

**VAPOR-LIQUID EQUILIBRIA IN THE SYSTEMS METHYL OLEATE +
METHANOL & METHYL OLEATE + WATER**

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ABSTRACT

Biodiesel is now considered the next generation of replacement for petroleum and they can be easily produced from esterification of fatty acid with alcohol and this process usually requires distillation to purify the biodiesel product. For column designs and process simulation, thermodynamic properties such as vapor-liquid equilibrium data of the related components are valuable. In this present study, vapor-liquid equilibrium data for the binary systems of methyl oleate + methanol and methyl oleate + water will be measured at isobaric condition (80kPa and atmospheric pressure). The mixtures were introduced into the equilibrium cell, heated to the desired temperature and at the same time maintaining the pressure. When the system had reached equilibrium, the samples were taken and underwent evaporation using rotary evaporator to remove the more volatile component. The results taken were then correlated with UNIQUAC and NRTL-RK thermodynamic activity coefficient models and it was found out that UNIQUAC is better fitted for methyl oleate + methanol system with absolute average relative deviation (AARD) of 0.0126-0.0409 compared to the NRTL-RK with AARD of 0.396-0.4176 while NRTL-RK is better fitted for methyl oleate + water system with AARD of 0.0004039-0.0463 compared to the UNIQUAC with AARD of 0.1703-0.1948. It was also found out that the pressure will affect separation speed. With the optimum separating condition of low pressure at high temperature, it can help the industry to design a more cost effective separation column.

ABSTRAK

Biodiesel sekarang dianggap sebagai pengganti minyak bumi dan mereka mudah dihasilkan dari pengesteran asid lemak dengan alkohol dan proses ini biasanya memerlukan penyulingan untuk mendapat produk biodiesel yang tulen. Untuk desain kolom dan simulasi proses, sifat termodinamik seperti data keseimbangan wap-cecair dari bahagian-bahagian berkaitan adalah sangat berharga. Dalam kajian ini, data keseimbangan wap-cecair untuk sistem binari metanol metil oleik + dan metil oleik + air akan diukur pada keadaan isobarik (tekanan 80kPa dan atmosfera). Campuran diperkenalkan ke dalam sel ekuilibrium, dipanaskan ke suhu yang dikehendaki dan pada masa yang sama tekanan akan dijaga. Apabila sistem telah mencapai keseimbangan, sampel akan diambil dan menjalani pengewapan menggunakan 'rotary evaporator' untuk menguap komponen yang lebih tidak stabil. Keputusan yang diambil kemudian dikorelasi dengan model UNIQUAC dan NRTL-RK aktiviti termodinamik pekali dan ditemui bahawa UNIQUAC lebih baik sesuai untuk sistem metil oleik + metanol dengan 'absolute average relative deviation' (AARD) dari 0.0126-0.0409 dibandingkan dengan NRTL-RK yang mempunyai AARD dari 0.396-0.4176 sementara NRTL-RK adalah lebih sesuai untuk sistem metil oleik + air dengan AARD dari 0.0004039-0.0463 berbanding dengan UNIQUAC dengan AARD dari 0.1703-0.1948. Hasil dari eksperimen ini juga mendapati bahawa tekanan akan mempengaruhi kelajuan pemisahan. Dengan keadaan pemisahan optimum iaitu pada tekanan rendah dan suhu yang tinggi, ini dapat membantu industri untuk mereka kolom pemisahan yang kos efektif.

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LIST OF ABBREVIATIONS

VLE		Vapor-Liquid Equilibrium
UNIQUAC		Universal QuasChemical
NRTL		Non Random Two Liquid
RK	-	Redlich Kwong
UNIFAC		Universal Functional Activity Coefficient
CPA-EoS		Cubic-Plus-Association Equation of State
AADT		Average Absolute Deviation in Temperature
ASOG	-	Analytical Solution of Group
VLLE	-	Vapor-Liquid-Liquid Equilibrium
LLE		Liquid-Liquid Equilibrium
HOC		Hayden and O'Connell
DMSO		Dimethyl Sulfoxide
FAME		Fatty Acid Methyl Ester
AARD		Absolute Average Relative Deviation

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CHAPTER 1

INTRODUCTION

Biodiesel has become a promising and sustainable short-term alternative fuel, as the continuous hike in crude oil prices, scarce resources of fossil energies and environmental concerns limit the usage of petroleum-based fuels. It consists of a blend of fatty acid alkyl esters that can be mixed in all proportions with regular diesel, is made from renewable sources and presents several environmental and economical benefits ^[1]. It is easily biodegradable, has a more favorable combustion profile, and offers no significant storage or transport problems.

Methyl oleate, a type of fatty acid ester, is one of the biodiesel derived from the esterification of free fatty acid with excess of alcohol. Pure methyl oleate appears as pale yellow oily liquid with boiling point of 218°C at 20mmHg. It is insoluble in water. Fatty acid esters can be used as the raw materials of emulsifiers or oiling agents for foods, spin finishes and textiles; lubricants for plastics; paint and ink additives; surfactants and base materials for perfumery, solvents or co solvents, oil carrier in agricultural industry, as lubricant and diluents for the products like oils ^[2]. It is also used in pharmaceutical applications such as emollients, perfuming agents and skin conditioning ^[3].

In a typical biodiesel production through esterification, the feed of free fatty acid and methanol will be introduced into the reactor for esterification process. The products then will be separated through separation column to retrieve excess methanol and to separate the biodiesel to get a high quality of it.

1.1 Importance of VLE Data on Separation

Vapor-Liquid Equilibrium is a condition in which liquid and gas is in equilibrium with each other meaning that the rate of vaporization is equal to the rate of condensation. Concentration of vapor in contact with its liquid is termed as vapor pressure or partial pressure if other gas(es) are present with the vapor at the same time. Vapor pressure of a liquid in equilibrium is usually temperature dependent. For the effective separation of the reaction mixture into its valuable components, the vapor-liquid equilibrium (VLE) data for the various mixtures are required. Concentrations of each component are often expressed as mole fractions in mixtures containing two or more components where their concentrations are compared in the vapor and liquid phases. When at a certain temperature, the total of partial pressures of all the components becomes equal to the overall pressure of the system such that vapors generated from the liquid displace any air or other gas which maintained the overall pressure and the mixture is said to be boiling and the corresponding temperature is the boiling point. A boiling point at an overall pressure of 1 atm is called the normal boiling point.

Vapor-liquid equilibrium (VLE) underpins the bulk of industrial separation processes, particularly in distillation processes. The composition of the liquid phase will be designated by the mole fraction of the more volatile component (lower boiling point), represented by x . The mole fraction of the other component will be represented $1 - x$. Likewise, the mole fraction of the vapor will be represented by y ,

with $1 - y$ being the composition of the other component in the vapor phase. When the liquid mixture is heated to its boiling point, the vapor produced will, in general, have a different composition than the liquid. Thus, boiling the mixture produces a partial separation of the components occurs. If the vapor is collected, it can be condensed and boiled again to further change the composition.

Distillation columns use this principle effectively repeating the separation process at individual trays within a column. Such columns may have over a hundred trays on which VLE is occurring.

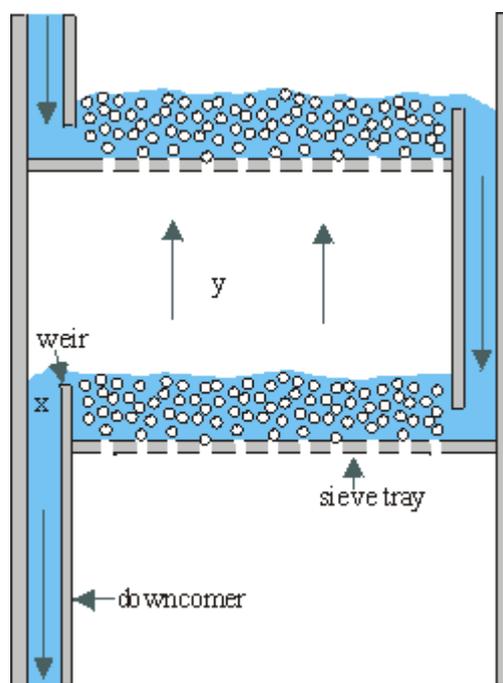


Figure 1.1: Separation Process in Distillation Column

Figure 1.1 shows a small section of a tray-type distillation column. Two sieve trays are shown. Hot vapor (shown in white) flows up through the holes in the sieve tray and vigorously bubbles through the liquid (shown in blue). The vapor and liquid mix on this tray and the new mixture boils. The composition of the liquid, x , leaving the tray will be enriched in the less volatile component while the composition of the vapor, y , will be enriched in the more volatile component. The vapor rises up to the

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next tray where it will contact a liquid of larger x and mixing and re-equilibration will again occur. The liquid leaving the tray will flow over the weir and down the downcomer to the next tray where it will mix with the vapor on that tray. In this way, x tends to become smaller at each lower tray, while y tends to increase at each tray higher in the column. VLE refers to the relationship between the x and y values on each tray.

Due to the fact that distillation columns are designed based on the boiling point properties of the components in the mixtures being separated, an in depth understanding in vapor liquid equilibrium is essential to the development of chemical processing and the design of separation equipment. Hence, the sizes, especially the height of distillation columns and number of trays required can be determined by the vapor liquid equilibrium (VLE) data for the specific mixtures. These data can be obtained experimentally or estimated using generalized methods which allow the calculation of the properties of the mixtures. Most systems in industrial application show deviations from ideal behavior.

1.2 Thermodynamic Representation of VLE Data

Thermodynamics provides the mathematical framework for the systematic correlation, extension, generalization, evaluation, and interpretation of data. Hence, it is the means by which the predictions of various theories of molecular physics and statistical mechanics may be applied to practical purposes. When thermodynamics is applied to vapor/liquid equilibrium, the goal is to find by calculation the temperatures, pressures, and compositions of phases in equilibrium.

1.2.1 Raoult's Law

One of the simplest representations of VLE data is the Raoult's Law. Raoult's law relates the vapor pressure of components to the composition of the solution. The law assumes ideal behavior. 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 approach zero, the behavior of gases approach the behavior of the ideal gas and Raoult's law is similar in that it assumes that the physical properties of the components are identical. The more similar the components, the more their behavior approaches that described by Raoult's law. A limitation of Raoult's Law is that it can be applied only to species of known vapor pressure, and this requires the species to be subcritical; meaning that it has to be at a temperature below its critical temperature. An important and useful feature of Raoult's Law is that it is valid for any species present at a mole fraction approaching unity, provided only the vapor phase is an ideal gas.

Using the example of a solution of two liquids, A and B, if no other gases are present the total vapor pressure, P_{tot} , above the solution is equal to the sum of the vapor pressures of the two components, P_A and P_B .

$$P_{tot} = P_A + P_B \quad (1.1)$$

If the two components are very similar, or in the limiting case, differ only in isotopic content, then the vapor pressure of each component will be equal to the vapor pressure of the pure substance, P^o , times the mole fraction in the solution. This is Raoult's law.

$$P_A = P_A^o x_A \quad (1.2)$$

Where,

P_A = partial pressure of the component A in mixture

P_A° = vapor pressure of the pure component A

x_A = mole fraction of the component A in solution (in mixture)

Thus the total pressure above solution of A and B, P_{tot} would be;

$$P_{tot} = P_A^\circ x_A + P_B^\circ x_B \quad (1.3)$$

P_A° can be calculated using Antoine Equation;

$$\ln P_A^\circ(\text{kPa}) = D - \frac{E}{(T(^{\circ}\text{C}) + F)} \quad (1.4)$$

Where,

D , E , and F = constants in Antoine Equation

1.2.2 K-Value Distribution Coefficient

VLE data can also be represented by the K-Value correlations. Equilibrium ratio, K_i , is a convenient way to measure the tendency of a given chemical species to partition itself preferentially between liquid and vapor phases.

$$K_i = \frac{y_i}{x_i} \quad (1.5)$$

The K-value measures the lightness of a constituent species, meaning the tendency to favor the vapor phase. When K_i is greater than unity, species i exhibits a higher concentration in the vapor phase; when less, a higher concentration in the liquid phase, and is considered a ‘heavy’ constituent. Moreover, the use of K-values

makes for computational convenience, allowing elimination of one set of mole fractions in favor of the other.

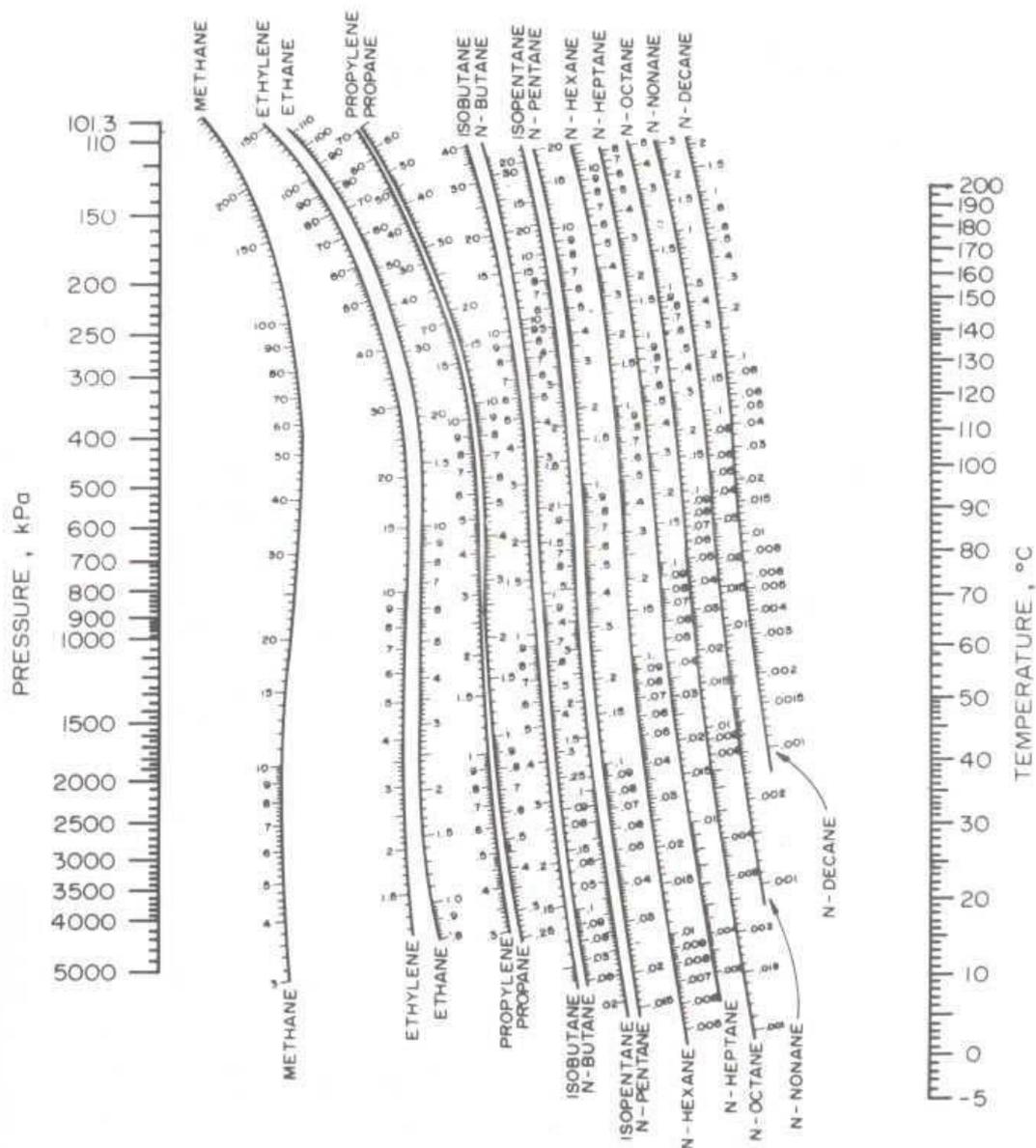


Figure 1.2: K-Values of Hydrocarbons as Functions of Temperature and Pressure

Figure 1.2 shows nomograph for the K-values of light hydrocarbons as functions of T and P, prepared by DePriester ^[4].

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1.2.3 Relative Volatility

In order to separate a binary mixture using distillation process, there must be differences in volatilities of the components, hence their boiling points. The greater the difference, the easier it is to do so. A measure for this is termed the relative volatility. The relative volatility of component ‘*i*’ with respect to component ‘*j*’ is as defined in equation 1.6.

$$\alpha = \frac{(y_i/x_i)}{(y_j/x_j)} = K_i/K_j \quad (1.6)$$

Where;

α = the relative volatility of the more volatile component *i* to the less volatile component *j*

y_i = the vapor-liquid equilibrium concentration of component *i* in the vapor phase.

x_i = the vapor-liquid equilibrium concentration of component *i* in the liquid phase.

y_j = the vapor-liquid equilibrium concentration of component *j* in the vapor phase.

x_j = the vapor-liquid equilibrium concentration of component *j* in the liquid phase.

$(y/x) = K$, commonly called the *K value* or *vapor-liquid distribution ratio* of a component.

When $\alpha = 1.0$, no separation is possible: both component-A and component-B are equally volatile. As the value of α increases above 1, separation by distillation becomes progressively easier.

Relative volatilities can be applied to both binary and multi-component systems. In the binary case, the relative volatility, α , between the light and heavy components can be used to give a simple relationship between the composition of the liquid phase and the composition of the vapor phase as shown in equation 1.7.

$$y = \frac{\alpha x}{1+(\alpha-1)x} \quad (1.7)$$

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1.3 Binary VLE Phase Diagram

Two types of vapor–liquid equilibrium diagrams are widely used to represent data for two-component (binary) systems. The first is a “temperature versus x and y ” diagram (Txy). The x term represents the liquid composition, usually expressed in terms of mole fraction. The y term represents the vapor composition. The second is a x versus y diagram. These types of diagrams are generated at a constant pressure. Since the pressure in a distillation column is relatively constant in most columns (the exception is vacuum distillation, in which the pressures at the top and bottom are significantly different in terms of absolute pressure level), a Txy diagram, and a xy diagram are convenient for the analysis of binary distillation systems.

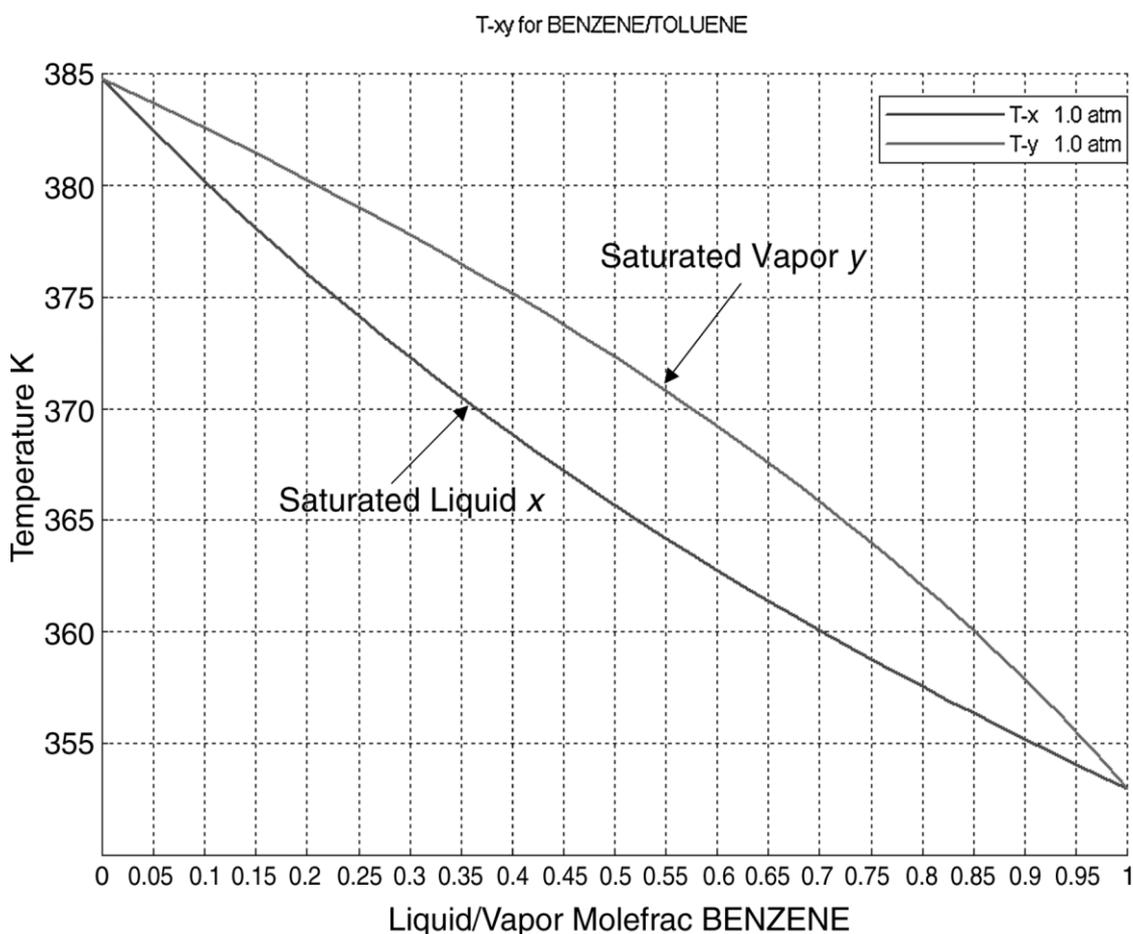


Figure 1.3: Example of T - xy Diagram

Figure 1.3 shows the Txy diagram for the benzene/toluene system at a pressure of 1 atm. The abscissa shows the mole fraction of benzene while the ordinate shows temperature. The lower curve is the “saturated liquid” line, which gives the mole fraction of benzene in the liquid phase, x . The upper curve is the “saturated vapor” line, which gives the mole fraction of benzene in the vapor phase, y . Drawing a horizontal line at some temperature and reading off the intersection of this line with the two curves give the compositions of the two phases. For example, at 370 K the value of x is 0.375 mole fraction benzene and the value of y is 0.586 mole fraction benzene. As expected, the vapor is richer in the lighter component. At the leftmost point is the pure toluene (0 mole fraction benzene), so the boiling point of toluene at 1 atm can be read from the diagram (384.7 K). At the rightmost point is the pure benzene (1 mole fraction benzene), so the boiling point of benzene at 1 atm can be read from the diagram (353.0 K). In the region between the curves, there are two phases; in the region above the saturated vapor curve, there is only a single “superheated” vapor phase; in the region below the saturated liquid curve, there is only a single “subcooled” liquid phase.

1.4 Problem Statement

The knowledge and the capability to describe the phase equilibria of systems formed by a fatty acid ester and an alcohol are of great interest in biodiesel production, where these mixtures can be found after the esterification unit which then must be separated to purify the biodiesel stream and to recover the unreacted alcohol. Despite this interest, little information is available on the vapor-liquid equilibrium data (VLE) of fatty acid ester + alcohol systems. Due to the lack of VLE data for biodiesel system particularly, methyl oleate + methanol and methyl oleate + water, VLE measurement of those systems will be carried out in this present work. The increase in the consumption of methyl oleate has caused the VLE data to become

more important as understanding in the systems' VLE data will help to design separation unit accurately for recovery of excess alcohol to minimize operating costs and environmental impact ^[1] and to control the alcohol content in biodiesel which is achieved through alcohol recovery sections in biodiesel production plant.

1.5 Objectives

The purpose of the research is to determine the vapor-liquid equilibrium data for methyl oleate + methanol and methyl oleate + water systems. Due to little availability of experimental data, the constants predicted by the group contribution models do not give very accurate predictions for systems containing methyl oleate as one of the components. The present study aims to contribute to the enlargement of available databank and hence enhance the predictive ability of the group contribution model. For the present study, we are going to;

- 1 Experimentally investigate isobaric vapor-liquid equilibrium data for methyl oleate + methanol and methyl oleate + water system at various pressures.
- 2 Correlate the measured data with activity coefficient models.

1.6 Scope of Study

In the present study, the effect of pressure on the system will be investigated. The pressures to be experimented will be 80kPa and atmospheric pressure. The experimental data obtained will be correlated with UNIQUAC & NRTL phase equilibrium data.

1.7 Rationale and Significance

The data acquired can help us to design the separation process and the separation column such as the height and number of trays needed for the column. Accurate design of separation unit for recovery of alcohol can help minimize the operating cost, increase the plant efficiency, and control the content of alcohol in biodiesel, hence controlling the quality of the biodiesel produced. At the same time, an accurate design of separation process can boost the production of biodiesel; hence minimize the usage of petrol-based diesel which eventually can help in reducing greenhouse gas emission and also the usage of fossil fuels.