Thermodynamic Analysis of Transesterification of Palm Oil to Biodiesel

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NUR FATHANAH NORHAYALIM

ABSTRACT

This project is concerning the thermodynamic analysis on the transesterification of palm oil to Biodiesel. Eventhough the chemical process for Biodiesel production have been worldwide used, the computation of phase and chemical equilibrium involve in the reaction is still lacking. Therefore this project will analyze the product composition of the transesterification reaction when it is in equilibrium. Equilibrium state is very important as at this state, the measurable properties of the system do no undergo any noticeable changes under a particular set of condition. The maximum allowable conversion of the ester will also be calculated by manipulation of reactant ratio, different operating temperature and type of alcohol (methanol/ethanol). The method used to calculate the equilibrium composition is stoichiometric method. In this method, the palm oil or specifically Triolein and glycerol will be assumed in pure liquid phase meanwhile alcohol and ester will be in solution phase. The activity coefficient is estimated using UNIFAC Group Contribution method. There are also some of the properties like Gibbs free energy of formation and enthalpy of formation that is estimated using properties estimation method, the Joback and Constantinou and Gani method. From the results, it can be concluded that when the reactant ratio is increased, the equilibrium concentration for the ester increase. The proposed ratio of alcohol to triolein ratio would be 5:1. As for manipulation of operating temperature, for methyl oleate system when temperature increase conversion will also increase and for ethyl oleate conversion is decrease when temperature is increased. When different type of alcohol is used, methanol gives much higher conversion compared to ethanol. This is expected as methanol has more advantages in term of physical and chemical properties.

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NOMENCLATURE

$G_{T,P}$ - Gibbs Free Energy at constant temperature and pressure.
S - Entropy
W - Work done
f_i - Fugacity of species i in the gas mixture
f_i^0 - Fugacity of species i at its standard state
G_i - Gibbs free energy of pure species i at operating condition
ΔG^0_{fi} - Standard Gibbs free energy of formation of species i
n_i - number of mole of species i
n - Total number of moles
γ_i - Activity coefficient of species i
x_i - mole fraction of species i
R - Gas constant
T - Temperature of the system
nG - total Gibbs free energy of the system
ν_i - stoichiometric coefficient
A_i - chemical species
α - extent of reaction
μ_i - chemical potential of component *i*
μ_i^o - chemical potential of component *i* at standard state
Π - cumulative product operator

K - equilibrium constant

Φi - volume fraction of component *i*

z - coordination number

qi - molecular surface parameter of component *i*

θi - area fraction of component *i*

l_i - constant

Γ_k - residual activity coefficient of group k

$\Gamma_k^{(i)}$ - residual activity coefficient of group k which in molecule *i*

r_i - molecular size parameter of component *i*

R_k - group size parameter

Q_k - group surface parameter

x_j - mol fraction of component j

v_{kj} - stoichiometric coefficient of group k in component j

θ_m - area fraction of group m

Ψ_{mn} - group interaction parameter

a_{mn} - group interaction parameter

ε - extent of reaction

y - equilibrium composition

Q thermodynamic function for a mixture

$\Delta H^0{}_{fi}$ Enthalpy of formation of species i

$\Delta G^0{}_{f,T}$ Standard Gibbs free energy of formation of species i at operating temperature

$\Delta G^0{}_{f,To}$ Standard Gibbs free energy of formation of species i at standard temperature

N_k number of first order group of type k in the molecule

f1k contribution for the first order group labeled 1k

M_j number of second order group of type j in the molecule

f2j contribution for the second order group labeled 2j

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

With rapidly increasing crude oil prices, limited fossil fuels, and intensified environment pollution, it is increasingly necessary to develop alternative clean and renewable energy sources like Biodiesel [1]. Nowadays Biodiesel has become the most widely accepted renewable alternative fuel for diesel engines due to its technical, environmental and strategic advantages. It has enhanced biodegradability, reduced toxicity and improved lubricity in comparison with conventional diesel fuels. The advantage of Biodiesel can further being explained as below:

a) Biodiesel is derived from crop oil, therefore it is naturally non-toxic. [2] [4]
b) By blending biodiesel with conventional diesel as low as 5%, the lubricity of the fuel can be improved .[2] [4]
c) Biodiesel also can be used directly as usage in the existing engine, without engine modification. Biodiesel can be pumped, stored and burned just like petroleum diesel fuel, and can be used pure, or in blends with petroleum diesel fuel in any proportion. [2]
d) Lower carbon dioxide emission than conventional diesel. [3]

Biodiesel is a fuel that being created from vegetable oils, animal fats, and greases through a chemical process called transesterification process[3]. This process involves the reaction between the natural oil with short chain alcohol such as methanol and ethanol and then refining the mixture to create molecules which can be easily burned in a diesel engine.

It is well known that the product composition of a transesterification reaction is governed by equilibrium thermodynamics [5]. Equilibrium thermodynamic investigates the product composition for transesterification system when the system is approaching the equilibrium. Equilibrium state is very important as at this state, the measurable properties of the system do no undergo any noticeable changes under a particular set of condition [6]. And if the equilibrium is subjected to some changes, it will definitely affect the rate of the reaction. By changing the concentration, temperature and pressure of any of the reactants and products the position of the equilibrium can be changed. The effect of these changes can be explained by the Le Chatelier’s principle.

1.2 PROBLEM STATEMENT

The transesterification process has long been a preferred method of producing biodiesel fuel. The technology behind most plant that produces biodiesel is using this type of process. Eventhough the chemical process have been worldwide used, the computation of phase and chemical equilibrium involve in the reaction is still needed. The phase and chemical equilibrium problem is extremely important for predicting fluid phase behavior for a very large number of separation process applications. Therefore it is important to know the equilibrium distribution of reaction mixture involve in the transesterification for this clean burning alternative fuel.

1.3 OBJECTIVE AND SCOPE OF STUDY

Below is the objective of this project:

a) To analyze the equilibrium composition and yield of Biodiesel in transesterification of palm oil.
b) To know the maximum allowable conversion of palm oil to Biodiesel by manipulating a different reactant ratio and different operating condition.

The scope of this project will be focusing on finding the equilibrium composition and yield of Biodiesel. The equilibrium composition can be determined by stoichiometric method or Gibbs Energy Minimization method. The former is inapplicable to pure liquid or solid species in the reaction system. Meanwhile for a heterogeneous system, the approach using the minimization of the Gibbs free energy is commonly used for thermodynamic analysis [7].

In this research, effect of type of alcohol (methanol/ethanol) need in the transesterification reaction will be determined. In order to find the equilibrium composition and the maximum allowable conversion, a simulation algorithm will be developed using Excel. In addition, the miscibility of all reaction components will be assumed to make the computation easy. The parameters that will be varied are alcohol to oil ratio and temperature. Pressure can be neglected as the operating pressure used in this reaction is low pressure. The range of optimum operation condition that yields maximum yield (> 90%) of Biodiesel will also be identified.

1.4 RELEVANCY OF PROJECT

The new regulation in Malaysia for Diesel selling specification stated that there should be at least 5% of palm oil blending with conventional Diesel [8]. Therefore any research or knowledge about Biodiesel is very important and valuable to the development of this alternative fuel not only in Malaysia but also worldwide. In addition, the thermodynamic analysis especially the equilibrium composition yield of Biodiesel production has not yet being thoroughly investigated due to the complex composition of palm oil.

1.5 FEASIBILITY OF PROJECT WITHIN THE SCOPE AND TIME FRAME

This project mainly involves calculation and simulation using software where the simulation requires manipulation of the operating condition and the reactant ratio. The reactant ratio should follow the principle of transesterification where the natural oil needs to be the limiting reactant and alcohol is in excess. In addition, calculation of stoichiometric equation and Gibbs free energy is not simple because the author’s knowledge about this complex reaction is still average. All of this factor is time consuming and will require a timeline of one year as given.

CHAPTER 2

LITERATURE REVIEW

2.1 BIODIESEL PRODUCTION PROCESS

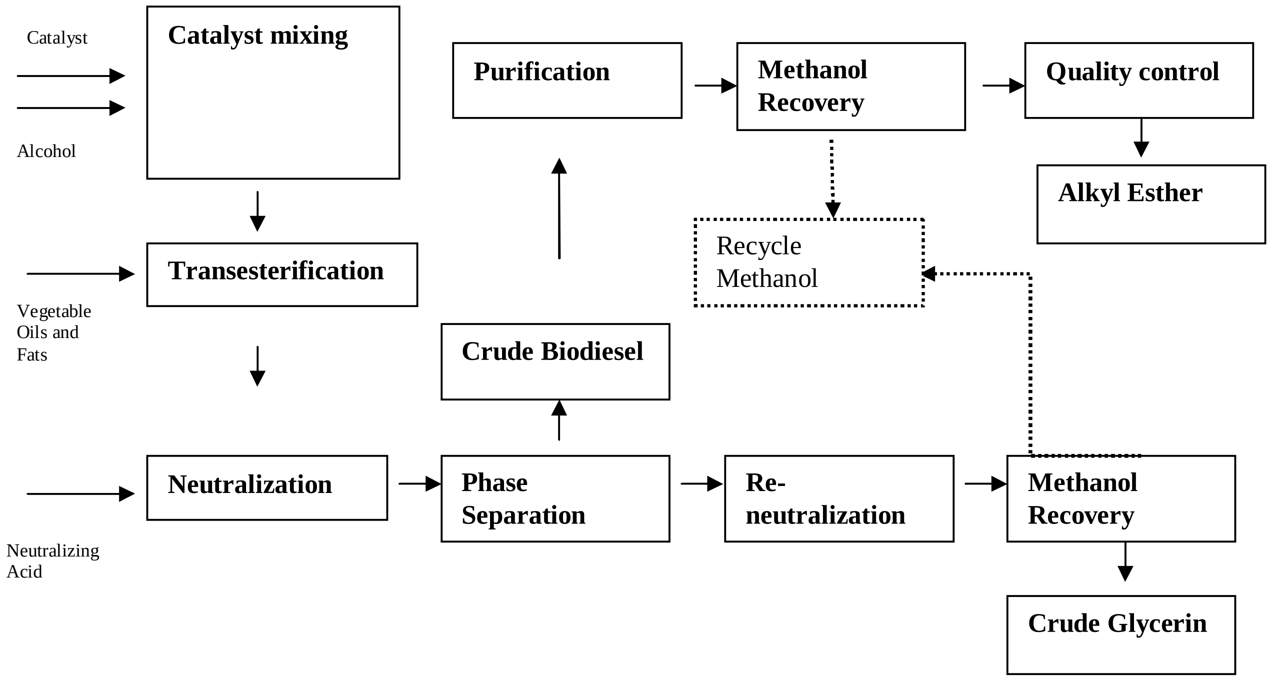


Figure 1: Biodiesel Production Process [3], [9], [10]

Above diagram shows the Biodiesel production process. Basically there are three basic routes to biodiesel production from oils and fats [10]:

- Base catalyzed transesterification of the oil.
- Direct acid catalyzed transesterification of the oil.
- Conversion of the oil to its fatty acids and then to biodiesel.

However mostly biodiesel today is produced by base catalyzed transesterification of the oil. This situation is due to the reactions' advantages where it utilizes low temperature and pressure, produces high conversion up to 98% with minimal side reactions and reaction time, has direct conversion to Biodiesel without intermediate compound and need no exotic materials of construction.

Transesterification is a process that involves reaction between the natural oil and alcohol with strong base catalyst such as sodium hydroxide and potassium hydroxide in order to produce alkyl ester and glycerin [4] [11]. However, for this project which focusing on finding the equilibrium composition of Biodiesel, the activity of the catalyst will not be considered because the purpose of catalyst is to increase the rate of the reaction and do not involve directly in the reaction.

Figure 1 shows the steps applied in producing Biodiesel using base catalyzed reaction. In this reaction, firstly the alcohol and catalyst will be mixed where the catalyst is dissolved in the alcohol using standard agitator or mixer. Since this project will not take account the catalyst activity or the residence time, therefore it can be assumed that only alcohol is fed into the reactor. The alcohol is charged into a closed reaction vessel and the oil or fat is added. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol. The reaction mix is kept just above the boiling point of the alcohol to speed up the reaction and the reaction takes place. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters.

Care must be taken to monitor the amount of water and free fatty acids in the incoming oil or fat. If the free fatty acid level or water level is too high it may cause problems with soap formation and the separation of the glycerin by-product downstream.

Once the reaction is complete, two major products will exist which is glycerin and biodiesel. Each has a substantial amount of the excess methanol that was used in the reaction. The reacted mixture is sometimes neutralized at this step if needed. The glycerin phase is much denser than biodiesel phase and the two can be gravity separated with glycerin simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster.

Once the glycerin and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. In others systems, the alcohol is removed and the mixture neutralized before the glycerin and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is re-used. Care must be taken to ensure no water accumulates in the recovered alcohol stream.

Nevertheless the purpose of this study is to find the chemical equilibrium, yield of Biodiesel and maximum allowable conversion in the transesterification of palm oil. Therefore the production will be focusing only on the reactor part. The simplest method for producing alcohol esters is to use a batch, stirred tank reactor where alcohol to triglyceride ratios are from 4:1 to 20:1 (mole:mole)[3], [9]. However the most common ratio is 6:1 ratio [3], [9]. The operating temperature is usually about 65°C (338 K), if methanol is used and around 78°C (351 K) if ethanol is used.

2.2 PALM OIL COMPOSITION

The transesterification process of palm oil to Biodiesel is very complicated due to the complex structure of palm oil. Therefore a model compound which obtained from the palm oil itself need to be used. Known as triglyceride of oleic acid called olein, this model compound will be chosen for this project.

Palm oil is extracted from the mesocarp of the fruit of the palm *Elaeis guineensis*. The mesocarp comprises about 70 - 80% by weight of the fruit and about 45 -50% of this mesocarp is oil. Palm oil is like all natural fats and oils which comprise mainly Triglyceries, mono and diglycerides. Palm oil also contains free fatty acids, moisture, dirt and minor components of non oil fatty matter which practically referred to unsaponifiable matter [11].

Triglycerides are formed from combination of a single molecule of glycerol with three fatty acids. The property of a triglyceride will depend on the different fatty acids that combine to form the triglyceride. The fatty acids are different depending on the chain length and degree of saturation. The short chain fatty acids has lower melting point and are more soluble in water. Meanwhile the longer chain fatty acids have higher melting points. Below show the composition of fatty acid in the palm oil [11]:

a) C12:0 Lauric
b) C14:0 Myrstic
c) C16:0 Palmitic
d) C18:0 Stearic
e) C18:1 Oleic
f) C18:2 Linoleic

Palmitic and Oleic acid make the largest composition of fatty acid in the palm oil [11]. If the fatty acid is oleic acid, then after reacting with glycerol it will form triolein, glycerion trioleate or commonly known as olein.

2.3 ALCOHOL

Alcohol plays an important role in transesterification reaction because it is used to drive the reaction to completion and also the fuel property of Biodiesel obtained.[12]. The ratio of alcohol used in the reaction will definitely give an impact towards the conversion as more excess of alcohol used, the conversion will also likely become high. Other than the ratio, the type of alcohol used also gives effect towards the ester conversion. For this study, there will be two types of alcohol that will be investigated which is methanol and ethanol.

2.3.1 Methanol

In the transesterification process, the natural oil is chemically acidic; the methanol is chemically a base. This chemical reaction breaks the fat molecules in the natural oils and converts it into a methyl ester, which is the biodiesel fuel, and glycerol. Among all the alcohols used in biodiesel production, the most commonly preferred one is methanol because of its low price and physical and chemical advantages (polar and the shortest chain alcohol). It can easily react with triglycerides, and catalyst, and also can be dissolved inside it faster compared with the other alcohols.

2.3.2 Ethanol

Unlike methanol, creating ethyl-esters biodiesel using ethanol is not a simple process. However, Ethanol is also a preferred alcohol in this process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment [13]. However, the acidity of ethanol is low, thus the reactivities of its reactions with catalysts in order to produce alkoxide anion, which is the real active catalyst in transesterification, are low as well. Because of this, extremely high molar alcohol ratios such as 66:1 need to be used. Moreover, in spite of these unacceptable high alcohol values in terms of the economical point of view, the ester yield is low as well as the amount of contaminants inside the produced ester (biodiesel) fuel such as mono- and diglycerides showing that the reaction is not complete [12].

2.4 BIODIESEL AND GLYCEROL

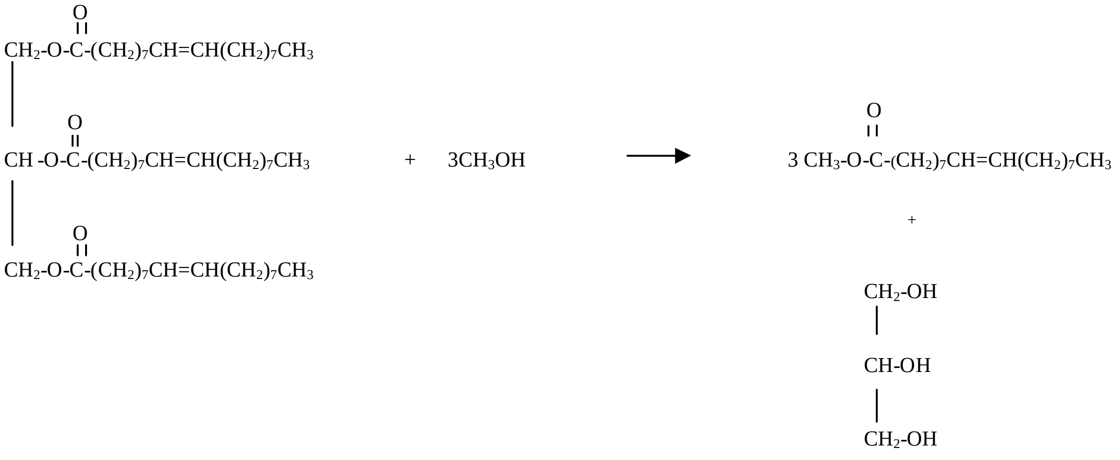
The ester fuel produced contain in its structure the bonds of the alcohol used in the transesterification. It means the monoalkyl esters produced through transesterification are termed as biodiesel. This alkyl group of the fuel is the alkyl radical of the alcohol used[12]. If methanol is used, the biodiesel produced is methyl ester and in the case of ethanol usage, ethyl ester will be produced. The model compound for palm oil is triolein, therefore the reaction of triolein with methanol will produce methyl oleate meanwhile reaction of triolein with ethanol will produce ethyl oleate.

2.4.1 Methyl Oleate

Transesterification of methanol and triolein will produce methyl oleate. Usually in many research and journal found, methyl oleate often becomes the biodiesel product chosen. This might due to methanol where years it has become the alcohol used in Biodiesel study and thus with bundle of information about methyl oleate-methanol, methyl oleate always being selected as the biodiesel product used in the study.

Below show the chemical reaction in producing methyl oleate [3], [9]:

1 triolein + 3 Methanol = 3 Methyl Oleate + 1 glycerol



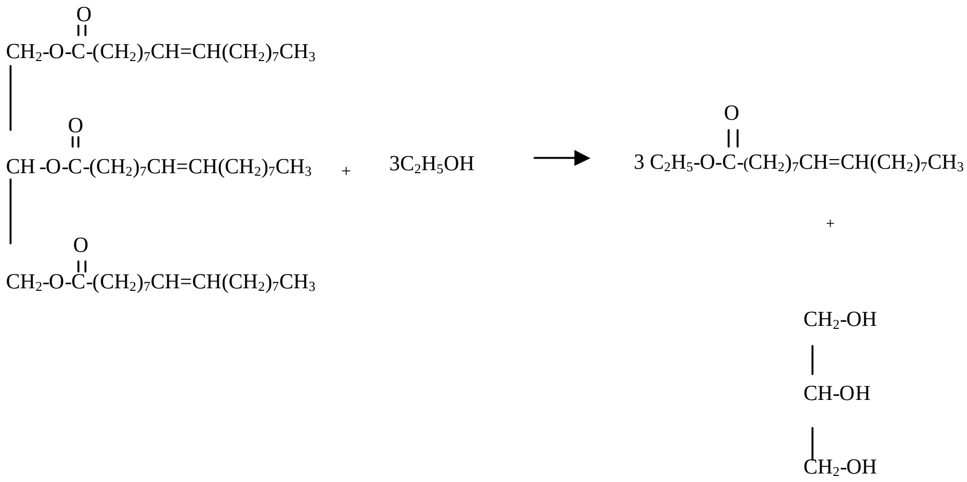
$$\begin{array}{l} CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ | \\ CH\text{ -}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ | \\ CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \end{array} \quad + \quad 3CH_3OH \quad \longrightarrow \quad \begin{array}{c} 3\ CH_3\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ + \\ \begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{array} \end{array}$$

2.4.2 Ethyl Oleate

The transesterification of triolein and ethanol will produce ethyl oleate. Ethyl oleate also can be produced by human body during ethanol intoxication.

Below show the chemical reaction in producing ethyl oleate [3], [9]:

1 triolein + 3 Ethanol = 3 Ethyl Oleate + 1 glycerol



2.4.3 Glycerol

Glycerol is the by-product in transesterification process of palm oil to Biodiesel. Biodiesel will undergo certain type of separation process in order to remove glycerol and also alcohol from its system. Alcohol vapor will be compressed and recycled back to be used as the feed [14]. Meanwhile glycerol can be reused to produce triolein by reacting it with oleic acid.

2.5 EQUILIBRIUM COMPOSITION

Reaction equilibrium can be mathematically described by the equilibrium equation and the reaction equilibrium composition can be calculated by solving this equation. The equilibrium composition can either be found using stoichiometric equation or Gibbs Free Energy Minimization. However for this study, the stoichiometric equation method will be used as the method is more detail and can be easily understand. Either way, both of the methods are explained in this section.

2.5.1 Gibbs free energy Minimization Method

Gibbs free energy can be used to describe equilibrium at conditions of constant temperature and pressure. A global minimum of the Gibbs free energy corresponds to the true equilibrium solution. However, there is difficulty in minimization of Gibbs free energy method in finding its global minimum since for many systems found by chemical engineers the Gibbs free energy function is very complex and can have multiple local minima [16]. Nevertheless, in 1973 Luus and Jaakola proposed a direct search optimization method using random search points and region reduction, and successfully used it for minimization of Gibbs free energy for a single phase situation [17].

In order to understand the fundamental of equilibrium at constant temperature and pressure, we must first understand the most basic Gibbs free energy minimization method [18], [19].

The function of G as a arbiter of equilibrium is analogous to that of the entropy in determining the equilibrium state of isolated systems. If volume and internal energy are fixed, the entropy is a maximum at equilibrium. This criterion is concisely described by:

$dS_{U,V} = 0$ at equilibrium of an isolated system (2.1)

where the subscripts denote the constraints on the system and the vanishing of dS indicates a maximum entropy at equilibrium. If an isolated system is off equilibrium, its entropy must increase as it spontaneously moves towards equilibrium:

$dS_{U,V} > 0$ disequilibrium of an isolated system (2.2)

The equilibrium condition of Eq(2.1) is of minimal practical consequence because the constraints of constant U and V are rarely imposed on real systems. Instead, the usual properties that are specified during a process are total pressure and temperature. With these constraints, the equilibrium criterion is no longer the entropy maximum of Eq (2.1) but the minimization of the Gibbs free energy. This criterion, which is derived below, forms the foundation of the thermodynamics of multiphase and multicomponent as well as equilibrium in chemically reacting systems.

For the practically important case of constant T and p, the equation can be as follow:

$dW_{ext} = -dG_{T,p}$ (2.3)

where the subscript T,p indicates that these two properties are held constant during any change in the system. With this constraint, the Gibbs free energy decreases as the system performs work (other than expansion work) on its surroundings.

A useful definition of a system in equilibrium is one that cannot perform useful(non-expansion) work. The criterion of equilibrium for closed systems constrained by fixed T and p is:

$dG_{T,p} = 0$ (at equilibrium) (2.4)

.

Equation (2.4) states that G is an extremum at equilibrium under the constraint of fixed T and p. However, it does not indicate whether the extremum is maximum or a minimum. Equation (2.3) clarifies this point: if a system could perform useful work, its Gibbs free energy would necessarily decrease, or

dGT,p < 0 (disequilibrium) (2.5)

The appropriate interpretation of Eq (2.5) is that a system at constant T and P will spontaneously seek to minimize its Gibbs free energy. This process occurs whether or not the system performs external work in moving towards its equilibrium state. Equations (2.4) and (2.5) give conditions on G for equilibrium and spontaneous change, respectively, that are analogous to Eqs (2.1) and (2.2) for S.

At equilibrium in an isolated system, the entropy is maximized; if pressure and temperature are fixed, the Gibbs free energy is minimized. Between entropy and Gibbs Free energy, the latter is by far the most important by virtue of the constant p-T restriction, which is much more practical than the constant U-V condition required of the maximum-entropy criterion.

Below show the equations for Gibbs Energy Minimization method:

$$nG = \sum n_i G_i = \sum n_i \Delta G_{fi}^o + RTn_i \ln \frac{f_i}{f_i^o} \qquad (2.6) \quad [19]$$

Liquid phase reaction, thus $\ln \frac{f_i}{f_i^o} = \gamma_i x_i$ (2.7) [16]

Substitute equation (3.2) in equation (3.1)

$$nG = \sum n_i \Delta G_{fi}^o + \sum n_i RT \ln \gamma_i + \sum n_i RT \ln x_i \qquad (2.8)$$

Equation (3.3) is the objective for this method where it needs to be minimized due to below constraint.

$$\sum n_i a_{ji} = b_j \qquad (2.9) \quad [19]$$

The number of gram atoms of element j in a mole of species i, $\mathbf{a_{ji}}$ with the number of moles of species i, $\mathbf{n_i}$ need to be equal with the total number of gram atoms of element j in the reaction mixture, $\mathbf{b_j}$ where $\mathbf{n_i}$ also is being used in the Gibbs equation.

2.5.2 Stoichiometric Equation Method

Analysis of chemical equilibrium for industrial production is an important part of chemical engineering practice. Stoichiometric method begins with understanding the generalized stoichiometry of a reaction. The reaction equation may be written as

$$\sum vi_i \, A_i = 0 \qquad (2.10)\ [18]$$

Where A_i's represent chemical species and the v_i's are the stoichiometric coefficients which are taken positive for products and negative for reactants.

$$\frac{dn_1}{v_1} = \frac{dn_2}{v_2} = \cdots = \frac{dn_i}{v_i} = d\alpha \qquad (2.11)$$

All the ratios are equal and are equated to a change in α which will be called extent of reaction. Thus a single variable α can be used to express the extent of reaction and stoichiometric calculations can be performed systematically.

The number of moles of each species present then can be obtained by integration of the extent of reaction using appropriate boundary conditions. The number of moles of any species presents at any extent reaction then can be generalized to

$$n_i = n_{0i} + v_i\alpha \qquad (2.12)$$

When the composition change is the result of a single chemical reaction, the equation (2.10) can be written as

$$dn_i = v_i d\alpha \qquad (2.13)$$

And by substituting above equation into fundamental equation for a process involving a composition change and occurring in a closed system, we yields:

$$dG = VdP - SdT + \left(\sum v_i\mu_i\right)d\alpha \qquad (2.14)$$

And by differential equation reveals

$$\sum v_i\mu_i = \left(\frac{\partial G}{\partial \alpha}\right)_{T,P} \qquad (2.15)$$

As we know, $dG_{T,P} = 0$ applied to variations constrained to constant temperature and pressure which originate from an equilibrium state. Applying this condition to equation above results in:

$$\left(\frac{\partial G}{\partial \alpha}\right)_{T,P} = 0 \tag{2.16}$$

Or

$$\sum v_i \mu_i = 0 \tag{2.17}$$

Equation above is the condition of equilibrium for a chemical reaction but in this form it has little utility. A more useful relation may be obtained by expressing the chemical potentials in term of fugacities.

$$\mu_i = \mu_i^o + RT \ln \frac{f_i}{f_i^o} \tag{2.18}$$

Substitute this equation into equation (2.17), the condition of equilibrium becomes

$$\sum v_i \mu_i^o + RT \sum vi \ln \frac{f_i}{f_i^o} = 0 \tag{2.19}$$

Or

$$\frac{\sum v_i \mu_i^o}{RT} = -\sum \ln \frac{f_i}{f_i^o} \tag{2.20}$$

Or

$$\frac{\sum v_i \mu_i^o}{RT} = -\ln \prod \frac{f_i}{f_i^o} \tag{2.21}$$

And can be further simplified by using equilibrium constant K:

$$\frac{\sum v_i \mu_i^o}{RT} = -\ln \mathrm{K} \tag{2.22}$$

μ_i^o is the chemical potential of component i when its standard state and that chemical potentials are identical with Gibbs Free Energies. Thus,

$$\frac{\Delta G^o}{RT} = -\ln K \tag{2.23}$$

K is defined as summation of fugacity ratio in the component. Meanwhile fugacity ratio can be defined same as:

$$\frac{f_i}{f_i^o} = \gamma_i \, x_i \tag{2.24}$$

Therefore equating both equation of K, value of x can be obtained and used to find the extent of reaction in the equilibrium mixture to find the number of moles of each component and finally the equilibrium concentrations.

2.5.2.1 Activity Coefficient Model

Activity coefficient, γ_i is one of the parameters in stoichiometric method. It will be discussed here as the method to obtain it is quite complicated. This parameter will be obtained from activity coefficient model such as Margules Equation, Van Laar Equation and Wilson Equation.

However if the reaction is ideal solution, then $\boldsymbol{\gamma_i}$ will be assumed equal to 1. Comparison has been made to the three models where the Margules and Van Laar equation can be rearranged to linear form and not Wilson equation [18]. Therefore for simplicity the author will only consider Margules Equation and Van Laar equation. Following are these equations in the linear form [18]:

<u>The Margules Equation</u>

$$\ln \gamma_1/x_2^2 = A_{12} + 2(A_{21}-A_{12})x_1 \tag{2.25}$$

$$\ln \gamma_2/x_2^2 = A_{21} + 2(A_{12}-A_{21})x_2 \tag{2.26}$$

The Van Laar Equation

$$1/\ln \gamma_1^{1/2} = 1/B_{12}^{1/2} + (B_{12}^{1/2} / B_{21})(x_1/x_2) \quad (2.27)$$

$$1/\ln \gamma_2^{1/2} = 1/B_{21}^{1/2} + (B_{21}^{1/2} / B_{12})(x_2/x_1) \quad (2.28)$$

In these equations the A's and B's are adjustable parameters which must be determined from an experimentally derived set of γx data. Because each equation contains only two parameters, a minimum of one Vapor-Liquid Equilibrium (VLE) data point is sufficient to determine them. This one data point provides T, P, x_1, and y_1 and allows the calculation of γ_1 and γ_2 which along with the values of x_1 and x_2 may be substituted into the equations to provide a set of two equations and two unknown parameters.

All the parameters in these equations are obtained from an experimentally determined isothermal set of γx data by fitting straight line to plot:

a) Margules Equation – plot $\ln \gamma_1/x_2^2$ vs. x_1 and $\ln \gamma_2/x_2^2$ vs. x_2

b) Van Laar Equation – plot $1/\ln \gamma_1^{1/2}$ vs. x_1/x_2 and $1/\ln \gamma_2^{1/2}$ vs. x_2/x_1

This procedure is useful when data for only one component are available but its disadvantage is that it yields a set of parameters from the plot for each component. As the two sets of parameters will rarely be in agreement, some type of averaging procedure must be used to obtain a single set. This problem can be avoided if the data for both components are combined through the function $\mathbf{Q}$ where $\mathbf{Q}$ is related to the excess Gibbs free energy of mixing [18].

$$\mathbf{Q} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (2.29)$$

Thus, instead of two sets of γx data, there is a single set of $\mathbf{Q}$x data as follow:[20]

The Margules Equation

$$\mathbf{Q} / x_1 x_2 = A_{12} + 2(A_{21} - A_{12})x_1 \quad (2.30)$$

The Van Laar Equation

$$x_1x_2/\mathbf{Q} = 1/B_{12} + [\,(B_{12}-B_{21})/(B_{12}B_{21})]\,x_1 \qquad (2.31)$$

Unfortunately for this study, the vapor-liquid equilibria experimental data for binary methyl oleate-methanol and ethyl oleate-ethanol at the respected temperature and pressure are difficult to find. Thus, an estimation of activity coefficients from group-contribution method is used.

2.5.2.2 Group Contribution Method

In the group contribution method, the basic idea is that whereas there are thousands of chemical compounds of interest in chemical technology, the number of functional groups that constitute these compounds is much smaller. Therefore, if we assume that a physical property of a fluid is the sum of contributions made by the molecule's functional groups, we obtain a possible technique for correlating the properties of a very large number of fluids in terms of a much smaller number of parameters that characterize the contributions of individual groups.[20]

Any group-contribution method is necessarily approximate because the contribution of a given group in one molecule is not necessarily the same as that in another molecule. The fundamental assumption of a group contribution method is additivity: the contribution made by any group within a molecule is assumed to be independent of that made by any other group in that molecule. This assumption is valid only when the influence of any one group in a molecule is not affected by the nature of other groups within that molecule.

There are two method used in estimation of activity coefficients from group contribution method namely analytical solution of group (ASOG) and UNIFAC. However in this project, UNIFAC method will be chosen.

In concept, the UNIFAC method follows the ASOG method, where activity coefficients in mixtures are related to interactions between structural groups. The essential features are:

1. Suitable reduction of experimentally obtained activity coefficient data to yield parameters characterizing interactions between pairs of structural groups in nonelectrolyte system.
2. Use of those parameters to predict activity coefficients for other systems that have not been studied experimentally but that contain the same functional groups.

Basically, the UNIFAC method is the combination of ASOG method and UNIQUAC equation. The UNIQUAC equation often gives good representation of vapor-liquid and liquid-liquid equilibria for binary and multicomponent mixtures containing a variety of nonelectrolyte. In multicomponent mixture, the UNIQUAC equation for the activity coefficient of component *i* is:

$$\ln \gamma_i = \underbrace{\ln \gamma_i^C}_{\text{combinatorial}} + \underbrace{\ln \gamma_i^R}_{\text{residual}} \tag{2.32}$$

Where

$$\ln \gamma_i^C = \ln \frac{\Phi i}{xi} + \frac{z}{2} qi \ln \frac{\theta i}{\Phi i} + l_i - \frac{\Phi i}{xi} \sum_j x_j l_j \tag{2.33}$$

$$\ln \gamma_i^R = \sum_k v_k \left(\ln \Gamma_\mathrm{k} - \ln \Gamma_\mathrm{k}^{(\mathrm{i})} \right) \tag{2.34}$$

The combinatorial contribution to the activity coefficient depends only on the sizes and shapes of the molecules present. Meanwhile the residual contribution to the activity coefficient depends on group areas and group interaction. The residual equation is not part of UNIQUAC equation and is extracted from solution-of-groups concept from ASOG method.

For combinatorial part:

$$\Phi_\mathrm{i} = \frac{r_i x_i}{\sum_j r_j x j_j} \tag{2.35}$$

Where $r_i = \sum_k v_k^{(i)} R_k$ (2.36)

Parameter R_k is given in the table provided in the book ‘Properties of Gases and Liquid’

z = 10

z is a constant number

$$q_i = \sum_k v_k^{(i)} Q_k \tag{2.37}$$

Parameter Q_k is given in the table provided in the book ‘Properties of Gases and Liquid’

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{2.38}$$

$$l_i = \frac{z}{2}\,(ri - qi) - \,(ri - 1) \tag{2.39}$$

For residual part:

$$\ln \Gamma_k = Q_k \left[1 - ln\left(\sum_m \theta_m \Psi_{mk}\right) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}}\right] \tag{2.40}$$

Equation above also holds for $\ln \Gamma_{\mathrm{k}}^{(\mathrm{i})}$

Where $\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}$ (2.41)

$$\Psi_{\mathrm{mn}} = \exp\left(-\frac{a_{mn}}{\mathrm{T}}\right) \tag{2.42}$$

$$x_m = \frac{V_j^i}{\sum v_j^i} \tag{2.43}$$

2.6 PROPERTIES ESTIMATION METHOD

Properties estimation method is used when there is no experimental data available at hand. Estimation carries the meaning of approximate. It may be based on theory, on correlations of experimental values or on a combination of both. A theoretical relation although not strictly valid, it will still serve adequately in specific cases. An ideal system for the estimation of a physical property would be able to serve below criteria [20]:

a. Provide reliable physical and thermodynamic properties for pure substance and for mixtures at any temperature, pressure and composition.
b. Indicate the phase (solid, liquid or gas)
c. Require a minimum of input data.
d. Choose the least-error route.
e. Indicate the probable error.
f. Minimize computation time.

In this case, property estimation method is used to estimate the Gibbs energy of formation $\Delta G^o_{f,T}$ and enthalpy of formation $\Delta H^o_{f,T}$. The method used is Joback and Constantinou and Gani (CG) Method.

Joback method assigns contributions to common molecular groupings such as –CH3, -NH2 and –COOH. Research done show by using Joback method the average absolute error for Gibbs of formation at 298.15K is about 9.9 (for carbon more than 3) meanwhile for enthalpy of formation at 298.15K, the average absolute error is around 10.2% (for carbon more than 3). However Joback method will be optional. It will only be used when the property estimated by Constantinou and Gani does not fit with this research requirement. Below show the calculation of Gibbs of formation and enthalpy of formation at 298.15K:

$$\Delta G_f^o = 53.88 + \left[\sum_k N_k (gf1k)\right] \tag{2.44}$$

$$\Delta H_f^o = 68.29 + \left[\sum_k N_k(hf1k)\right] \qquad (2.45)$$

Constantinou and Gani developed an advanced group contribution method based on the UNIFAC group but enhanced by allowing for more sophisticated functions of the desired properties and by providing contributions at a ‘Second Order’ level. The functions give more flexibility to the correlation while the Second order partially overcomes the limitation of UNIFAC which cannot distinguish special configurations such as isomers, multiple groups located close together, resonance structures etc. at the First Order [20].

This method is much more complicated and more accurate compared to Joback Method. It assigns contributions to common molecular groupings and allows interactions with next nearest neighbors to the atom or group. This allowance is generally the limits for estimation method because allowance for atoms or groups that are two or more atoms removed from the one of interest treats very small effects but still making the technique quite cumbersome[20].

Below show the equation employed in obtaining Gibbs energy of formation $\Delta G^o_{f,T}$ and enthalpy of formation $\Delta H^o_{f,T}$ of Triolein.

$$\Delta G_f^o = -14.83 + \left[\sum_k N_k(gf1k) + W \sum_j M_j(gf2j)\right] \qquad (2.46)$$

$$\Delta H_f^o = 10.835 + \left[\sum_k N_k(hf1k) + W \sum_j M_j(hf2j)\right] \qquad (2.47)$$

The value of W is set to zero for first order calculations and unity for second-order calculations.

A research is done using all substances in Appendix A from the Properties of Gases and Liquids book, to compare the absolute percentage error between experimental value and calculated value using Constantinou and Gani Method. The calculated value can be divided into two; first order group and second order group. From standard enthalpy of formation value, the average absolute percentage error for first order is 8%. Meanwhile for second order, the average absolute percentage error is 4.7%. This demonstrates that by including second order group in Constantinou and Gani Method, a more accurate result can be obtained. The trend is basically same with result from standard Gibbs of formation value where for the average absolute percentage error for first order (12%) is more than second order group (10%).

With low error in this method, it implies that Constantinou and Gani method is reliable and applicable in estimating the property of the substance. Other than that, it also requires a minimum of input data and minimizes the computation times.

2.7 CONVERSION

In defining conversion, reactants should be choose as the basis of calculation and then relate the other species involve in the reaction to this basis. In virtually all instances it is best to choose the limiting reactant as the basis of calculation [21]. The stoichiometric relationships and design equation is developed by considering the general equation below:

$$aA + bB \rightarrow cC + dD$$

The uppercase letters represent chemical species and the lowercase letters represent stoichiometric coefficients. Taking species A as our basis calculation, the reaction expression is divided through by stoichiometric coefficient of species A, in order to arrange the reaction expression in the form such as below in order to put every quantity on a "per mole A" basis, the limiting reactant.

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

Now in order to quantify how far a reaction has proceeds to the right hand side of the equation or how many moles of C are formed for every mole A consumed, the convenient way is to define the parameter of conversion. The conversion of X_A is the number of moles of A that have reacted per mole of A that fed to the system:

$$X_A = \frac{Moles\ of\ A\ reacted}{Moles\ of\ A\ fed}$$

For irreversible reaction, the maximum conversion is 1.0 which is the complete conversion meanwhile for reversible reaction, the maximum conversion would be the equilibrium conversion (X_e). Therefore $X_{max} = X_e$

CHAPTER 3

METHODOLOGY

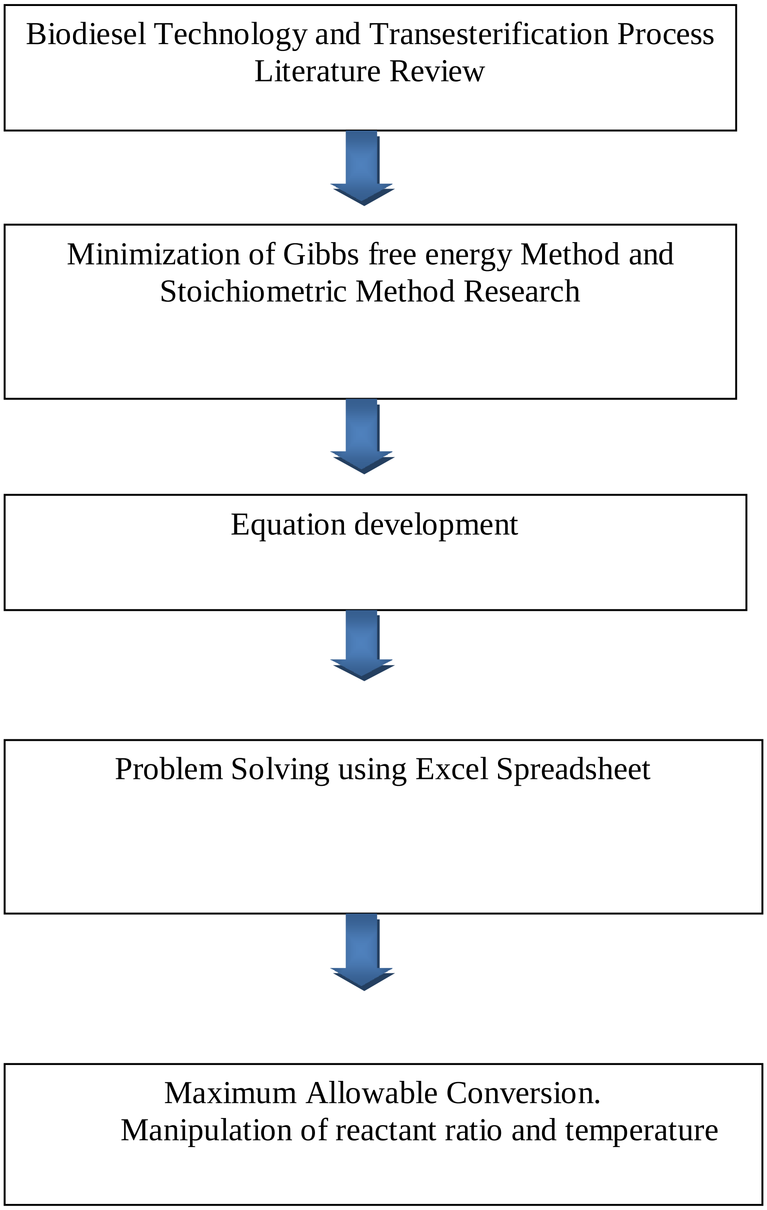


Figure 2: Methodology

3.1 EQUATION DEVELOPMENT

Stoichiometric Method is chosen as the method used to identify the equilibrium composition of transesterification process as the information about it is more detail and can be easily understand. There will be two models applied in this study by which the two models will be differ in number of phase exist. In first model, there are two pure liquid phase and one solution phase. Meanwhile in second model, there will be one pure liquid phase and two solution phase.

3.1.1 First Model

In this model the triolein and glycerol will be in liquid phase meanwhile alcohol and ester will be in one solution phase. It can be concluded that the alcohol only dispersed to ester by using this model.

The transesterification reaction from palm oil to Biodiesel can be simplified as below:

Triglyceride (T) + 3 Alcohol (A) = 3 Ester (E) + Glycerol (G)

Degree of freedom

P = 3 liqid phases (T, A+E, G)
C = 4 components (T, A, E, G)
r = 1 reaction

$F = C - P + 2 - r = 4 - 3 + 2 - 1 = 2$ degrees of freedom

Two types of operating condition need to be chosen to fix the system. It can be temperature, pressure, or initial composition. Since pressure effect is negligible for low pressure liquid-phase reaction, temperature and initial composition is chosen as two independent variables to define the system.

1. For a given temperature, K will be calculated by Eq (3.1).

$$K(T)=\exp\left(\frac{-\Delta G_T^o}{RT}\right)=\exp\left(\frac{-\sum_i \nu_i \Delta G_{fi,T}^o}{RT}\right) \tag{3.1}$$

$\Delta G_{f,T}^{o}$ will be determined by Gibbs Hemholtz Equation

$$K(T)=\frac{\left(\hat{f}_E/f_E^o\right)^3\left(\hat{f}_G/f_G^o\right)}{\left(\hat{f}_T/f_T^o\right)\left(\hat{f}_A/f_A^o\right)^3} \tag{3.2}$$

Since Triolein and Glycerol are pure liquid phases,

$$\left(\hat{f}_T/f_T^o\right)=\left(\hat{f}_G/f_G^o\right)=1$$

For liquid solution (A+E),

$$\left(\hat{f}_E/f_E^o\right)=\gamma_E x_E\left(\frac{f_E}{f_E^o}\right)\cong\gamma_E x_E\,, \tag{3.3}$$

Similarly $\left(\hat{f}_A/f_A^o\right)\cong\gamma_A x_A$ (3.4)

Thus,

$$K(T)=\left(\frac{\gamma_E x_E}{\gamma_A x_A}\right)^3=\left[\frac{\gamma_E x_E}{\gamma_A(1-x_E)}\right]^3 \tag{3.5}$$

2. Values for mol fraction of alcohol, x_A and ester, x_E will be assumed such that $x_A + x_E = 1$.
3. Then, at the same temperature, the activity coefficient of ester, $\gamma_E(T, x_E)$ and alcohol, $\gamma_A(T, x_A)$ will be found using estimation of activity coefficient using Group Contribution Method UNIFAC.
4. The values of x_A and x_E then can be corrected from Eq (3.5).
5. Step 2 is repeated until convergence is achieved.

6. The concentrations or moles of the components in the equilibrium mixture can be calculated using the reaction stoichiometry as follow:

	T	+	3A	=	3E	+	G
Initial:	n_{T0}		n_{A0}		n_{E0}		n_{G0}
Extent:	ε		$3\ \varepsilon$		$3\ \varepsilon$		ε
Equili:	$(n_{T0}-\varepsilon)$		$(n_{A0}-3\varepsilon)$		$(n_{E0}+3\varepsilon)$		$(n_{G0}+\varepsilon)$

7. From the reaction stoichiometry, the extent of reaction, ε is calculated.

$$\frac{n_A}{n_{\mathrm{E}}+n_{\mathrm{A}}}=\frac{n_{AO}-3\varepsilon}{(n_{\mathrm{E0}}+3\varepsilon)+(n_{\mathrm{A0}}-3\varepsilon)}=\frac{n_{\mathrm{AO}}-3\varepsilon}{n_{\mathrm{E0}}+n_{\mathrm{A0}}}=x_{\mathrm{A}} \tag{3.6}$$

8. The number of moles for each component can now be calculated using below equation.

$$n_i=n_{i0}+\nu_i\varepsilon \tag{3.7}$$

9. Following with the total number of moles Σn_i.

$$\sum n_i=n_{\mathrm{T}}+n_{\mathrm{A}}+n_{\mathrm{E}}+n_{\mathrm{G}}=(n_{\mathrm{T0}}-\varepsilon)+(n_{\mathrm{A0}}-3\varepsilon)+(n_{\mathrm{E0}}+3\varepsilon)+(n_{\mathrm{G0}}+\varepsilon)=\sum n_{i0} \tag{3.8}$$

10. And lastly, equilibrium concentrations of each component, y_i is obtained.

$$y_i=\frac{n_i}{\sum n_i} \tag{3.9}$$

3.1.2 Second Model

Second Model

In the second model, there will be two liquid solutions phase and one pure liquid phase. The solution phase is alcohol and ester and alcohol and glycerol. Different from first method, glycerol now become the solution phase and only triolein stay as the pure liquid phase. Below show the transesterification of palm oil to Biodiesel reaction:

Triglyceride (T) + 3 Alcohol (A) = 3 Ester (E) + Glycerol (G)

Degree of Freedom

P = 3 liqid phases (T, A+E, A+G)
C = 4 components (T, A, E, G)
r = 1 reaction
F = C – P + 2 – r = 4 – 3 + 2 – 1 = 2 degrees of freedom

Two types of operating condition need to be chosen to fix the system. It can be temperature, pressure, or initial composition. Since pressure effect is negligible for low pressure liquid-phase reaction, temperature and initial composition is chosen as two independent variables to define the system.

1. For a given temperature, *K* will be calculated by Eq (3.1).

$$K(T) = \exp\left(\frac{-\Delta G_T^o}{RT}\right) = \exp\left(\frac{-\sum_i \nu_i \Delta G_{fi,T}^o}{RT}\right) \tag{3.10}$$

$\Delta G_{f,T}^{o}$ will be determined by Gibbs Hemholtz Equation

$$K(T) = \frac{\left(\hat{f}_E / f_E^o\right)^3 \left(\hat{f}_G / f_G^o\right)}{\left(\hat{f}_T / f_T^o\right)\left(\hat{f}_A / f_A^o\right)^3} \tag{3.11}$$

For pure liquid phase T, $\left(\hat{f}_T / f_T^o\right)$ = 1

For liquid solution 1 (A+E),

$$\left(\hat{f}_E / f_E^o\right) = \gamma_{E1} x_{E1} \left(\frac{f_E}{f_E^o}\right) \cong \gamma_{E1} x_{E1}\, , \;\; \left(\hat{f}_A^1 / f_A^o\right) \cong \gamma_{A1} x_{A1}$$

For liquid solution 2 (A+G),

$$\left(\hat{f}_G / f_G^o\right) = \gamma_{G2} x_{G2} \left(\frac{f_G}{f_G^o}\right) \cong \gamma_{G2} x_{G2}\, , \;\; \left(\hat{f}_A^2 / f_A^o\right) \cong \gamma_{A2} x_{A2}$$

For phase equilibrium,

$$\left(\hat{f}_A / f_A^o\right) = \left(\hat{f}_A^1 / f_A^o\right) = \left(\hat{f}_A^2 / f_A^o\right) = \gamma_{A1} x_{A1} = \gamma_{A2} x_{A2} \qquad (3.12)$$

Thus,

$$K(T) = \frac{(\gamma_{E1} x_{E1})^3 (\gamma_{G2} x_{G2})}{(\gamma_{A1} x_{A1})^3} = \frac{\gamma_{E1}^3 (1 - x_{A1})^3 \gamma_{G2} (1 - x_{A2})}{(\gamma_{A1} x_{A1})^3} \qquad (3.13)$$

2. The values for mol fraction of alcohol 1, x_{A1} and ester, x_{E1} is assumed such that $x_{A1} + x_{E1} = 1$.
3. At specified operating temperature, T, the activity coefficient of ester $\gamma_{E1}(T, x_{E1})$ and activity coefficient of alcohol 1,$\gamma_{A1}(T, x_{A1})$ is calculated using a suitable activity coefficient model.
4. The initial value for mol fraction of alcohol 2, x_{A2} will be assumed such that $x_{A2} < 1$.
5. The activity coefficient of glycerol, $\gamma_{G2}(T, x_{G2})$ is calculated using a suitable activity coefficient model.
6. The value of x_{A2} from Eq (5) is corrected using γ_{G2} value obtained above.
7. Step 5 is repeated until convergence of x_{A2}.
8. The activity coefficient of alcohol 2, $\gamma_{A2}(T, x_{A2})$ is calculated using the same activity coefficient model as in step 5.
9. The value of x_{A1} is obtained from equation (4), using the current x_{A2}, γ_{A2}, and γ_{A1}.

10. Step 3 is repeated until convergence of x_{A1}.
11. After convergence of x_{A1} and x_{A2}, the concentrations or moles of the components in the equilibrium mixture can be calculated from the reaction stoichiometry as follow:

	T	+	3A	=	3E	+	G
Initial:	n_{T0}		n_{A0}		n_{E0}		n_{G0}
Extent:	ε		$3\ \varepsilon$		$3\ \varepsilon$		ε
Equili:	$(n_{T0}-\varepsilon)$		$(n_{A0}-3\varepsilon)$		$(n_{E0}+3\varepsilon)$		$(n_{G0}+\varepsilon)$

12. From the reaction stoichiometry,the extent of reaction,ε can now be calculated by using below equation:

$$n_A = n_{A1} + n_{A2} = \frac{(n_{\mathrm{E0}} + 3\varepsilon)x_{A1}}{1 - x_{\mathrm{A1}}} + \frac{(n_{\mathrm{G0}} + \varepsilon)x_{A2}}{1 - x_{\mathrm{A2}}} = n_{\mathrm{A0}} + 3\varepsilon \tag{3.14}$$

13. The number of moles for each component (triolein, alcohol, ester and glycerol) is calculated using equation (3.7).

$$n_i = n_{i0} + \nu_i \varepsilon \tag{3.15}$$

14. Followed by the total number of moles in the mixture as in equation (3.8).

$$\sum n_i = n_{\mathrm{T}} + n_{\mathrm{A}} + n_{\mathrm{E}} + n_{\mathrm{G}} = (n_{\mathrm{T0}} - \varepsilon) + (n_{\mathrm{A0}} - 3\varepsilon) + (n_{\mathrm{E0}} + 3\varepsilon) + (n_{\mathrm{G0}} + \varepsilon) = \sum n_{i0} \tag{3.16}$$

15. With that, the equilibrium concentrations for each of the components, *i* can be directly obtained using equation (3.9).

$$y_i = \frac{n_i}{\sum n_i} \tag{3.17}$$

3.2 SOFTWARE

3.2.1 MATLAB

MATLAB is a high-level technical computing language and interactive environment for algorithm development, data visualization, data analysis, and numeric computation. This software will be used to check the validity of value of activity coefficient obtained by calculation using the UNIFAC method [22].

3.2.2 Microsoft Excel

Microsoft Excel spreadsheet is written application that features calculation, graphing tools, pivot table and a macro programming language. The equations computation for equilibrium composition for this study will be developed using Microsoft Excel spreadsheet.

3.3 MAXIMUM ALLOWABLE CONVERSION

In order to obtain maximum allowable conversion for this system, the parameters to be manipulated are reactant ratio and temperature. For reactant ratio, natural oil needs to be the limiting reactant and alcohol is in excess. The reactant ratio will be manipulated likely starting from 3:1 to 10:1 (mole:mole). As for temperature and pressure, it will start at the boiling point of the alcohol and atmospheric pressure and gradually decrease until the maximum conversion is achieved. The conversion of palm oil (triolein) to biodiesel (ester) is calculated using the difference of number of moles in the Triolein at initial and at the end of the reaction divided by number of moles at initial. The equation for the conversion can be shown as below:

$$Conversion = \frac{n_{io} - n_i}{n_{io}} \times 100 \qquad (3.18)$$

3.4 GANTT CHART

No	Detail. Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Topic Awarded	🟦													
2	Preliminary Report (Research)		🟦	🟦											
3	Submission of Preliminary Report				⬛										
4	Minimization of Gibbs Free Energy and Stoichiometric Method research					🟦	🟦	🟦	🟦						
5	Submission of Progress Report and Seminar								⬛						
6	Equation Development									🟦	🟦	🟦			
7	Result Gathering												🟦	🟦	
8	Submission of Interim Report													⬛	
9	Oral Presentation														⬛

Table 1: Gantt chart for Semester 1

No	Detail.Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1	Activity coefficient by UNIFAC method	🟦	🟦	🟦	🟦	🟦														
2	Submission of Progress Report I					⬛														
3	Equation Development for second method					🟦	🟦	🟦	🟦											
4	Equilibrium composition								🟦	🟦	🟦									
4	Submission of Progress Report II										⬛									
6	Maximum conversion										🟦	🟦								
7	Poster Exhibition											⬛								
8	Project Work Continue												🟦	🟦	🟦					
9	Submission of Dissertation (softbound)														⬛					
10	Oral Presentation																		⬛	⬛
11	Submission of Dissertation (hard bound)															⬛	⬛	⬛	⬛	⬛

Table 2: Gantt Chart for semester 2

CHAPTER 4

RESULT AND DISCUSSION

In the first phase of this study, the author will focus on finding equilibrium composition of transesterification of palm oil to biodiesel by using stoichiometric equation method. For easier computation to find the equilibrium composition and maximum allowable conversion, the miscibility of all reaction components will be assumed where all the reaction components are in liquid phase. In order to solve the equation, firstly the parameters involved must be identified:

4.1 PARAMETER

4.1.1 Gibbs Energy of Formation, $\Delta G^{0}{}_{fi}$

Gibbs free energy of formation for methanol, ethanol and glycerol is directly obtained from the Gibbs free energy of formation function of temperature. However it is different for Triolein, Methyl Oleate and Ethyl Oleate. The Gibbs free energy of formation for those components will be obtained from Properties Estimation Methods, Joback and Constantinou and Gani Method. Joback and Constantinou and Gani Method will give the value of Gibbs free energy of formation only at standard temperature 298 K. Therefore another equation needs to be used in correlation with the value from Joback and Constantinou and Gani method. The equation used is Gibbs Hemholtz Equation. This equation will require enthalpy of formation constant a, b, c, d. However the constant cannot be obtained and thus the enthalpy of formation will be assumed constant and using Joback and Constantinou and Gani method again, the enthalpy of formation at 298

K is acquired. Below is the summary of properties estimation method used by each component:

Components	Property Estimation Method
Triolein for methyl oleate	Joback
Triolein for ethyl oleate	Constantinou and Gani (CG)
Methyl Oleate	Constantinou and Gani (CG)
Ethyl Oleate	Constantinou and Gani (CG)

Table 3: Property estimation method for each component

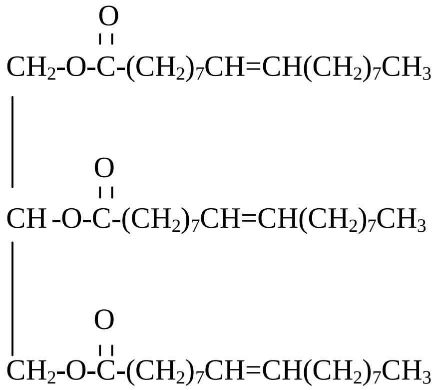
The reason why Joback method is used instead of Constantinou and Gani in estimation of Gibbs of formation of triolein for methyl oleate is it produces a value where the Gibbs of reaction is close to the positive value. When the Gibbs of reaction is close to positive value, the K(T) produced will become small and thus avoid the possibility of obtaining negative value for equilibrium composition. Below summary show using Joback for Triolein and CG method for methyl oleate produces the highest value for Gibbs free energy of reaction for triolein-methyl oleate system:

Number of try	Component	Method/ Source of Gibbs of formation	DG reaction (kJ/mol)
Try 1	Triolein	Joback	-51.571
	Methyl Oleate	Database	
Try 2	Triolein	Joback	-61.30
	Methyl Oleate	Joback	
Try 3	Triolein	Joback	-12.094
	Methyl Oleate	CG	
Try 4	Triolein	CG	-52.177
	Methyl Oleate	CG	
Try 5	Triolein	CG	-101.375
	Methyl Oleate	Joback	

Table 4: DG reaction using various methods of Gibbs of formation

The first step in Joback and Constantinou and Gani Method for estimation of properties is to identify the groups that exist in the component. Below show the groups that exist in Triolein, Methyl Oleate and Ethyl Oleate and how to obtain the enthalpy of formation and Gibbs free energy of formation using these methods.

Triolein



$$\begin{array}{l} CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ | \\ CH\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ | \\ CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \end{array}$$

1. Joback Method

The groups for triolein are forty four CH2, six =CH, one CH, three CH3 and three COO. Using the information above, the group values can be obtained from table C2 and C3 in The Properties of Gases and Liquids Fifth Edition book.

Group k	Nk	hf1k	Nk * hf1k	gf1k	Nk * gf1k
CH3	3	-76.45	-229.35	-43.960	-131.880
CH2	44	-20.64	-908.16	8.420	370.480
CH	1	29.89	29.89	58.360	58.360
=CH	6	37.97	227.82	48.530	291.180
COO	3	-337.92	-1013.76	-301.950	-905.850
		Total	-1893.56	Total	-317.71

Table 5: Property estimation using Joback approach for Triolein

Using the values and substitute in equation (2.44) and (2.45), the Gibbs free energy of formation and enthalpy of formation for triolein at 298 K is -263.83 kJ/mol and -1825.27 kJ/mol respectively.

2. Constantinou and Gani Method

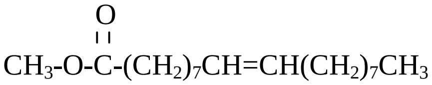
The first order groups for triolein are forty four CH2, three CH=CH, one CH, three CH3 and three COO. Using the information above, the group values can be obtained from table C6 and C7 in The Properties of Gases and Liquids Fifth Edition book.

Group k	Nk	hf1k	Nk * hf1k	gf1k	Nk * gf1k
CH2	44	-20.763	-913.572	8.231	362.164
CH=CH	3	69.939	209.817	92.900	278.700
CH	1	-3.766	-3.766	19.848	19.848
CH3	3	-45.947	-137.841	-8.030	-24.090
COO	3	-313.545	-940.635	-281.495	-844.485
		Total	-1786	Total	-207.863

Table 6: Property estimation using Constantinou and Gani approach for Triolein

Using the values and substitute in equation (2.44) and (2.45), the Gibbs free energy of formation and enthalpy of formation for triolein at 298 K is -222.693kJ/mol and -1775.16 kJ/mol respectively.

Methyl Oleate



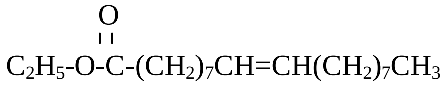
$CH_3\text{-}O\text{-}\overset{\overset{O}{||}}{C}\text{-}(CH_2)_7CH{=}CH(CH_2)_7CH_3$

Group k	Nk	hf1k	Nk * hf1k	gf1k	Nk * gf1k
CH2	14	-20.763	-290.682	8.231	115.234
CH=CH	1	69.939	69.939	92.900	92.900
CH3	2	-45.947	-91.894	-8.030	-16.060
COO	1	-313.545	-313.545	-281.495	-281.495
		Total	-626.182	Total	-89.421

Table 7: Property estimation using Constantinou and Gani approach for Methyl Oleate

The group values can be obtained from table C2 and C3 in The Properties of Gases and Liquids Fifth Edition. Substitute the above values in equation (2.44) and (2.45), the Gibbs free energy of formation and enthalpy of formation for Methyl Oleate at 298 K is -104.251 kJ/mol and -615.347 kJ/mol respectively.

Ethyl Oleate



$$C_2H_5\text{-}O\text{-}\overset{\overset{O}{||}}{C}\text{-}(CH_2)_7CH{=}CH(CH_2)_7CH_3$$

The first order groups for ethyl oleate are fifteen CH2, one CH=CH, one CH, two CH3 and one COO. Using the information above, the group values can be obtained from table C2 and C3 in The Properties of Gases and Liquids Fifth Edition.

Group k	Nk	hf1k	Nk * hf1k	gf1k	Nk * gf1k
CH2	15	-20.763	-311.445	8.231	123.465
CH=CH	1	69.939	69.939	92.900	92.900
CH3	2	-45.947	-91.894	-8.030	-16.060
COO	1	-313.545	-313.545	-281.495	-281.495
		Total	-646.945	Total	-81.19

Table 8: Property estimation using Constantinou and Gani approach for Ethyl Oleate

Using the values and substitute in equation (2.46) and (2.47), the Gibbs free energy of formation and enthalpy of formation for ethyl oleate at 298 K is -96.02 kJ/mol and -636.11 kJ/mol respectively.

Inserting the Gibbs free energy and enthalpy of formation at 298 K from above Constantinou and Gani approach into constant enthalpy of Gibbs Hemholtz equation, the Gibbs free energy of formation can now be calculated. Below show the derivation of Gibbs Hemholtz equation when the enthalpy of formation is assumed to be constant [17],[19]:

$$\begin{aligned}
\frac{d(\Delta G_f^o / RT)}{dT} &= \frac{-\Delta H_f^o}{RT^2} \\
\int_{T_o}^{T} d(\Delta G_f^o / RT) &= -\int_{T_o}^{T} \frac{\Delta H_f^o}{RT^2} \\
\frac{\Delta G_f^o}{RT} - \frac{\Delta G_{f,T_O}^o}{RT} &= -\Delta H_f^o \int_{T_o}^{T} \frac{dT}{RT^2} \\
&= -\Delta H_f^o \left[\frac{-1}{T} \right]_{T_O}^{T} \\
&= -\Delta H_f^o \left[\frac{1}{T} - \frac{1}{T_O} \right] \\
\Delta G_f^o &= T \left[\frac{\Delta G_{f,T_O}^o}{T_o} + \Delta H_f^o \left(\frac{1}{T} - \frac{1}{T_O} \right) \right]
\end{aligned}$$

Table 9 and 10 show the result of Gibbs free energy of formation for each molecule at respective temperature:

Methanol-Methyl Oleate system

Molecule (i)	ΔG_f^o (kJ/mol)		
	T=333 K	T=323 K	T=313 K
Triolein	-80.4394	-92.4523	-144.5486
Methanol	-157.6394	-158.9622	-160.2737
Methyl Oleate	-44.2229	-61.3738	-78.5247
Glycerol	-432.7824	-437.3167	-441.8295

Table 9: Gibbs free energy of formation of molecule involved

Ethanol-Ethyl Oleate system

Molecule (i)	ΔG_f^o (kJ/mol)		
	T=345 K	T=335 K	T=325 K
Triolein	22.1595	-29.9368	-82.0331
Ethanol	-157.0392	-159.3444	-161.6341
Ethyl Oleate	-10.8380	-28.9618	-47.0857
Glycerol	-427.3137	-431.8730	-436.4115

Table 10: Gibbs free energy of formation of molecule involved

4.1.2 Activity Coefficient, γ_i

As mentioned in the literature review section, due to the insufficient data of vapor liquid equilibria of methyl oleate-methanol system and ethyl oleate-ethanol system, thus an estimation of activity coefficients from Group-Contribution method is chosen. The Group-Contribution method selected is UNIFAC. There are two methods used in this study: (First method: T,A+E,G and Second method: T, A+E, A+G) by which T=Triolein, A=Alcohol, E=Ester and G=Glycerol. Therefore there will be four sets of activity coefficients in this study (since there are methyl oleate methanol system and ethyl oleate ethanol system). Below show the method employed in obtaining the activity coefficient [20]:

1. Firstly we need to identify group in the system.
   1.1 First Method

Methyl oleate - methanol system

Group Identification						
Molecule (i)	**Name**	**Main No.**	**Sec No.**	**vji**	**Rj**	**Qj**
Methyl-oleate (1)	CH_3	1	1	2	0.9011	0.848
	COO	41	77	1	1.38	1.2
	CH_2	1	2	14	0.6744	0.54
	CH=CH	2	6	1	1.1167	0.867

Table 11: Group identification for methyl-oleate

Group Identification						
Molecule (i)	**Name**	**Main No.**	**Sec No.**	**vji**	**Rj**	**Qj**
Methanol (2)	CH_3	1	1	1	0.9011	0.848
	OH	5	14	1	1	1.2

Table 12: Group identification for methanol

Ethyl oleate – ethanol system

Group Identification						
Molecule (i)	**Name**	**Main No.**	**Sec No.**	**vji**	**Rj**	**Qj**
Ethyl-oleate (1)	CH_3	1	1	2	0.9011	0.848
	COO	41	77	1	1.38	1.2
	CH_2	1	2	15	0.6744	0.54
	CH=CH	2	6	1	1.1167	0.867

Table 13: Group identification for ethyl oleate

Group Identification						
Molecule (i)	**Name**	**Main No.**	**Sec No.**	**vji**	**Rj**	**Qj**
Ethanol (2)	CH_3	1	1	1	0.9011	0.848
	CH_2	1	2	1	0.6744	0.54
	OH	5	14	1	1	1.2

Table 14: Group identification for ethanol

1.2 Second Method

For second method, the needed activity coefficient is for both solutions (first solution: alcohol and ester, second solution: alcohol and glycerol). The group identification for first solution is the same as first method meanwhile for second solution, methanol and and ethanol are the same as in table 11 and 12. Group identification for glycerol is shown as below:

Group Identification						
Molecule (i)	**Name**	**Main No.**	**Sec No.**	**vji**	**Rj**	**Qj**
Glycerol (1)	CH2	1	2	2	0.6744	0.54
	CH	1	3	1	0.4469	0.228
	OH	5	14	3	1	1.2

Table 15: Group identification for glycerol

2. COMBINATORIAL PART. With information above, the parameters in combinatorial part can be found (here x_1 and x_2 will be assumed such that $x_1 + x_2=1$).

$$l_i = \frac{z}{2}(ri - qi) - (ri - 1) \quad (2.39)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (2.38)$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (2.37)$$

$$r_i = \sum_k v_k^{(i)} R_k \quad (2.36)$$

$$\Phi_\mathrm{i} = \frac{r_i x_i}{\sum_j r_j x j_j} \quad (2.35)$$

3. Substitute all in combinatorial equation as in equation (2.33).

$$\ln\gamma_i^C = \ln\frac{\Phi i}{xi} + \frac{z}{2} qi \ln\frac{\theta i}{\Phi i} + li - \frac{\Phi i}{xi}\sum_j x_j l_j \quad (2.33)$$

4. RESIDUAL PART. Firstly the group interaction parameters, a_{mn}. This parameter can be obtained from Table 8-24 in book 'Properties of Gases and Liquid' and by pairing the main group that exist in the molecule or the mixture. Along with that is group interaction parameter, ψ_{mn} which can be obtained using equation (2.42). Below is the result:

Group-interaction parameter			
a1,1	0	**ψ1,1**	1
a1,41	387.1	**ψ1,41**	0.3181
a41,1	529	**ψ41,1**	0.2091
a41,41	0	**ψ41,41**	1
a1,2	86.02	**ψ1,2**	0.7753
a2,1	-35.36	**ψ2,1**	1.1103
a2,2	0	**ψ2,2**	1
a41,2	1397	**ψ41,2**	0.0160
a2,41	48.33	**ψ2,41**	0.8668
a1,5	986.5	**ψ1,5**	0.0540
a5,1	156.4	**ψ5,1**	0.6296
a5,5	0	**ψ5,5**	1
a5,2	457	**ψ5,2**	0.2587
a5,41	190.3	**ψ5,41**	0.5695
a2,5	524.1	**ψ2,5**	0.2121
a41,5	88.63	**ψ41,5**	0.7693

Table 16: Group interaction parameter for each group in the mixture

For methyl oleate-methanol system, there are 3 main groups in molecule (1) which is 1(CH_3 and CH_2), 41(COO) and 2 (CH=CH). Meanwhile for molecule (2), there are 2 main groups which are 1 (CH_3) and 5 (OH). Therefore as for overall mixture, 4 main groups exist.

As for ethyl oleate-ethanol system, the main group for its molecule (1) is slightly the same with methyl oleate. The different is only at CH_2 group where the number of group CH_2 in ethyl oleate is more than methyl oleate. Meanwhile for molecule (2), other than CH_3 and OH group, CH_2 group also exist.

For glycerol-methanol system, there are 2 main groups for molecule (1) which is 1(CH2 and CH) and 5(OH) and also 2 main groups in molecule (2); 1(CH3) and 5(OH).

The number of main group in glycerol-ethanol system is almost the same with glycerol-methanol system. Molecule (2) in this system also has 2 main groups, however at main group (1), there are additional of CH2 group.

5. Compute the mole fraction of each group, x_m by using equation (2.43) and the area fraction of group m, θ_m by using equation (2.41).

$$x_m = \frac{V_j^i}{\sum v_j^i} \tag{2.43}$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{2.41}$$

6. Obtain the residual activity coefficient of group k in the molecule *i*, $\Gamma_k^{(i)}$ by using equation (2.40). For methyl oleate methanol system, there would be 4 groups of component in molecule methyl oleate and as for molecule methanol; there would be 2 groups of component. Hence, there are total of 6 values of $\Gamma_k^{(i)}$. Meanwhile for ethyl oleate ethanol system there are total of 7 values of $\Gamma_k^{(i)}$. Glycerol methanol

system will have total of 6 values of $\Gamma_{\mathrm{k}}^{(\mathrm{i})}$. and glycerol ethanol system will have 7 values of $\Gamma_{\mathrm{k}}^{(\mathrm{i})}$.

Below show the example of calculation for ln $\Gamma_{\mathrm{CH3}}^{(\mathrm{methanol})}$.

$$\ln\Gamma_{k} = Q_{k}\left[1-ln\left(\sum_{m}\theta_{m}\Psi_{mk}\right)-\sum_{m}\frac{\theta_{m}\Psi_{km}}{\sum_{n}\theta_{n}\Psi_{nm}}\right] \tag{2.40}$$

$$\ln\Gamma_{CH3} = Q_{CH3}\left[1-ln\left(\sum_{m}\theta_{m}\Psi_{mCH3}\right)-\sum_{m}\frac{\theta_{m}\Psi_{CH3m}}{\sum_{n}\theta_{n}\Psi_{nm}}\right]$$

n and m can be any other groups in molecule (1). Therefore:

$$\ln\Gamma_{CH3} = Q_{CH3}\begin{bmatrix} 1-\ln(\theta_{CH3}\Psi_{CH3-CH3}+\theta_{OH}\Psi_{OH-CH3}) \\ -\dfrac{\theta_{CH3}\Psi_{CH3-CH3}}{\theta_{CH3}\Psi_{CH3-CH3}+\theta_{OH}\Psi_{OH-CH3}}+\dfrac{\theta_{OH}\Psi_{CH3-OH}}{\theta_{CH3}\Psi_{CH3-OH}+\theta_{OH}\Psi_{OH-OH}} \end{bmatrix}$$

The calculation is repeated for other group for both molecule in both system methyl-oleate and methanol, ethyl-oleate and ethanol, glycerol-methanol and glycerol-ethanol.

7. Find the mol fraction of each group, X_k for the mixture. For methyl oleate methanol system and ethyl oleate ethanol system, there are 5 groups of component exist in each mixture. Meanwhile for glycerol ethanol and glycerol methanol system, 4 groups of component will be exist in each mixture. The example of calculation for X_{CH3} in methyl oleate-methanol system can be shown as below.

$$X_{k} = \frac{\sum_{j}x_{j}v_{kj}}{\sum_{j}x_{j}\sum_{k}v_{kj}} \tag{4.3}$$

$$X_{CH_3} = \frac{x_{MO}\,v_{CH3/MO}+x_{MEOH}v_{CH3/MEOH}}{\begin{matrix}x_{MO}(v_{CH3,MO}+v_{COO,MO}+v_{CH2,MO}+v_{CH=CH,MO}+v_{OH,MO}) \\ +\,x_{MEOH}(v_{CH3,MEOH}+v_{COO,MEOH}+v_{CH2,MEOH}+v_{CH=CH,MEOH}+v_{OH,MEOH})\end{matrix}}$$

Where MEOH = methanol

MO = methyl oleate

The calculation will be repeated for each group in the mixture.

8. Obtain the area fraction of each group, θ_k for the mixture by using equation (2.41).

$$\theta_k = \frac{Q_k X_k}{\sum_n Q_n X_n} \tag{2.41}$$

9. Along with that, the residual activity coefficient of group k in the mixture, Γ_k is obtained by using the same equation (2.40) as the residual activity coefficient of group k in the molecule, $\Gamma_k^{(i)}$.

$$\ln \Gamma_k = Q_k \left[1 - ln \left(\sum_m \theta_m \Psi_{mk}\right) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}}\right] \tag{2.40}$$

10. Substitute all the values: v_k, Γ_k , $\Gamma_k^{(i)}$ into the residual equation as in equation (2.34).

$$\ln \gamma_i^R = \sum_k v_k \left(\ln \Gamma_k - \ln \Gamma_k^{(i)}\right) \tag{2.34}$$

11. After substituting both the combinatorial part and residual part in equation (2.32), finally activity coefficients can be achieved.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{2.32}$$

4.2 RESULT INTERPRETATION

4.2.1 FIRST MODEL

4.2.1.1 METHYL-OLEATE METHANOL SYSTEM

T	333 K	**Equilibrium concentration,y_i**	**Component/Ratio (A:T)**	**3:1**
γE	2.2497		Triolein (T)	0.028023
γA	4.1547		Methanol (A)	0.084070
χE	0.88791		Methyl-Oletate (E)	0.665930
χA	0.11209		Glycerol (G)	0.221977

Table 17: Equilibrium concentration of components in Methyl-Oleate methanol system at T=333 K

T	323	**Equilibrium concentration,y_i**	**Component/Ratio (A:T)**	**3:1**
γE	2.2492		Triolein (T)	0.028074
γA	4.1535		Methanol (A)	0.084222
χE	0.88770		Methyl-Oletate (E)	0.665778
χA	0.11230		Glycerol (G)	0.221926

Table 18: Equilibrium concentration of components in Methyl-Oleate methanol system at T=323 K

T	313	**Equilibrium concentration,y_i**	**Component/Ratio (A:T)**	**3:1**
γE	2.2491		Triolein (T)	0.028087
γA	4.1532		Methanol (A)	0.084260
χE	0.88765		Methyl-Oletate (E)	0.665740
χA	0.11235		Glycerol (G)	0.221913

Table 19: Equilibrium concentration of components in Methyl-Oleate methanol system at T=313 K

4.2.1.1.1 Different Reactant Ratio

The reactant molar ratio, alcohol to triolein is manipulated starting from molar ratio 3:1 and in increasing manner. The purpose is to see which of the ratio will produce the highest equilibrium concentration or yield of Biodiesel. Thou, a higher ratio like 8:1 or 10:1 will not be favorable because excess alcohol means extra cost especially due to alcohol recovery process.

However the equilibrium concentration becomes negative value when the molar ratio started to increase to 4:1. Therefore the data above only show the equilibrium composition at molar ratio 3:1 and change in equilibrium composition (increase or decrease) toward increasing of reactant ratio could not be observe. However this shows that at only molar ratio of 3:1, the equilibrium concentration of the system has already achieved its maximum concentration. This means the triolein has almost fully convert into Biodiesel at only molar ratio of 3:1.

4.2.1.1.2 Different Operating Temperature

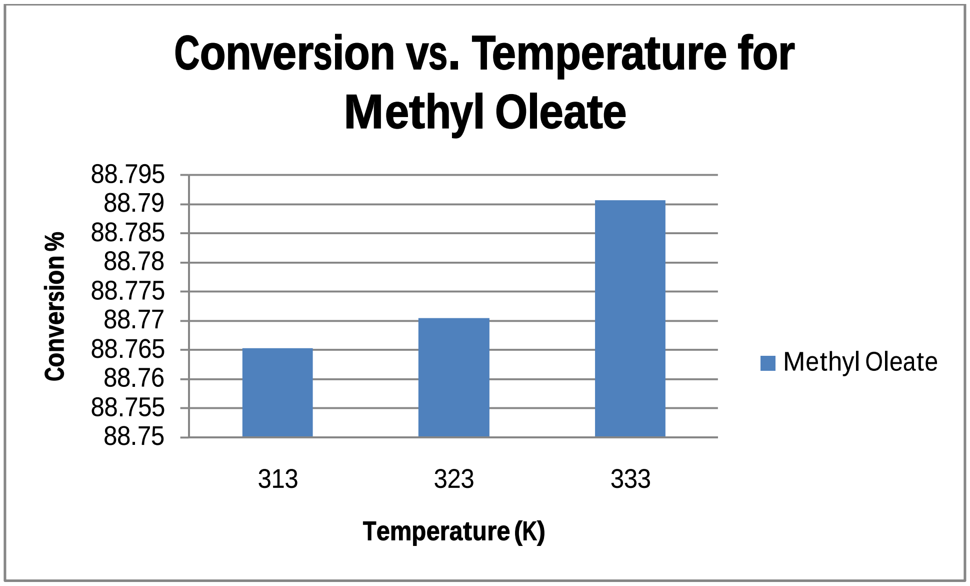


Figure 3: Conversion of Methyl Oleate by manipulation of temperature

The purpose of temperature manipulation is to see which one of the operating temperature that will give the highest maximum conversion. The operating temperature of this system is manipulated at 333 K, 323 K and 313 K. Higher temperature than 333 K is not used as above the boiling point of methanol, methanol will be evaporated and thus the vapor liquid equilibrium (VLE) has to be considered by which in this study the reaction is assumed to be only in liquid phase.

From Figure 4, the conversion is showing an increasing trend when the temperature is increased. This might be due to the fact that transesterification reaction is an endothermic reaction and thus favoring a higher temperature in order to produce a higher conversion. This can be explained by the equilibrium theory where an endothermic reaction requires heat in order to change from reactant to product. Therefore if the temperature decreasing, it will tend to go the left hand side and cause lower conversion.

The Gibbs free energy of this reaction is -12.094 kJ/mol. Due to the negative value, the forward reaction would be spontaneous. However the equilibrium constant for this system at temperature 333 K is 78.9 which is moderate. When the value of equilibrium constant is neither very high nor very small, we conclude that the reaction occurs both in forward and backward direction and equilibrium will be attained after certain period of time.

In addition if the temperature becomes too low, it can effect the kinetic of the system where in other word the kinetic is limited. The system will also take longer time to achieve the equilibrium. Thus, an optimum temperature should be the temperature that compromises both thermodynamically and kinetically namely 333 K as at this temperature the equilibrium concentration has already maximum.

4.2.1.2 ETHYL-OLEATE ETHANOL SYSTEM

T	345 K	**Equilibrium concentration**	**Component/Ratio (A:T)**	**3:1**
γE	2.309377		Triolein (T)	0.024818812
γA	5.924482		Ethanol (A)	0.074456437
χE	0.900725		Ethyl-Oleate (E)	0.675543563
χA	0.099275		Glycerol (G)	0.225181188

Table 20: Equilibrium concentration of components in Ethyl-Oleate ethanol system at T=345 K

T	335	**Equilibrium concentration**	**Component/Ratio (A:T)**	**3:1**
γE	2.315039		Triolein (T)	0.024178473
γA	5.944859		Ethanol (A)	0.072535418
χE	0.903286		Ethyl-Oleate (E)	0.677464582
χA	0.096714		Glycerol (G)	0.225821527

Table 21: Equilibrium concentration of components in Ethyl-Oleate ethanol system at T=335 K

T	325	**Equilibrium concentration**	**Component/Ratio (A:T)**	**3:1**
γE	7.200497		Triolein (T)	0.023445409
γA	0.879137		Ethanol (A)	0.070336228
χE	0.003118		Ethyl-Oleate (E)	0.679663772
χA	0.996882		Glycerol (G)	0.226554591

Table 22: Equilibrium concentration of components in Ethyl-Oleate ethanol system at T=325 K

4.2.1.2.1 Different Reactant Ratio

The data for ethyl oleate ethanol system shows only data for reactant ratio 3:1 as higher than that ratio, the equilibrium composition will produce negative value. However, this shows that at molar reactant ratio 3:1, the conversion already achieves its maximum with conversion of 90.07% at temperature of 345 K.

4.2.1.2.2 Different Operating Temperature

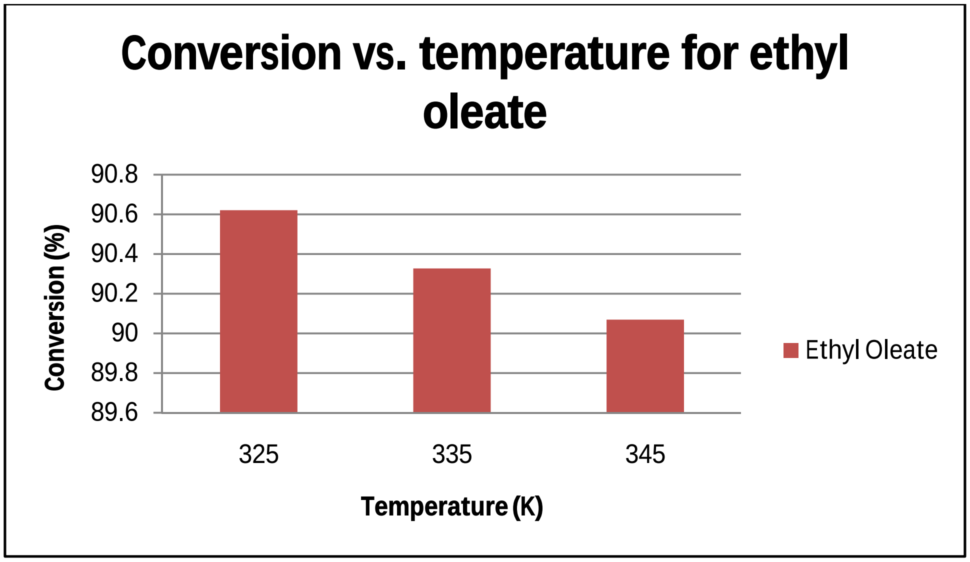


Figure 4: Conversion of Ethyl Oleate by manipulation of temperature

The operating temperature for a Biodiesel reaction system is depending on the boiling point of the alcohol used. In this case, ethanol has the boiling point around 72 degree celcius or 345 K. Therefore, the manipulated operating temperature will be started at 345 K, followed by 335 K and 325 K. From Table 14, Table 15 and Table 16 and Figure 4, decreasing the temperature resulted in higher equilibrium concentration and conversion. This trend can be explained by the equilibrium theory where an exothermic reaction will favor a lower temperature when higher conversion is required. However since we have to comply with effect in kinetic change and since the difference of conversion between 345 K and 325 K is not high (0.6%), the optimal temperature should be 345 K.

4.2.1.3 DIFFERENT TYPE OF ALCOHOL

The conversion for each system is observed at the respective reactant molar ratio of 3:1 only since at molar ratio of 3:1, the equilibrium concentration for methyl oleate methanol system already achieve its maximum and since the optimum temperature is when thermodynamic and kinetic compromise, only consider the conversion at temperature of 333 K for methyl oleate methanol system and temperature of 345 K for ethyl oleate ethanol system. The conversion of Biodiesel will used Triolein as the basis calculation since Triolein is the limiting reactant. The equation of conversion can be shown as below:

$$X_T = \frac{N_{TO} - N_T}{N_{TO}} \times 100$$

Type of alcohol used	Conversion (%)
Methanol	88.79
Ethanol	90.07

Table 23: Conversion for both system

As Table 23 show, the conversion for ethyl oleate is much higher than methyl. This result is not parallel with research by H. Sanli and M.Canakci [25] where methanol will gives better conversion when compared to other solvent like ethanol and propanol. The methanol's structure where it has only one carbon and therefore it will produce higher reactivity and higher conversion. Low reactivity can definitely cause harder transesterification reaction and consequently the reaction time to completeness of the reaction become longer.

Since in this method, the distribution of alcohol is only to ester, thus the result obtained will not be so precise. Therefore second method will be used in order to verify this condition.

4.2.2 SECOND METHOD

4.2.2.1 METHYL-OLEATE METHANOL AND GLYCEROL-METHANOL SYSTEM

T	333 K	Equilibrium Composition	Component/Ratio (A:T)	3:1	4:1	5:1
X_{A1}	0.168453009		Triolein (T)	0.1201	0.0615	0.0224
X_{A2}	0.684339787		Methanol (A)	0.3604	0.3845	0.4005
			Methyl-Oletate (E)	0.3896	0.4155	0.4328
			Glycerol (G)	0.1299	0.1385	0.1443

Table 24: Equilibrium concentration of components in Methyl-Oleate methanol system at T=333 K

T	323 K	Equilibrium composition	Component/Ratio (A:T)	3:1	4:1	5:1
X_{A1}	0.168630285		Triolein (T)	0.1203	0.0616	0.0225
X_{A2}	0.684845726		Methanol (A)	0.3608	0.3849	0.4009
			Methyl-Oletate (E)	0.3892	0.4151	0.4324
			Glycerol (G)	0.1297	0.1384	0.1441

Table 25: Equilibrium concentration of components in Methyl-Oleate methanol system at T=323 K

T	313 K	Equilibrium composition	Component/Ratio (A:T)	3:1	4:1	5:1
X_{A1}	0.168675360		Triolein (T)	0.1203	0.0617	0.0226
X_{A2}	0.684974318		Methanol (A)	0.3609	0.3850	0.4010
			Methyl-Oletate (E)	0.3891	0.4150	0.4323
			Glycerol (G)	0.1297	0.1383	0.1441

Table 26: Equilibrium concentration of components in Methyl-Oleate methanol system at T=313 K

4.2.2.1.1 Different reactant ratio

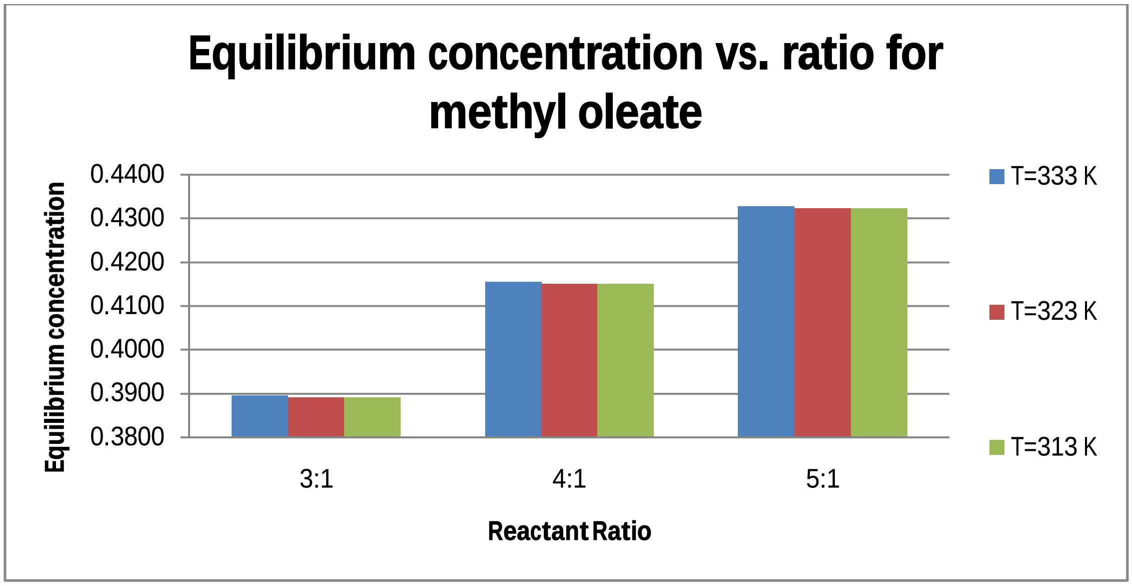


Figure 5: Equilibrium concentration vs. ratio for methyl oleate for second method

Above figure shows when the reactant ratio (alcohol to triolein molar ratio) is increase, the equilibrium concentration also increases. This result applies for all temperatures 333 K, 323 K and 313 K. This increasing trend is due to the more excess of alcohol used. Excess alcohol is needed as it will drive the reaction towards completion.

The reactant ratio for methyl oleate system in second method is manipulated starting from ratio 3:1 to 4:1 and 5:1. The reason for small different of reactant ratio chosen to be manipulated is due to at ratio 6:1, the system starts producing negative value for the equilibrium composition. Therefore it can be concluded that ratio 5:1 is the maximum ratio that can be used in order to produce high conversion of methyl oleate. Below show the summary of conversion using different ratio at constant temperature 333 K.

Ratio	Conversion
3:1	51.94178317
4:1	69.25571089
5:1	86.56963862

Table 27: Conversion at different molar ratio for methyl oleate system

4.2.2.1.2 Different operating temperature

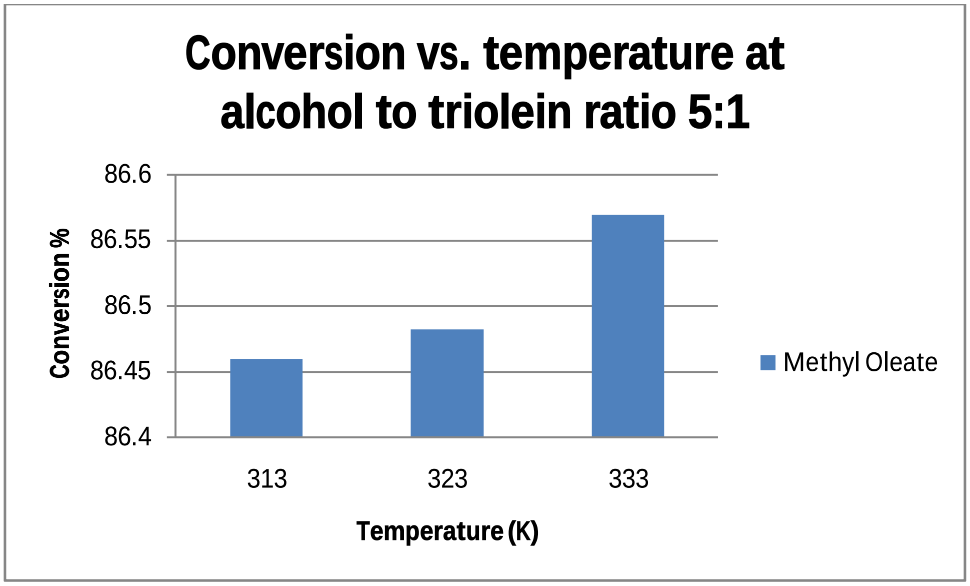


Figure 6: Conversion vs. temperature for methyl oleate system at ratio 5:1

From above figure, conversion increase as temperature increase. This MIGHT be due to transesterification reaction for methanol is an endothermic reaction, thus it favors high temperature in order to produce high conversion. Since at highest allowable temperature, 333 K (higher than 333 K, methanol will start to evaporate) achieves highest conversion, thus it will be the optimal temperature for this system.

Observe that the ratio used to see the effect of temperature changes is 5:1. This is due to the maximum allowable ratio is 5:1 whereby this means above than this ratio, the equilibrium composition starts produce negative value and thus invalid conversion produced.

4.2.2.2 ETHYL-OLEATE ETHANOL AND GLYCEROL-ETHANOL SYSTEM

T	345 K	Equilibrium composition	Component/Ratio (A:T)	3:1	4:1	5:1
X_{A1}	0.143324840		Triolein (T)	0.2052	0.1522	0.1168
X_{A2}	0.929704057		Ethanol (A)	0.6155	0.6565	0.6839
			Ethyl-Oletate (E)	0.1345	0.1435	0.1495
			Glycerol (G)	0.0448	0.0478	0.0498

Table 28: Equilibrium concentration of components in ethyl oleate ethanol system at T=345 K

T	335 K	Equilibrium composition	Component/Ratio (A:T)	3:1	4:1	5:1
X_{A1}	0.142195069		Triolein (T)	0.2028	0.1496	0.1142
X_{A2}	0.925295713		Ethanol (A)	0.6083	0.6489	0.6759
			Ethyl-Oletate (E)	0.1417	0.1511	0.1574
			Glycerol (G)	0.0472	0.0504	0.0525

Table 29: Equilibrium concentration of components in ethyl oleate ethanol system at T=335 K

T	325 K	Equilibrium composition	Component/Ratio (A:T)	3:1	4:1	5:1
X_{A1}	0.140819548		Triolein (T)	0.1999	0.1466	0.1110
X_{A2}	0.919860646		Ethanol (A)	0.5997	0.6397	0.6663
			Ethyl-Oletate (E)	0.1503	0.1603	0.1670
			Glycerol (G)	0.0501	0.0534	0.0557

Table 30: Equilibrium concentration of components in ethyl oleate ethanol system at T=335 K

4.2.2.2.1 Different reactant ratio

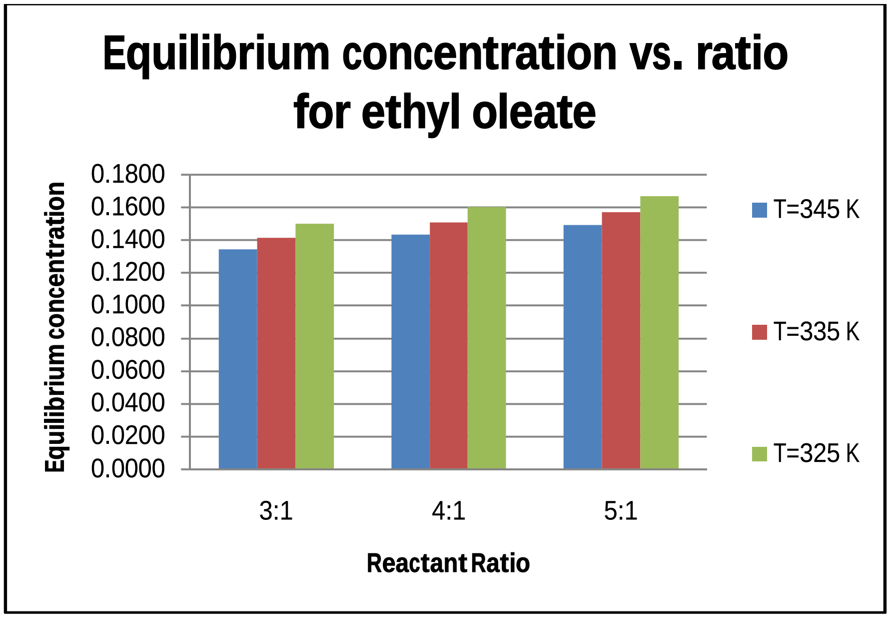


Figure 7: Equilibrium concentration vs. ratio for ethyl oleate for second method

From Figure 7 above, it shows that when the reactant ratio increases, the equilibrium composition also increases. This is parallel with the theory where when more excess of alcohol is used, the composition of product should be higher as more excess of alcohol is consumed to drive the reaction towards completion.

4.2.2.2.2 Different operating temperature

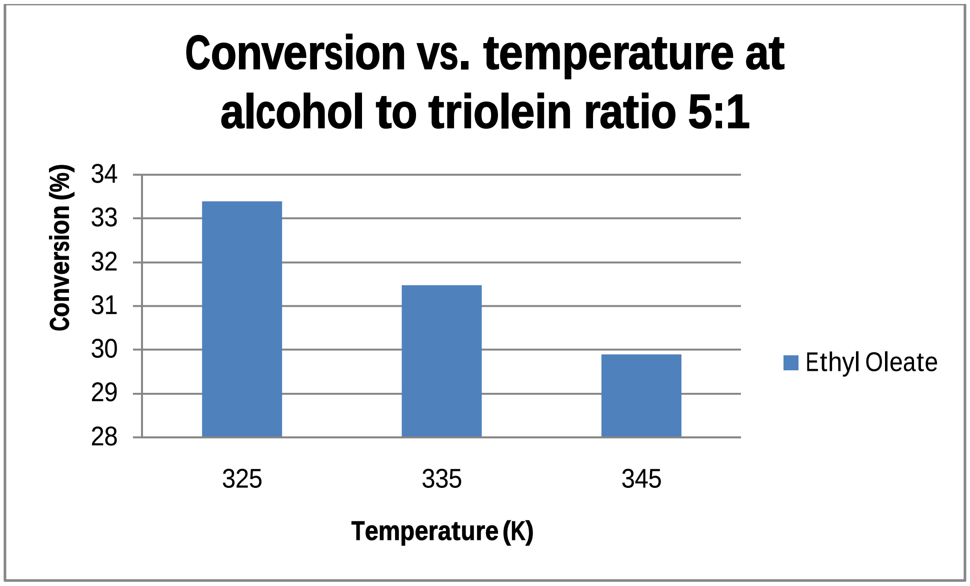


Figure 8: Equilibrium conversion vs. temperature at alcohol to triolein ration 5:1

The conversion for ethyl oleate when temperature is increase shows decreasing trend. This is the same with the first method where the conversion increases when temperature is decrease. Nevertheless, this shows that transesterification of reaction of triolein and ethanol is somehow an exothermic reaction. Exothermic reaction will favor lower temperature in order to achieve high conversion. This can be explained by the Le Chatelier principle where exothermic reaction release energy, thus if temperature decreases, the system will tend to go to the right hand side of equation and thus produce more conversion.

However a very low temperature can effect the kinetic of the system. Therefore the temperature taken should be temperature that agree with both kinetic and thermodynamic (conversion). In this case is 345 K as if comparison is made between conversion at 325 K and 345 K, the conversion different is only 3.5%.

4.2.2.3 DIFFERENT TYPE OF ALCOHOL

For the second method, alcohol is distributed to both products in the system: ester and glycerol. If we take the alcohol to triolein molar ratio 5:1 and temperature of 333 K for methyl oleate and temperature of 345 K for ethyl oleate, the comparison of conversion between these alcohols can be made. The temperature taken is the optimal temperature for both systems. Below table shows conversion of each ester:

Type of Alcohol used	Conversion (%)
Methanol	86.57%
Ethanol	29.89%

Table 31: Conversion comparison between different types of alcohol used

Using methanol achieves higher conversion compared with using ethanol for biodiesel production. This is parallel with the research by H.Sanli, M. Canakci where using methanol should gives higher conversion. As mentioned earlier, this is be due to the structure of methanol which proposes higher reactivity. High reactivity will drive reaction to completeness and thus higher conversion.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The first part of this project is focusing on understanding and developing the Minimization of Gibbs Free Energy equations and Stoichiometric method equation meanwhile the second part will continue on developing the simulation program using Excel spreadsheet in order to find the equilibrium composition and maximum conversion. In the first part, the Stoichiometric method is chosen as it is detail and easy to understand. Using this method, the equilibrium composition is obtained by using extent of reaction. This extent of reaction is found from mol fraction that being predicted using the equilibrium constant equation.

From this study, it shows that when the reactant molar ratio is increased, the equilibrium concentration will also increase. This might be due to the excess of alcohol being used that able to complete the reaction. Comparison of conversion in methyl oleate for both system shows using first method achieves higher conversion, 88.79% vs. 51.94% (at molar ratio 3:1). It is the same with ethyl oleate where the first method achieves higher conversion 90.07% vs. 17.93%.

The trend for temperature is also the same where in both method, methyl oleate conversion increase when temperature increases and in ethyl oleate, conversion decreases when temperature increases. Therefore it can be concluded that transesterification reaction of triolein and methanol is endothermic meanwhile transesterification reaction of triolein and ethanol is exothermic.

First model is distributed only to ester. Therefore the thermodynamic analysis on equilibrium composition will not be as precise as the second method. The distribution of alcohol in second method is to both product; ester and glycerol. Therefore the result in second method will be more reliable.

Thus proposed alcohol used is methanol with alcohol to triolein ratio 5:1 and temperature of 333 K.

As the recommendation, since there are some of the properties such as Gibbs free energy of formation and enthalpy of formation of some components are estimated using property estimation method, in the future there should be experimental value for this type of components as estimation value will definitely has errors compared to the real values.

Other than that, there is no data mention whether transesterification reaction is exothermic or endothermic because from the result it shows that using ethanol is showing exothermic reaction meanwhile using methanol is endothermic reaction. Therefore experiment should be done in order to investigate whether using different types of alcohol gives different result in term of the temperature trend.

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APPENDIX

Appendix 1: Physical and Chemical Properties of Substance

a) Triolein

Appearance	Colorless viscous liquid
Molecular Formula	$C_{57}H_{104}O_6$
Molecular weight	885.4321
Density g/cm^3	0.9210
Melting Point °C	-5.5
Boiling Point °C	818.7
Flash Point °C	302.6
Solubility	Soluble in chloroform: 0.1 g/mL

Table 32: Physical and Chemical Properties of Olein [23]

b) Methanol

Appearance	Colorless liquid
Molecular Formula	CH_3OH
Molecular weight	32.04
Density g/cm^3	0.7918
Melting Point °C	-98
Boiling Point °C	64.7
Flash Point °C	11
DH_f constant	A = -188.188 B = -4.9823e-02 C= 2.0791e-05
$G_{f\ at}$ 298 K (kJ/mole)	-162.51

Table 33: Physical and Chemical properties of methanol [24], [25]

c) Ethanol

Appearance	Clear Colorless liquid
Molecular Formula	C_2H_5OH
Molecular weight	46.0414
Density g/cm^3	0.7900
Melting Point °C	-114.1
Boiling Point °C	78
DH_f constant	A = -216.961 B = -6.9572E-02 C= 3.1744E-05
$G_{f\ \text{at}}$ 298 K (kJ/mole)	-168.28

Table 34: Physical and chemical properties of ethanol [26], [25]

d) Methyl Oleate

Appearance	Clear liquid
Molecular Formula	$C_{19}H_{36}O_2$
Molecular weight	296.48
Density g/cm^3	0.8700
Melting Point °C	-19.9
Boiling Point °C	217
Solubility	Insoluble
DH_f constant	A = -531.982 B = -3.7562E-01 C= 1.9684E-04 D=2.6007E-08 E=-2.7203E-11
$G_{f\ \text{at}}$ 298 K (kJ/mole)	-117.00

Table 35: Physical and chemical properties of methyl oleate [27],[25]

e) Glycerol

Appearance	Clear liquid
Molecular Formula	C_3H_8O
Molecular weight	92.09
Density g/cm^3	1.2600
Melting Point °C	18
Boiling Point °C	290
Flash point °C	190
DH$_f$ constant	A = -559.438 B = -9.2185 E-02 C= 4.5003E-05
G$_{f \text{ at}}$ 298 K (kJ/mole)	-448.89
Solubility	Miscible in water

Table 36: Physical and chemical properties of glycerol [28],[25]