following experiments

1. Determine the vapour liquid relationship at equilibrium for binary components systems at atmospheric and elevated pressures.
2. Study the effect of initial mixture compositions upon boiling temperature and vapour liquid phase

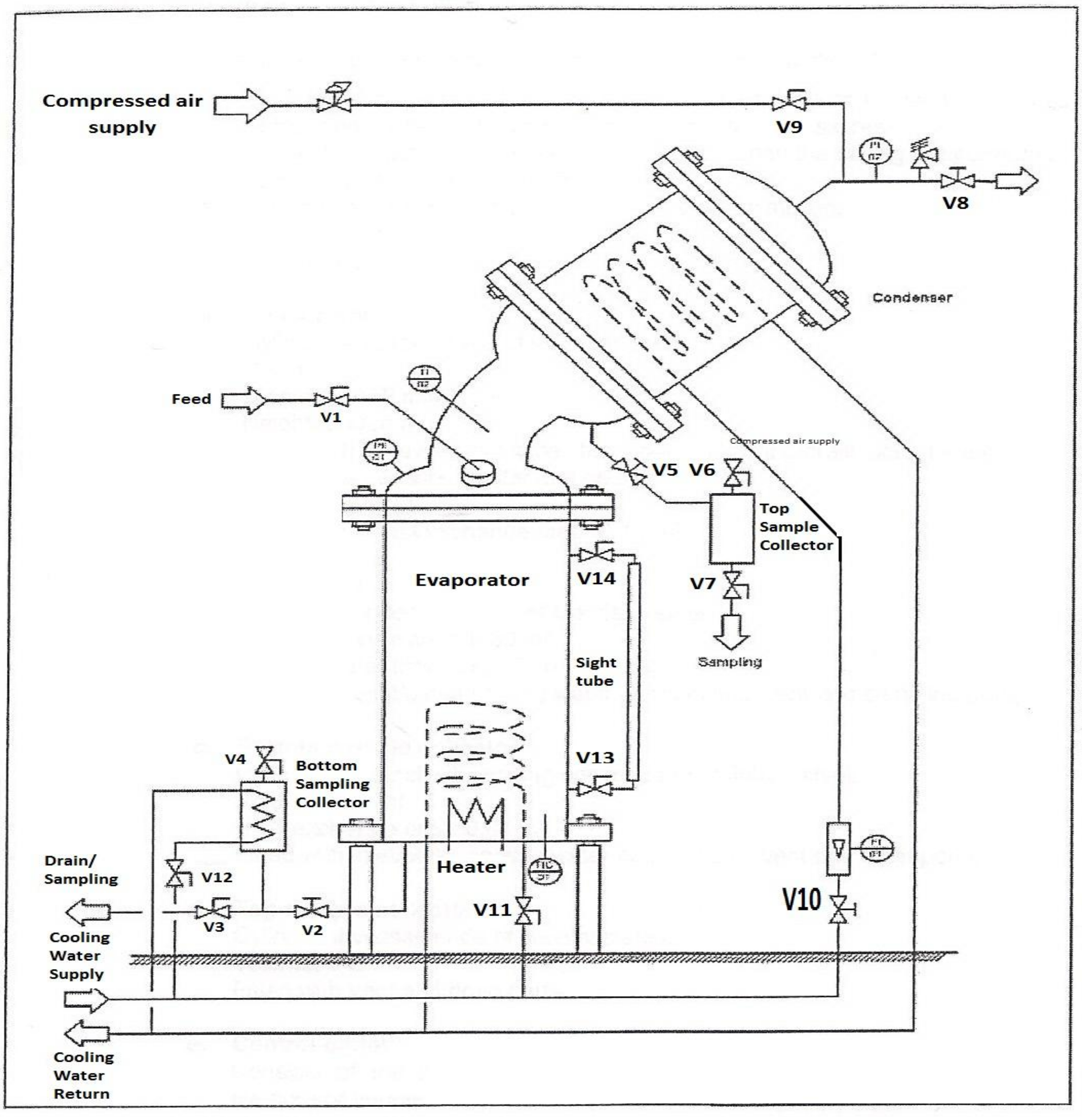


Figure 3.1: Vapour Liquid Equilibrium Unit

3.2 Calibration Curve

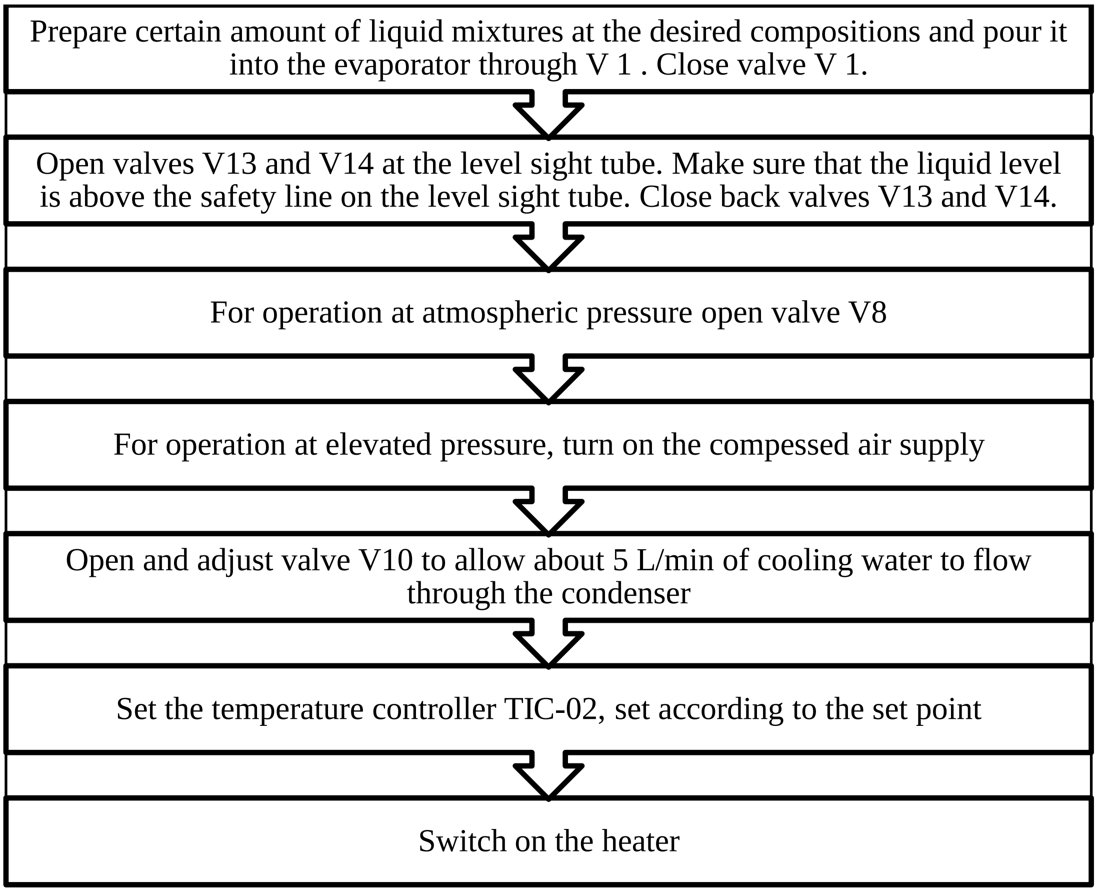
Eleven samples of MTBE-MeOH mixtures as listed in Table 3.2 were prepared. The refractive indices of each sample were measured using Atogo Refractometer at normal condition. The data obtained were used to construct a calibration curve which shows refractive indices versus mole fraction of MTBE. The calculation method for the calibration curve was shown in the Appendixes C.

Table 3.2: Calibration Curve volume compositions

MeOH(ml)	MTBE(ml)	Mole fraction MTBE
4.04858	107.155	0.9
8.097	95.249	0.8
12.145	83.343	0.7
16.194	71.437	0.6
20.242	59.53	0.5
24.291	47.624	0.4
28.34	35.718	0.3
32.388	23.812	0.2
36.4372	11.906	0.1

3.3 General Experiment Procedures

The general experiment procedure is the standard procedure for all the experiments for the whole research project. The experiment operated at atmospheric pressure and at different temperature. Flowchart for this procedure is illustrated as in Figure 3.2.



Prepare certain amount of liquid mixtures at the desired compositions and pour it into the evaporator through V 1 . Close valve V 1.

Open valves V13 and V14 at the level sight tube. Make sure that the liquid level is above the safety line on the level sight tube. Close back valves V13 and V14.

For operation at atmospheric pressure open valve V8

For operation at elevated pressure, turn on the compessed air supply

Open and adjust valve V10 to allow about 5 L/min of cooling water to flow through the condenser

Set the temperature controller TIC-02, set according to the set point

Switch on the heater

Figure 3.2: Flowchart for general experimental procedure

3.3.1 Sampling Procedures

Sampling procedures involved two samples. Vapour sampling and liquid sampling is illustrated in Figure 3.3 and Figure 3.4. The entire valve can be referred to Figure 3.1

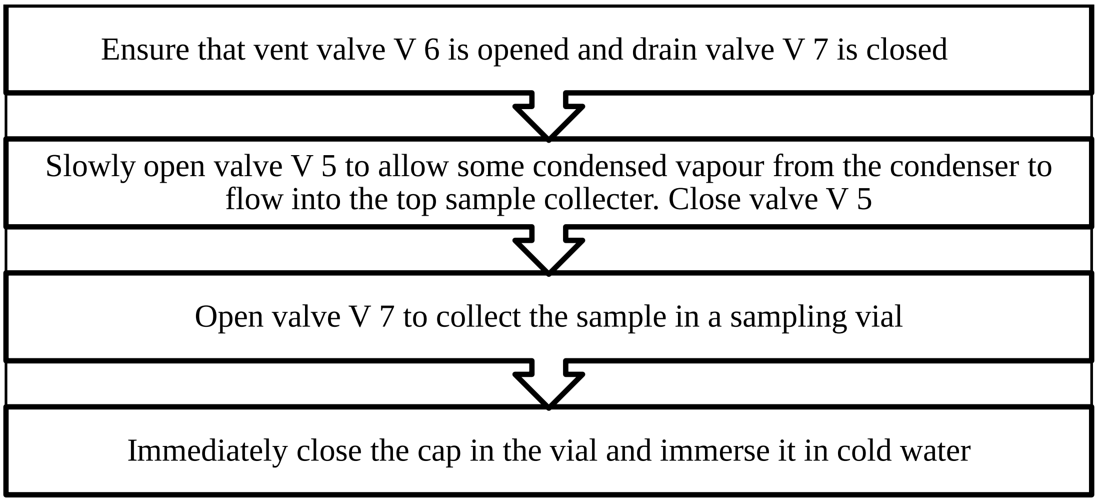


Figure 3.3: Sampling procedure for vapour samples

Liquid sampling procedure is similar to vapour sampling but the liquid samples were collected from the evaporator.

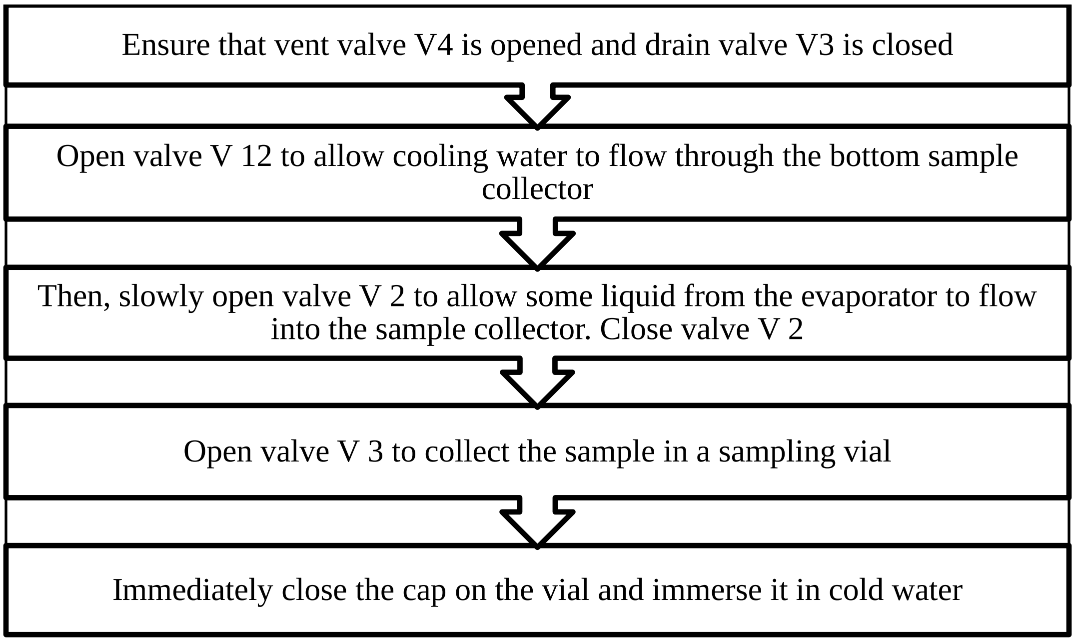


Figure 3.4: Sampling procedure for liquid samples

After collecting both liquid and vapour samples the samples RI Index were measured using Refractometer and the mole fraction of the samples was obtained using calibration curve.

3.4 Research Methodology

The research objective as mention in Chapter 1 is to investigate the effect of different temperature on Vapour Liquid Equilibrium of MTBE-Methanol binary mixture at constant atmospheric pressure 1atm and to investigate azeotropic point of the mixture. Thus the experiment were divided into three sets of experiments

I. Experiment 1: To construct Vapour Liquid Equilibrium Diagram at various Temperatures, thus the experiment ran at 60℃, 70℃ and 75℃. Get the value of *x* and *y* at each of the temperatures. Use these values for *x vs y* diagram.

II. Experiment 2: To construct Vapour Liquid Equilibrium Diagram complete with azeotropic point in order to investigate phenomena, thus ran the experiment at 60℃ .

Table 3.3: List of Data Collected

x	Liquid mole fraction of MTBE in binary mixture
y	Vapour mole fraction of MTBE in binary mixture
TT02	Temperature of Liquid Section in the Equipment
TT01	Temperature of Vapour Section in the Equipment

3.4.1 Effects of Temperatures on Vapor Liquid Equilibrium Diagram of MTBE-Methanol mixture

The operating temperature was firstly set at 60℃ and repeated with temperature 70 ℃ and 75℃. Different feed composition, of MTBE-methanol mixture was prepared as listed in Table 3.4 in Appendixes.

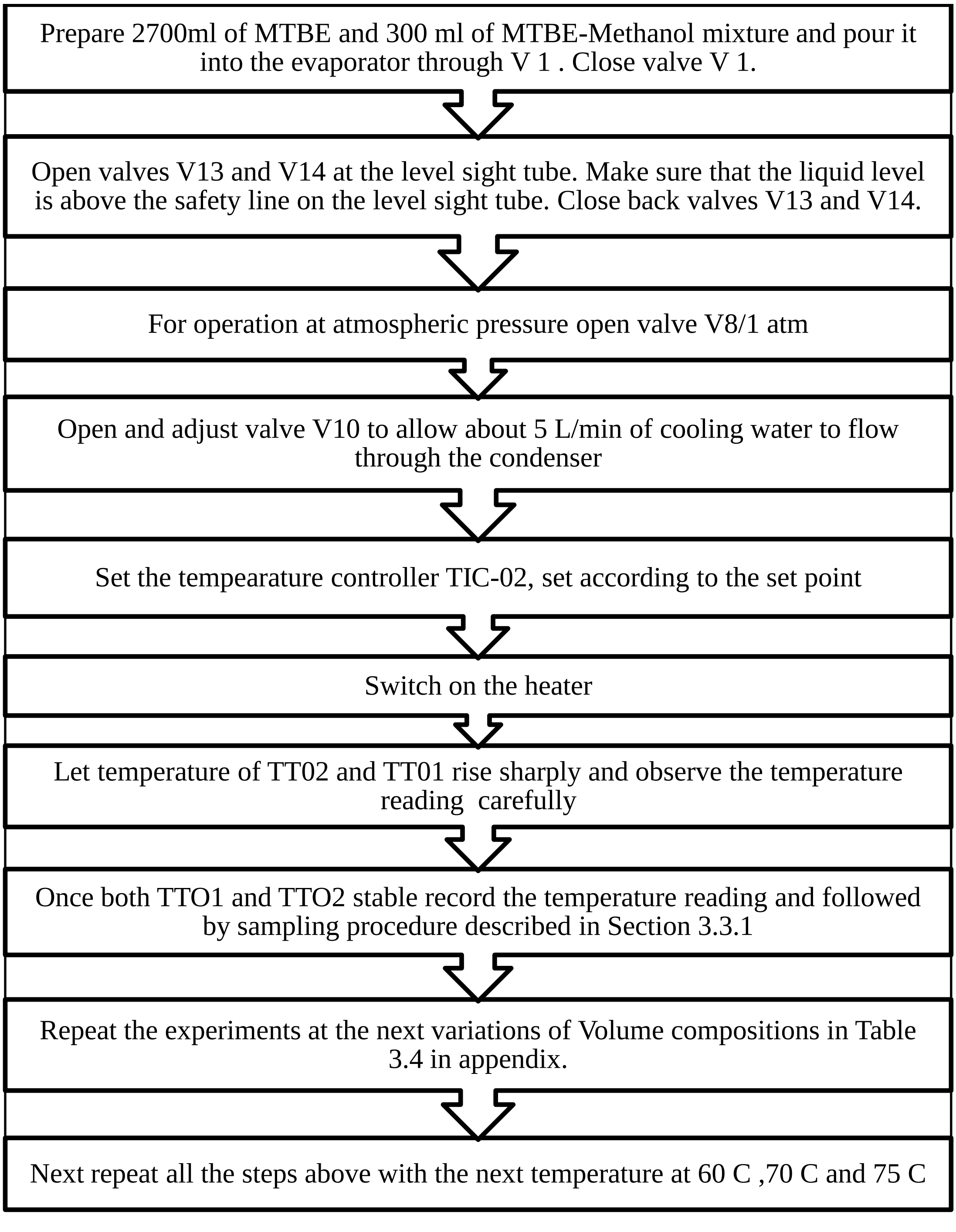
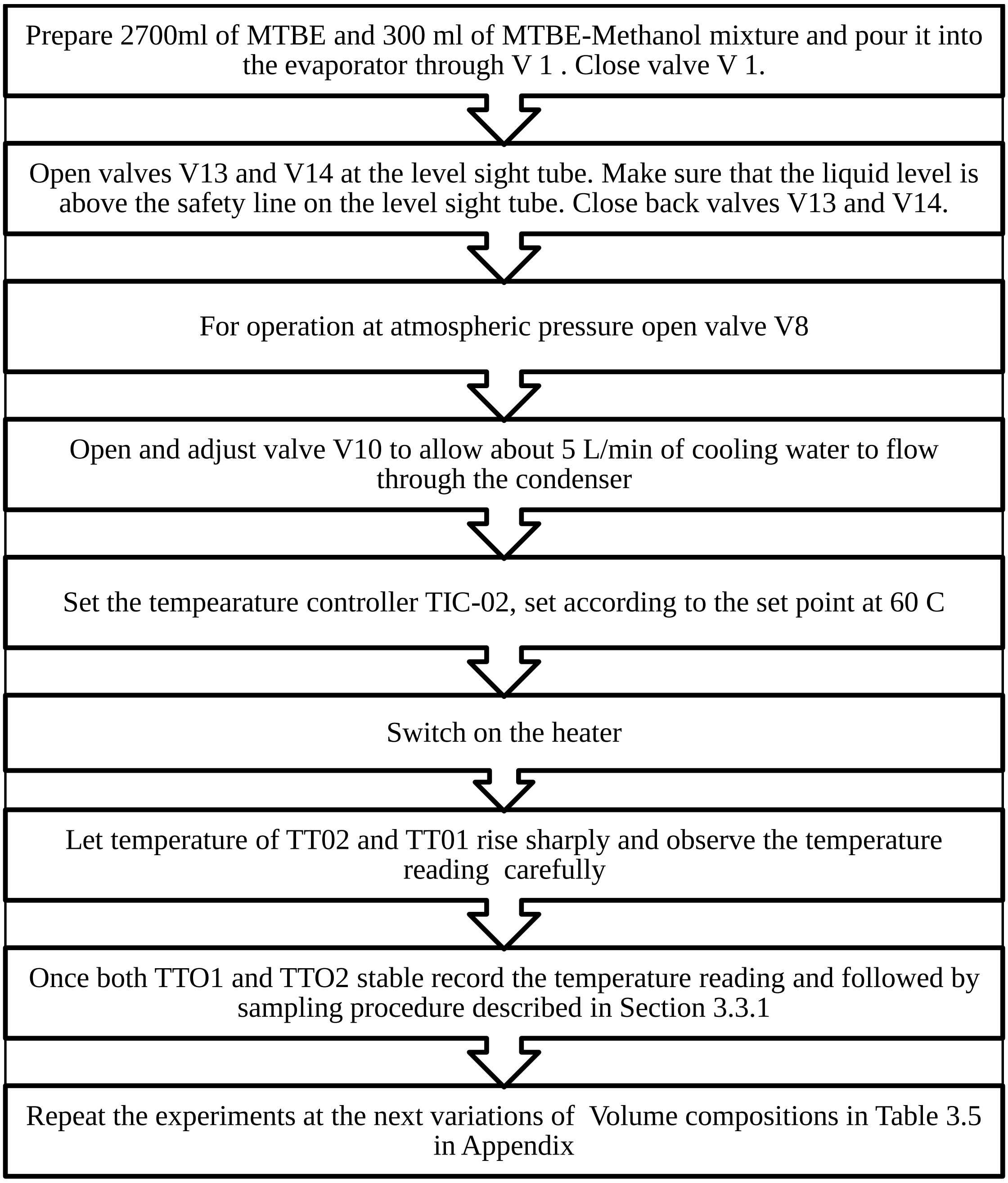


Figure 3.5: Effects of temperature on VLE diagram at 60℃, 70 ℃ and 75 ℃

3.4.2 VLE Diagram of MTBE-Methanol Mixture at 60 ℃ at Various Volume Fractions

Experiment was run at 60 ℃ with 15 variations of volume compositions as described in Table 3.5. All the data as describe in Table 3.3 were recorded to construct *x* and *y* diagrams and *T vs x&y* diagrams.



Prepare 2700ml of MTBE and 300 ml of MTBE-Methanol mixture and pour it into the evaporator through V 1 . Close valve V 1.

Open valves V13 and V14 at the level sight tube. Make sure that the liquid level is above the safety line on the level sight tube. Close back valves V13 and V14.

For operation at atmospheric pressure open valve V8

Open and adjust valve V10 to allow about 5 L/min of cooling water to flow through the condenser

Set the tempearature controller TIC-02, set according to the set point at 60 C

Switch on the heater

Let temperature of TT02 and TT01 rise sharply and observe the temperature reading carefully

Once both TTO1 and TTO2 stable record the temperature reading and followed by sampling procedure described in Section 3.3.1

Repeat the experiments at the next variations of Volume compositions in Table 3.5 in Appendix

Figure 3.6: Experiment procedure for 60 ℃ at various volume fractions

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Standard Curve

The results on standard curve obtained are shown in Table 4.1. Table 4.1 below showed the result from experiment and data from (Aim & Ciprain, 1980).. The data is an RI Index against the mole fraction of MTBE. The figure4.1 was constructed to compare between these two data.

Table 4.1: Result for Calibration Curve

Mole fraction MTBE	RI Experiment Data	RI (Aim & Ciprain, 1980)	Error %
1	1.3659	1.37	0.2992
0.9	1.3649	1.368	0.2266
0.8	1.3643	1.3673	0.2194
0.7	1.363	1.3673	0.3144
0.6	1.3611	1.3638	0.1979
0.5	1.3587	1.3611	0.1763
0.4	1.3555	1.357	0.1105
0.3	1.3514	1.3537	0.1699
0.2	1.3452	1.3478	0.1929
0.1	1.3374	1.3399	0.1865
0	1.3301	1.333	0.2175

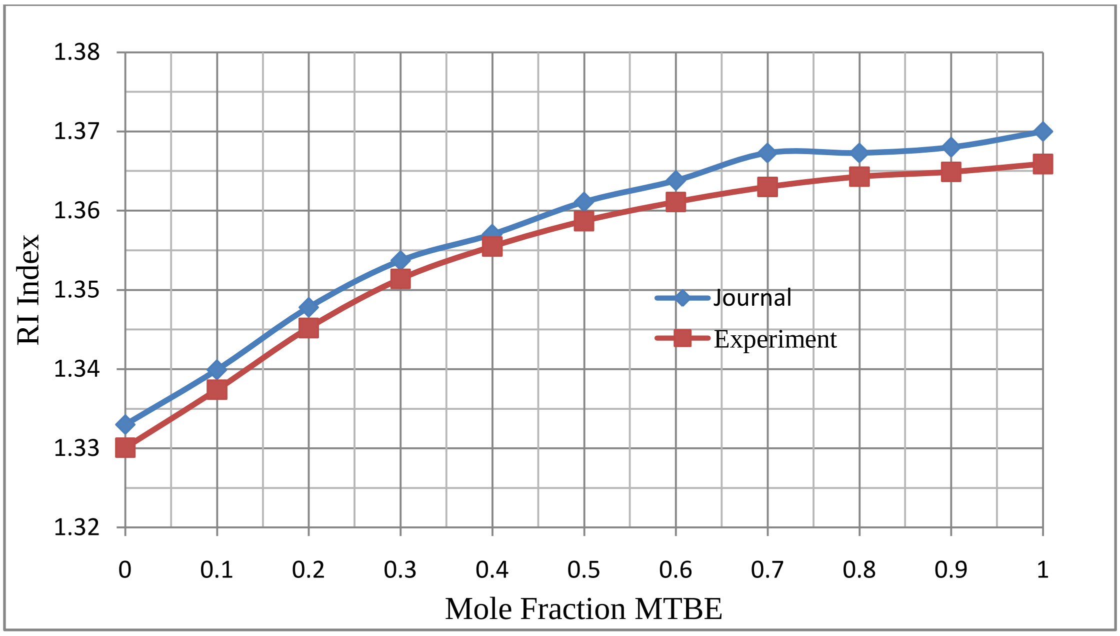


Figure 4.1: Calibration Curve

The results from Journal by (Aim & Ciprain, 1980) and from experiment were shown in the Figure 4.1 indicating only slight error between the two. Justifying the Refractometer used in this experiment can produce accurate results. The average error between the two is around 0.21%

4.2 Effects of Temperatures on Vapor Liquid Equilibrium Diagram of MTBE-Methanol mixture

These experiments were run at 60℃, 70℃, 75℃ .The data obtained are tabulated in Table 4.2 -4.4 and used to construct graph *y vs x*. *x* is the liquid fraction of MTBE while *y* is the vapor fraction of MTBE. In the experiments the data for *x* was obtained from the Liquid Samples Collector that came through Evaporator section of the equipment. Meanwhile *y* is the vapor fraction of MTBE that was collected at the condenser section. Other data obtained are the temperature of TT02 which is the temperature of the Liquid section of the equipment which also the temperature of the Evaporator. The TT01 is temperature of the Vapor section of the equipments. The pressure readings of the experiments are zero at all temperatures meant that pressure reading is 1 atm. Because the all the experiments were operated at constants pressure by opening the valve V8 that exposed the equipment at ambient pressure.

Using the *x* and *y* values to construct the diagram will give insight on how all these different temperatures performed in the *x* and *y* diagram. The patterns of the graph will be observed and compared to results obtain from the literature (Rebecca K. Toghiani, 1996) shown in the Figure 4.3.

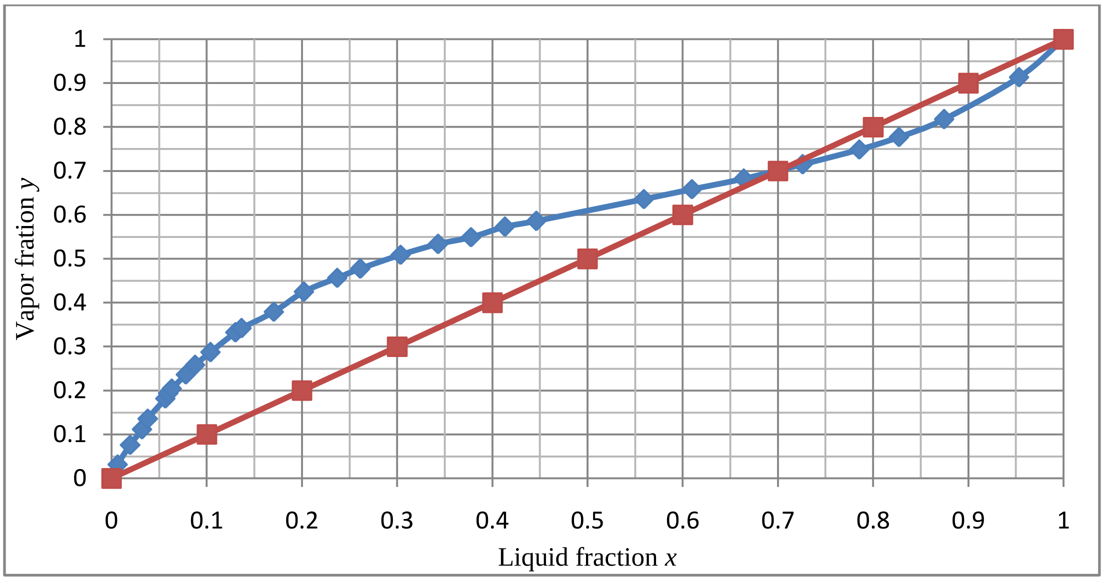


Figure 4.2: Graph of *y vs x* from Journal data (Rebecca K. Toghiani, 1996)

4.2.1 VLE of MTBE-MeOH at 60 ℃

At temperature 60 °C the graph of *x vs y* diagram shown in Figure 4.4This graph is similar to the graph shown in the Journal in Figure 4.3. This can be due to several reasons. The primary reason is at 60 °C the temperature is closer to both components boiling point. The boiling point of Methanol is 64 °C, MTBE 55.2 °C. The boiling point of both components is for 1 atm pressure. The graph in Figure 4.4 showed that there is an interception at *x*=*y* between 0.7~0.8. The interception showed that the diagram of *x* vs *y* formed an azeotropic phenomenon which is the vapor and liquid composition is equal. The type of azeotrope of this mixture is positive azeotrope.

The average volatility at 60 °C is 1.52. The average volatility is lower compared to relative volatility at 70 and 75 °C. The relative volatility at 70 °C is 1.6918 while at 75°C is 2.304. This means that the relative volatility is effectively influenced by temperature and thus pressure. The higher the temperature of the equipment means the pressure is higher thus affecting the relative volatility.

Table 4.2: Relative Volatility at 60 °C

							Average
α	1	1.15	1.35	1.92	2.9	0.84	1.52

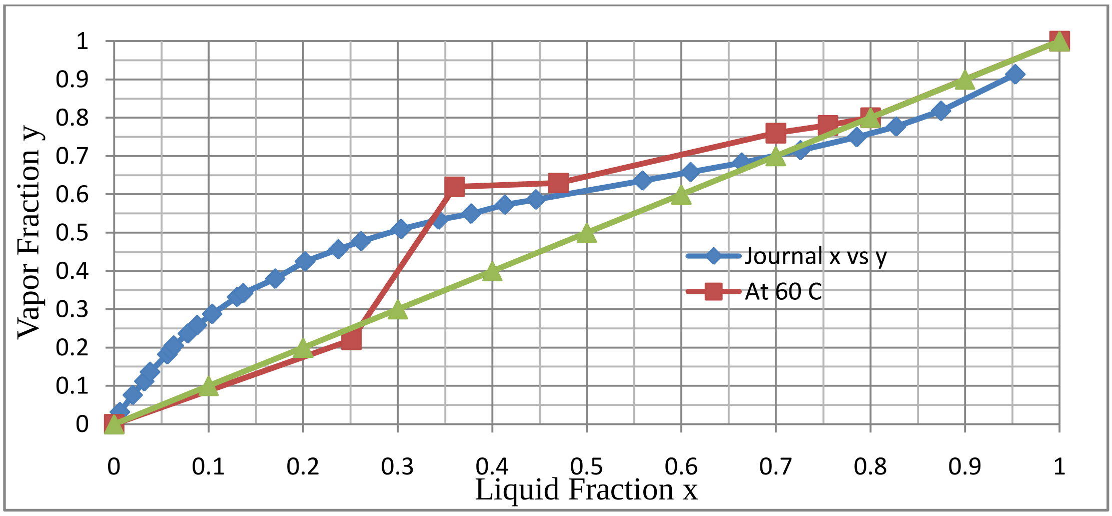


Figure 4.3: Diagram of *x vs y* at 60℃

4.2.2 VLE of MTBE-MeOH at 75 ℃

At temperature 75 °C the graph *x vs y* diagram as shown in Figure 4.5. The graph inclined towards *y* vapor fraction of MTBE. This is due to the facts that at 75 °C, the temperature is too high for the binary mixture components. Thus at operating temperature at 75 °C, most of the liquid inside the evaporator section vaporize to condenser section that will later be read as *y* value. This gives reasons as to why the graph inclined towards *y* axis. The graph also didn't show any interception as seen in Figure 4.4. Thus no azeotrope formed in this experiment.

Table4.3: Relative Volatility at 75 °C

							Average
α	4.04	1.39	1.85	1.71	2.33	2.48	2.3

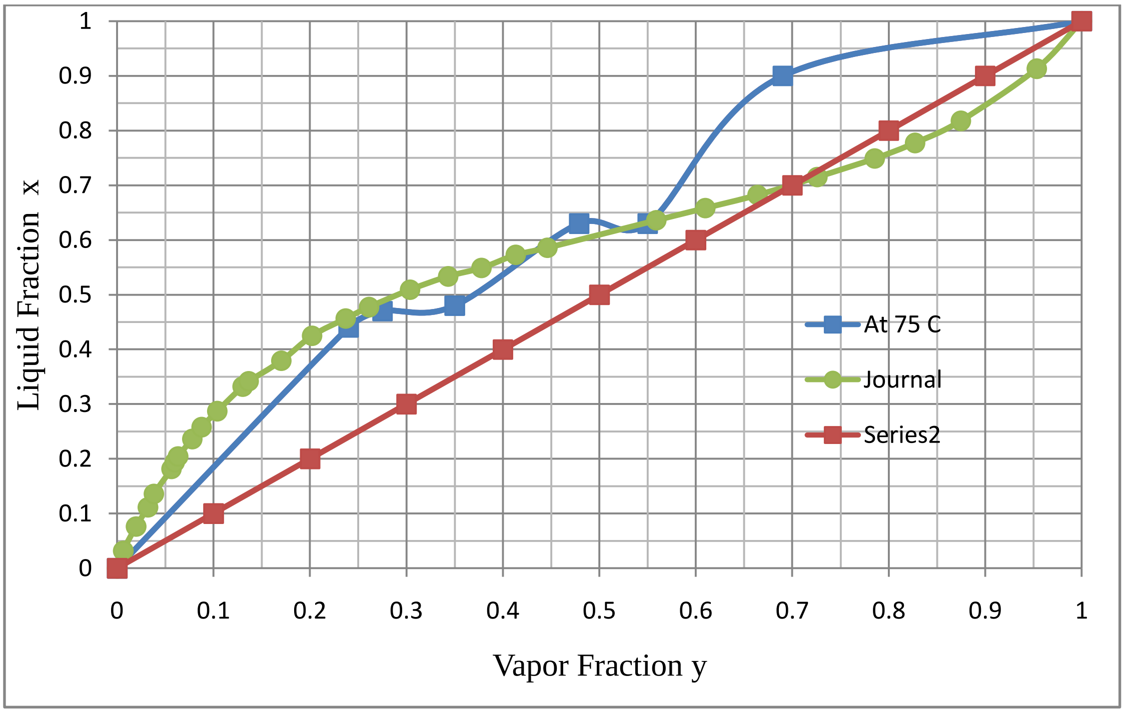


Figure 4.4: *x vs y* diagram at 75 °C

4.2.3 VLE of MTBE-MeOH at 70 ℃

At temperature 70 °C the graph is almost similar in terms of its patterns to the graph of *x vs y* diagram 60 °C .This due to the temperature being closer to the boiling point of both components boiling point. The graph show no interception meant no azeotrope formed. Comparing the Figure 4.5 and Figure 4.6, the latter graph showed to be inclined towards Liquid Fraction *x* because at 70 °C most of the MTBE-MeOH mixture is still in liquid form in comparison with the graph 75 °C which more inclined towards *y* value. Thus from the three graph of Figure 4.4-4.6 the best of graph that closely resembles the graph from Journal is at 60 °C Figure 4.4.

Table4.4: Relative Volatility at 70 °C

							Average
α	1.49	1.66	1.44	1.32	1.708	2.52	1.69

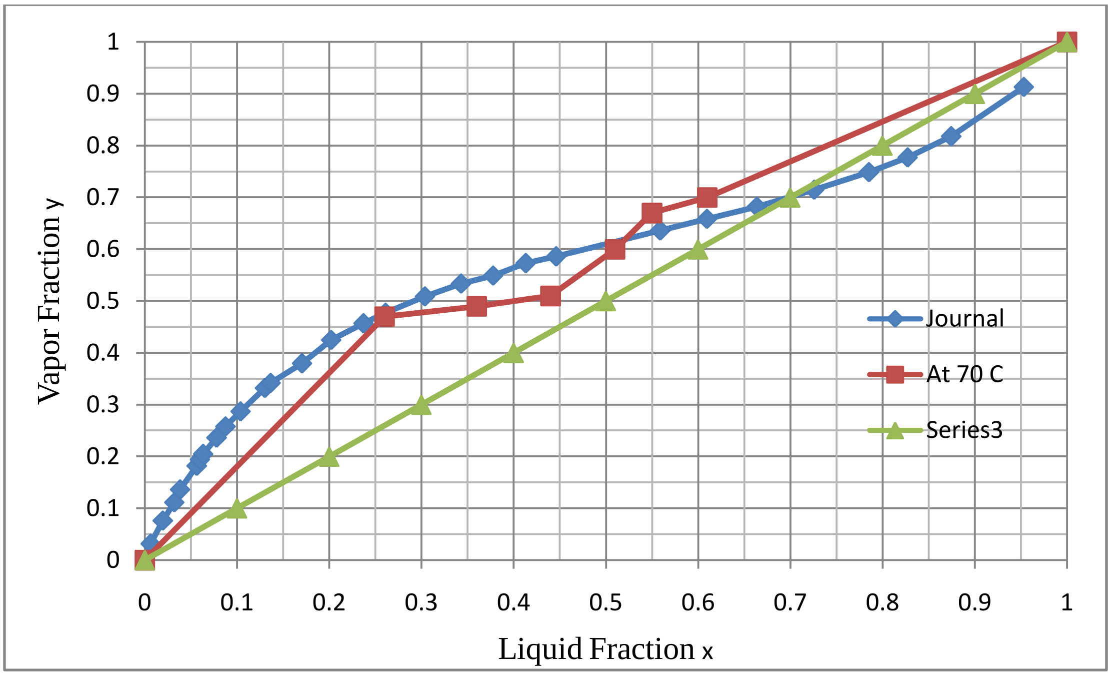


Figure 4.5: *x vs y* diagram at 70 °C

4.3 VLE Diagram of MTBE-MeOH Mixture at 60 ℃ at Various Volume Fractions

In this part of the experiments the decision were made to further the research in constructing Vapor Liquid Equilibrium Diagram with greater accuracy. The objective of the second experiment is to construct diagram of *y vs x* diagram and also *T vs x&y* diagrams. To achieve greater accuracy, a decision made to run the experiments at 60 °C and at more variations of volume compositions. By varying more volume compositions more data of *x* and *y* can be obtained and temperature data to construct *T vs x&y* diagrams. The temperature 60 °C was chosen because among the temperatures of 60 °C, 70℃ and 75 °C, 60 °C graphs of *y vs x* is more likely to produce azeotropic point. Hence the experiments were run with 14 volume variations as described in the Table 4.5 in Appendixes.

Discussing the Figure 4.7, the graph showed azeotropic point as it touched the *x*=*y* line or the equilibrium line. The figure showed azeotropic point at range 0.68~0.7 .This is compatible with the results from journal graph in Figure 4.3. Thus at 60 °C is the most suitable temperature that showed azeotropic point.

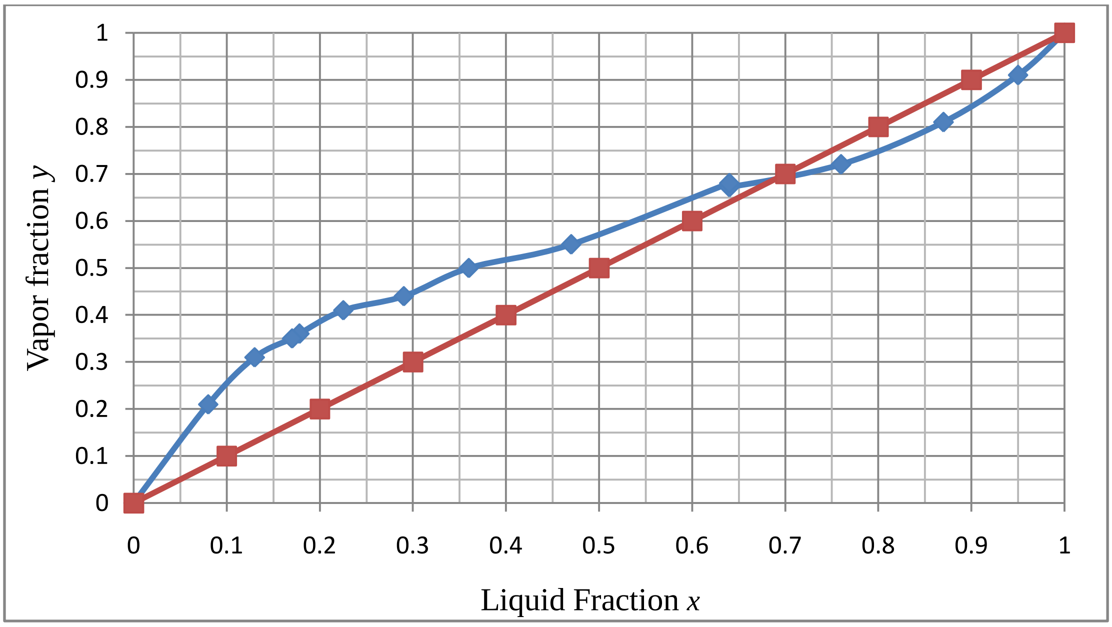


Figure 4.6: *x vs y* diagram at 60℃, with 14 volume variations

Table 4.5: Relative Volatility comparison

x_A	y_A	Relative Volatility α Journal	Relative Volatility α Experiment	Error %
1	1	None	None	None
0.95	0.91	0.5154	0.5321	3.252
0.87	0.81	0.6431	0.6370	0.944
0.76	0.72	0.8154	0.8120	0.413
0.64	0.671	1.2338	1.15087	6.721
0.64	0.68	1.7582	1.1953	32.014
0.47	0.55	2.0064	1.3782	31.307
0.36	0.5	2.3789	1.7777	25.268
0.29	0.44	2.7062	1.9236	28.917
0.22	0.41	2.3789	2.3935	0.617
0.17	0.36	2.7062	2.5976	4.012
0.17	0.35	2.9785	2.6289	11.735
0.13	0.31	3.3247	3.0066	9.565
0.08	0.21	3.6197	3.0569	15.546
			Average Error	13.101

Relative Volatility is a measure comparing the vapor pressure of the components in a liquid mixture of chemicals. For liquid mixture of two components or binary mixture at any given temperature and pressure the relative volatility is defined as

$$\alpha_{AB} = \frac{y_A/x_A}{y_B/x_B} = \frac{y_A/x_A}{1-y_A/1-x_A} \tag{4.1}$$

When the volatilities of both key components are equal, α = 1 and separation of the two by distillation would be impossible under the given conditions because the compositions of the liquid and the vapour phase are the same (azeotrope). As the value of α increase above 1, separation by distillation becomes progressively easier. When a binary mixture is distilled, complete separation of the two components is rarely achieved. Referring to the Table 4.2 the Relative Volatility obtained from the experiments was compared with Journal Relative Volatility (Gmehling, 2002) in an effort to measure the error between. As mentioned above if the Relative Volatility is below 1 the distillation is impossible, observing the Table 4.2 the Relative Volatility is less than 1 in between $x_A = y_A$= 1~0.7. The Relative Volatility between this ranges are in azeotropic condition. The value α starts to be above 1 when the range of $x_A = y_A$ =0.6~0.08 showed that separation is possible at this condition.

Discussing the Figure 4.8 at 60 ℃ the experiment were run at 14 volume variations by holding the MTBE volume constant throughout the experiments. Figure 4.9 is the diagram of *T vs x&y*. Figure 4.9 is the figure of combination of the result obtained in Table 4.2 a) b) and c) in Appendixes. The results that were taken to construct the graph are the temperature of TT02 and the value of *x* and y values MTBE in the mixture. Figure 4.8 is the graph that used all its values from experimental result, Figure 4.9 used temperature from journal and *x&y* value from experiment. Lastly the Figure 4.10 is the graph obtained from journal by (Rebecca K. Toghiani, 1996).

The reasons for comparing these three figures are to indentify which of experimental values are inaccurate. Comparing Figure 4.9 and 4.10, the graphs are very much identical. This showed that the values of *x* and *y* are accurate. Comparing Figure 4.8 with 4.9 the conclusion can be made that there is a slight inaccuracies in the value of temperature obtained in the experiments. This could be due to several reasons. The equipment is exposed to unwanted cooling effect from the surrounding, this disturbed the temperature accuracy. Observing carefully, in the Figure 4.8 and Figure 4.10 the *x* and *y* values against temperature is almost equal or identical. This are due to the facts that when referring to the Table 4.5 a) the volume differences of MTBE to Methanol are smaller.

The problem mostly endured throughout the experiments is when operating the equipments at volume compositions as in Table 4.2 b) and Table 4.2 c) shown in Appendixes. For Table 4.2 c) the volume of MTBE is high in comparisons to Methanol, when operating the experiments at constant pressure the vent V8 was left fully opened in order to operate at 1 atm. The boiling point of MTBE is low at 55.2 ℃, due to its low boiling point when the experiment is operating at 60 ℃, the MTBE that is in large volume will evaporate through to the condenser section and most of the vapour will comes out through vent V8. This will send unpleasant smell throughout the lab and can be considered hazardous. At a point of time, there is a need to partially close or fully close the vent V8. By shutting down the vent V8 change the operating condition of the experiments. The pressure will build up and this will increase the temperature reading. These are the reasons why in Figure 4.8 and at *x* > 0.7 and above the temperature give fluctuative reading.

Discussing further on Figure 4.8 until Figure 4.10, all the diagram of Temperature vs *x y* showed azeotrope at *x* and *y* 0.68~0.7. The diagram also showed that the binary mixture of MTBE-Methanol showed positive azeotrope. Positive azeotrope is when the azeotropic composition such in this mixture 0.68~0.7 of both vapor faction of MTBE and liquid fraction of MTBE have equal boiling point, of 51.4 ℃ . The positive azeotrope is a condition which both liquid fraction *x* and vapor fraction y of MTBE have lower boiling point compared to its components. The positive azeotrope boiling point of the binary mixture that is 51.4 ℃ is lower to both of the components boiling point which is 55.2 ℃ for MTBE and 64 .7℃ for Methanol. That is why positive azeotrope also called minimum boiling mixtures.

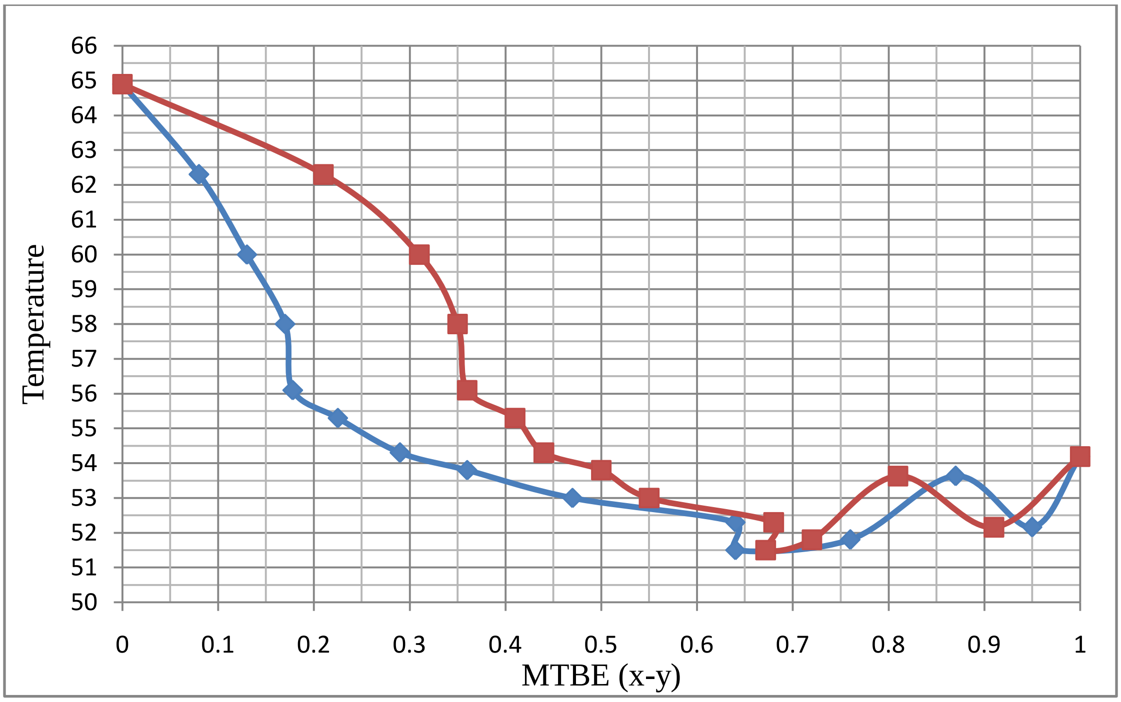


Figure 4.7: Temperature and *x y* values from experiment

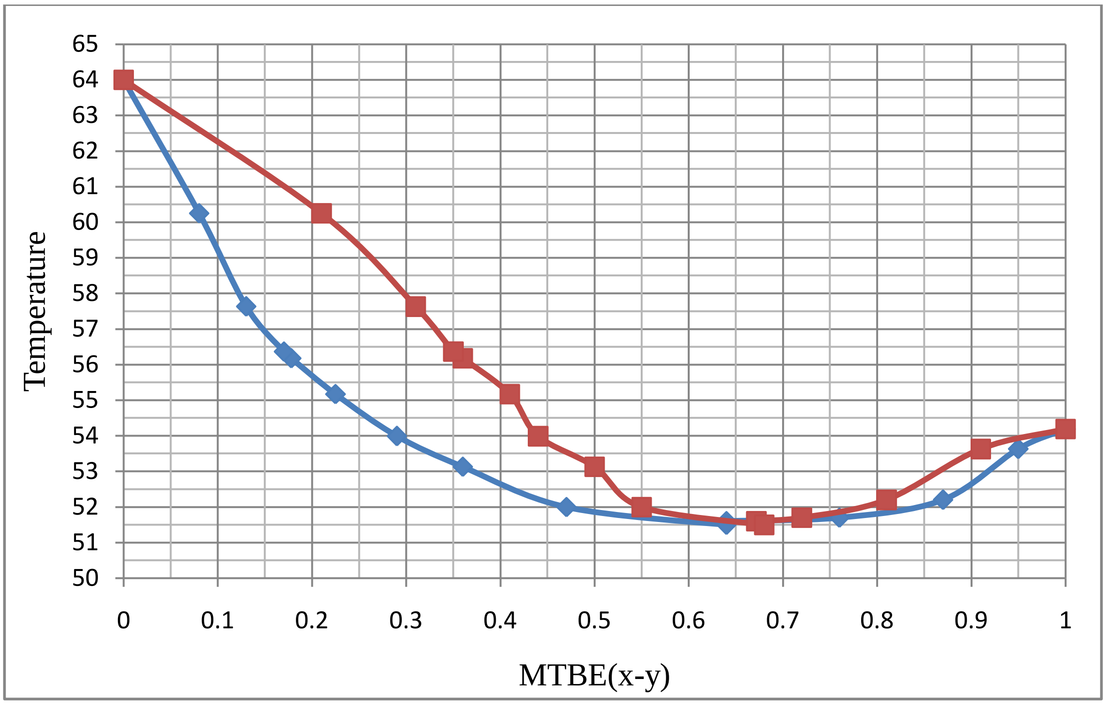


Figure 4.8: Temperature was taken from journal, *x* and *y* values from experiment

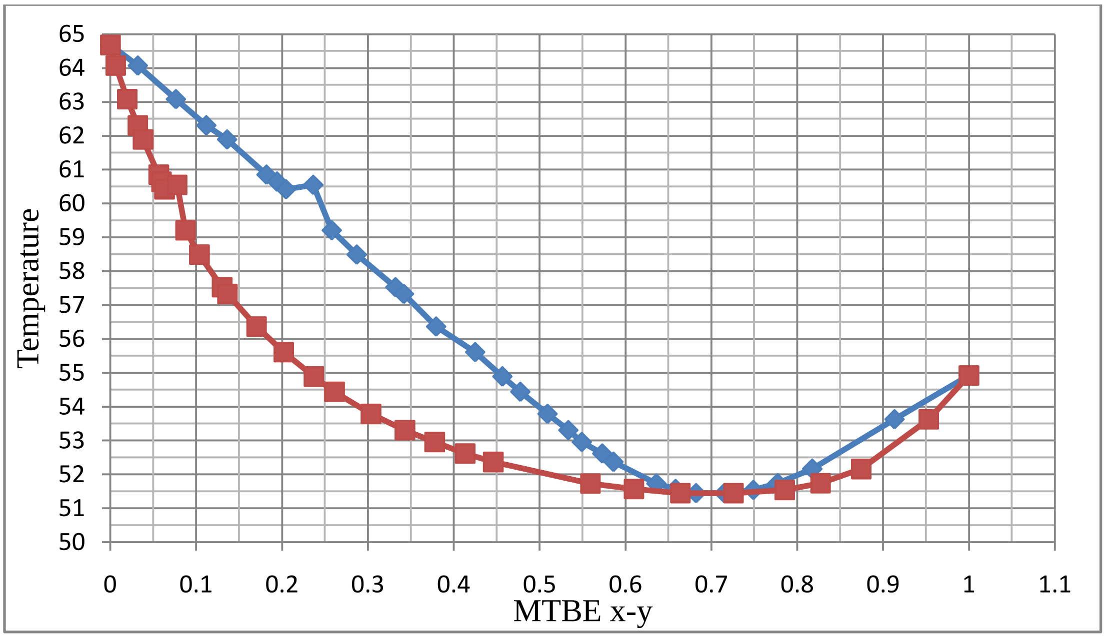


Figure 4.9: Graph Temperature vs *x y* diagram from Journal (Gmehling, 2002)

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Initially the experiment started with calibration curve compared to Journal showed positive result with slight error meant great accuracy. The first part is to find at which temperature between 60 ℃, 70℃ and 75 ℃. The suitable temperature chosen is 60 ℃. The mixture formed azeotropic point at vapour fraction and liquid fraction at 0.68~0.7. The temperature in which the mixture formed azeotropic condition is 51.4 ℃ which is lower to both of the components boiling point. This meant that the Vapour Liquid Equilibrium Diagram of MTBE-Methanol formed positive azeotrope or minimum boiling point mixture. The azeotrope of the mixture posed problems during distillation process.

5.2 Recommendation

The recommendations that can be suggested from this research are, once the azeotropic point has been identified. The research for entrainer that is cheap and efficient must continue to further improve the distillation process. Other suggestions that can be made, using this method to construct Vapour Liquid Equilibrium is much easier and straightforward compared to method suggested by most journals which required complicated calculation method. Last recommendation for this research are the vent V8 issues on should be addressed especially when operating components that is hazardous and have low boiling point.

APPENDICES A

Table 3.4: Volume variations for 60℃, 70℃, 75℃

MTBE (ml)	Methanol (ml)	x(MTBE)
2700	300	0.75
2700	380	0.7
2700	610	0.6
2700	900	0.5
2700	1350	0.4
2700	2100	0.3
2700	2750	0.25
2700	3300	0.21

Table 3.5: Volume variations at 60°C

MTBE (ml)	Methanol (ml)	Mole fraction MTBE
3000	100	0.91
3000	200	0.836
2700	380	0.7
2700	680	0.57
2700	900	0.5
2700	1350	0.4
2700	1750	0.344
2700	2100	0.3
2700	2750	0.25
2700	3300	0.21
1000	2000	0.145
1000	2800	0.1
1000	4200	0.074
1000	5000	0.05

APPENDICES B

Table 4.2 a): Volume variations

Temperature=60								
MTBE (ml)	Methanol (ml)	x(MTBE)	TT01	TT02	RI Index		*y* vapour	*x* liquid
					Vapour	Liquid		
2700	380	0.7	50.6	51.5	1.3655	1.3459	0.8	0.64
2700	680	0.57	50.8	51.8	1.3637	1.3644	0.72	0.76
2700	900	0.5	51.1	52.3	1.3628 1.3624	1.362 1.3621 1.3618	0.68	0.64
2700	1350	0.4	52	53	1.3602 1.3608 1.3606	1.3586 1.358	0.55	0.47
2700	1750	0.344	52.5 52.6	53.7 53.8 53.9	1.3598 1.356 1.3595	1.354 1.3539 1.3541	0.5	0.36
2700	2100	0.3	53 53.1	54.3 54.4 54.5	1.3577 1.3577	1.3507 1.351 1.3509	0.44	0.29
2700	2750	0.25	54.1	55.3 55.2 54.5	1.3568 1.3567 1.3567	1.3476 1.3478 1.3472	0.41	0.225
2700	3300	0.21	54.9 55	56.1 56.2 56.3	1.3546 1.3543	1.3437 1.3437	0.36	0.178

Table 4.2 b): Volume variations

Temperature=60								
MTBE (ml)	Methanol (ml)	x(MTBE)	TT01	TT02	RI Index		*y*	*x*
					Vapour	Liquid	vapour	liquid
1000	2000	0.145	55.1	56 57	1.354	1.3517	0.355	0.28
1000	2800	0.1		58	1.3548 1.3555	1.3431 1.3432	0.35	0.17
1000	4200	0.074		60	1.35 1.3486	1.3422 1.3399	0.31	0.13
1000	5000	0.05		62.3 62.1	1.346 1.347	1.3374 1.3365	0.21	0.08

Table 4.2 c): Volume variations

Temperature=60								
MTBE (ml)	Methanol (ml)	x(MTBE)	TT01	TT02	RI Index		*y*	*x*
					Vapour	Liquid	vapour	liquid
3000	100	0.91		52.16	1.365 1.3647	1.9657 1.9653	0.91	0.95
3000	200	0.836		53.63	1.3645 1.3647	1.3649	0.81	0.87

Table 4.2: Temperature 60 ℃

Temperature=60 ℃								
MTBE (ml)	Methanol (ml)	x(MTBE)	TT01 Vapour	TT02 Liquid	RI Index		Vapour *y*	Liquid *x*
					Vapour	Liquid		
2700	300	0.75	50.2	50.7	1.3647	1.3557	0.8	0.41
				50.9	1.3649	1.3558		
				51				
2700	380	0.7	50.3	51.1	1.3668	1.3534	0.8	0.64
				51.2		1.3623		
					1.3665			
2700	610	0.6	50.4	51.3	1.3655	1.364	0.9	0.75
					1.3656	1.3638		
					1.3653	1.3641		
2700	900	0.5	50.7	51.4	1.3648	1.3629	0.76	0.7
			50.8	51.6	1.3651			
				51.7	1.365			
2700	1350	0.4	51.5	52.3	1.3619	1.3584	0.63	0.47
			51.4	52.4	1.3625	1.3586		
				52.5				
2700	2100	0.3	52.4	53.5	1.3622	1.3552	0.62	0.36
			52.6	53.6	1.3618	1.3541		
			52.7	53.8	1.3616	1.3541		
2700	2750	0.25	53.3	54.1	1.3603	1.3486	0.55	0.25
			53.5	54.7	1.3599	1.3487		
			53.6	54.8	1.3594	1.3488		

Table 4.3: Temperature 75 ℃

Temperature=75 ℃								
MTBE (ml)	Methanol (ml)	x(MTBE)	TT01	TT02	RI Index		Vapour *x*	Liquid *y*
			Vapour	Liquid	Vapour	Liquid		
2700	300	0.75	50.2	51 51.1	1.366 1.3662 1.3659	1.3586 1.3588 1.36	0.93	0.5
2700	380	0.7	50.3	51.2	1.3651 1.366 1.3651	1.3627 1.3628	0.9	0.99
2700	610	0.6	50.4 50.5	51.3 51.4	1.3656 1.3651 1.3653	1.363	0.9	0.69
2700	900	0.5	50.8 50.9	51.7 51.8	1.3619 1.3615 1.3616	1.3604 1.3611 1.361	0.63	0.55
2700	1350	0.4	51.4 51.5	52.1 52.2 52.5	1.3619 1.3615 1.3616	1.3587 1.3593 1.3587	0.63	0.479
2700	2100	0.3	52.4	53.6 53.7	1.3588 1.3588 1.3588	1.3537 1.3539 1.3545	0.48	0.35
2700	2750	0.25	53.3 53.4 53.5	54.4 54.5 54.7	1.3583 1.3582 1.3583	1.3498 1.3497 1.3501	0.47	0.275
2700	3300	0.21	54.3 54.1	55.3 55.4 55.5	1.3564 1.357 1.3567	1.347 1.3476 1.3478	0.44	0.24

Table 4.4: Temperature 70 ℃

Temperature=70								
MTBE (ml)	Methanol (ml)	x(MTBE)	TT01	TT02	RI Index		Vapour y	Liquid x
			Vapour	Liquid	Vapour	Liquid		
2700	300	0.75	50.1	51.3	1.3436 1.3632	1.3614 1.358	0.7	0.61
2700	680	0.57	50.4	51.1	1.363 1.36	1.36	0.67	0.55
2700	900	0.5	50.7	51.5	1.361	1.359	0.6	0.51
2700	1350	0.4	51	52.1 52.2 52.5	1.359	1.357	0.51	0.44
2700	2100	0.3	52.3 52.5 52.6	53.2 53.3 53.8	1.3592	1.3545	0.49	0.36
2700	2750	0.25	53.5 53.6	54.8 54.9	1.3573 1.358	1.349	0.47	0.26

Table 4.5 a)

Temperature=60								
MTBE (ml)	Methanol (ml)	x(MTBE)	TT01	TT02	RI Index		*y*	*x*
					Vapour	Liquid	vapour	liquid
2700	380	0.7	50.6	51.5	1.3655	1.3459	0.8	0.64
2700	680	0.57	50.8	51.8	1.3637	1.3644	0.72	0.76
2700	900	0.5	51.1	52.3	1.3628 1.3624	1.362 1.3621 1.3618	0.68	0.64
2700	1350	0.4	52	53	1.3602 1.3608 1.3606	1.3586 1.358	0.55	0.47
2700	1750	0.344	52.5 52.6	53.7 53.8 53.9	1.3598 1.356 1.3595	1.354 1.3539 1.3541	0.5	0.36
2700	2100	0.3	53 53.1	54.3 54.4 54.5	1.3577 1.3577	1.3507 1.351 1.3509	0.44	0.29
2700	2750	0.25	54.1	55.3 55.2 54.5	1.3568 1.3567 1.3567	1.3476 1.3478 1.3472	0.41	0.225
2700	3300	0.21	54.9 55	56.1 56.2 56.3	1.3546 1.3543	1.3437 1.3437	0.36	0.178

Table 4.5 b)

Temperature=60								
MTBE (ml)	Methanol (ml)	x(MTBE)	TT01	TT02	RI Index		*y*	*x*
					Vapour	Liquid	vapour	liquid
1000	2000	0.145	55.1	56 57	1.354	1.3517	0.355	0.28
1000	2800	0.1		58	1.3548 1.3555	1.3431 1.3432	0.35	0.17
1000	4200	0.074		60	1.35 1.3486	1.3422 1.3399	0.31	0.13
1000	5000	0.05		62.3 62.1	1.346 1.347	1.3374 1.3365	0.21	0.08

Table 4.5 c)

Temperature=60								
MTBE (ml)	Methanol (ml)	x(MTBE)	TT01	TT02	RI Index		*y*	*x*
					Vapour	Liquid	vapour	liquid
3000	100	0.91		52.16	1.365 1.3647	1.9657 1.9653	0.91	0.95
3000	200	0.836		53.63	1.3645 1.3647	1.3649	0.81	0.87

APPENDICES C

The calculation method for Calibration curve is as follows:

Mole fraction 0.9 of MTBE in binary mixture, thus 0.1 moles for Methanol

$$0.9 = \frac{Density}{Molecular\ Mass} \times Volume(ml)$$

1 *cc* = 1 *ml*

$$0.9 = \frac{0.7404\ \mathrm{g/cc}}{88.15\ \mathrm{g/mol}} \times Volume(\mathrm{ml})$$

Volume of MTBE =<u>107.1515 *ml*</u>

0.1 mole fraction of Methanol

$$0.1 = \frac{0.7918\ \mathrm{g/cc}}{32.04\ \mathrm{g/mol}} \times Volume(\mathrm{ml})$$

1 *cc* = 1 *ml*

Volume of Methanol = <u>4.046 *ml*</u>

Mixing 107.1515 *ml* MTBE with 4.046 *ml* Methanol will produced 0.9 mole fraction of MTBE in MTBE-Methanol mixture. Next step gets the RI Index using Refractometer. Repeat the calculations and procedure above for 0.8 to 0.1 mole fraction MTBE. Construct the calibration curve of RI Index against mole fraction MTBE.

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