# Measurement of LLE For Biodiesel and Bio-Oil in Solvents

by

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Final Year Project Progress Report submitted in
partial fulfillment of the requirements for the
Bachelor of Chemical Engineerng (Hons)

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Universiti Teknologi PETRONAS
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# CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Enginering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
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SRI ISKANDAR, PERAK
SEPTEMBER 2011

# 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 acknowledgments, and that the original work contained here have not been undertaken or done by unspecified sources or persons.

AHMAD UMAIR BIN ZULKEFLI

# ABSTRACT

Biodiesel is an alternative fuel for internal combustion engines. It can reduce carbon monoxide (CO), hydrocarbon (HC) and particulate matter (PM) emissions, compared with diesel fuel, but there is also an increase in nitrogen oxides (NOx) emission. The combustion of diesel oil will produces carbon dioxide that contribute to global warming and sulfur that lead to acid rains. Furthermore, the high prices of fossil fuel make researchers find an alternative and renewable fuel. The diesel oil or methyl ester is produced in transesterification of triglycerides with methanol. It is called in other name with alcoholysis.

In the reaction of producing biodiesel, the product that is glycerol is formed simultaneously to methyl esters. This condition will complicate the reactant and product recovery and thus increase operation cost. The knowledge of the complex phase behaviours is essential in designing and optimizing the recovery. Therefore, an experimental investigation of the complex phase behaviours between methanol, different oils, and catalyst as reactants and methyl ester and glycerol as products need to be done to define suitable process conditions for reaction and product separation.

Hopefully this study will enhance the production of biodiesel from rubber seed oil in Malaysia.

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In the name of Allah, The Gracious, The Merciful

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# CHAPTER 1
# INTRODUCTION

## 1.1 BACKGROUND

Biodiesel is an alternative fuel for internal combustion engines. It can reduce carbon monoxide (CO), hydrocarbon (HC) and particulate matter (PM) emissions, compared with diesel fuel, but there is also an increase in nitrogen oxides ($NO_x$) emission. The combustion of diesel oil will produces carbon dioxide that contribute to global warming and sulfur that lead to acid rains. Furthermore, the high prices of fossil fuel make researchers find an alternative and renewable fuel [1]. The diesel oil or methyl ester is produced in transesterification of triglycerides with methanol. It is called in other name with alcoholysis.

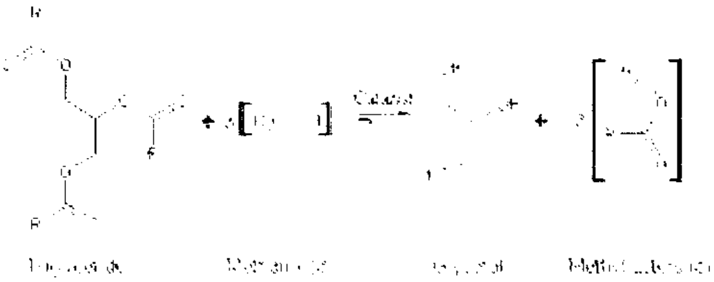


Figure 1.1: The reaction of producing biodiesel (Methy Esters)

The biodiesel are biodegrable, nontoxic, and reducing pollution. However, the vegetable oils have relative high viscosity and also high melting point. Converting with ethanol will reduce the viscosity and melting point in order to make it compatible to the engines. The mechanism of the transesterification is as below.

$$RCOOR' - R'OH \xrightleftharpoons{catalyst} RCOOR' - R'OH \qquad [1.1]$$

The most widely used vegetable oils for the production of biodiesel are taken from rape seeds, sunflowers, and soybean. In Malaysia, the natural rubber trees are widely spread and being another source of biodiesel. It has been reported that rubber Seed oils have oil rich seeds and the average of oil yield are 40%. [2]

## 1.2 PROBLEM STATEMENT

In the reaction of producing biodiesel, the product that is glycerol is formed simultaneously to methyl esters. This condition will complicate the reactant and product recovery and thus increase operation cost [3]. The knowledge of the complex phase behaviours is essential in designing and optimizing the recovery. Therefore, an experimental investigation of the complex phase behaviours between methanol, different oils, and catalyst as reactants and methyl ester and glycerol as products need to be done to define suitable process conditions for reaction and product separation.

## 1.3 OBJECTIVE AND SCOPES OF STUDY

The objective of this project is to investigate the phase behaviour of binary system for phase separation by measuring LLE of the reactant and product on binary phase diagram.

For this project, the scope of work will be focused on:

1. Synthesis of rubber Seed oil
2. Study of binary phase diagram system of reactant and product

## 1.4 RELEVANCY OF THE PROJECT

As previously mentioned, biodiesel are the alternative of substituting fossil fuel. In Malaysia, the spread of rubber trees is a chance to produce biodiesel from the rubber seeds. Thus, this project will enhance the usage of our sources that is rubber seed. Meanwhile, Jathropha oil is also reported as alternative rich oil and both sources are still in research stage and need more investigation on that.

## 1.5 FEASIBILITY OF THE PROJECT

For this project, the first semester will cover formulation of methodology by literature review. At final first semester and early second semester will be concentrated in experiment of the LLE measurement. Based on the draft methodology, the project's objectives are achievable within the time frame.

# CHAPTER 2

# LITERATURE REVIEW

## 1.1 LIQUID-LIQUID EQUILIBRIA

Liquid-liquid equilibria are of interest in extraction operations and are useful for developing a thermodynamic predictive and correlative method [4]. The three component liquid-liquid eqilibrium system at fixed temperature and pressure (always stated or implied) has, by the Phase Rule, only a single degree of freedom. The classic `triangular diagram' can in fact be regarded as a plot of three separate quantities against this single degree of freedom, which can be taken up by choosing the mol fraction of one component [5].

Liquid-liquid equilibrium measurement is essential in understanding the phase behavior of reactant and product of the process. The chemical equilibrium need to be taken into account when applying stability criteria and carrying out phase equilibrium calculations where the stability criteria to establish the conditions under which a liquid-phase split may occur [6].

Many works has been done by researchers by using LLE method for binary and ternary data in their production and purification work.Lee et al [7] has has using LLE data, including tie lines and phase boundaries for mixture containing water, methanol, fatty acid methyl esters and glycerol to accurately calculate the phase composition of each individuals liquid phase in process simulation.

Oliveira et al [8] in their work of transesterification reaction with ethanol have used LLE method to measure the ternary system of canola oil biodiesel, ethanol, and glycerol at temperatures between 303.15 and 333.15 K.

Vicenta et al [9] have used LLE for separation of tocopherol from olive oil using ethyl lactate. They studies on LLE at ambient temperature of three model system that are binary, pseudo-binary, and ternary.

## 1.2 JATROPHA OIL

Jatrophacurcas L. is a drought – resistant shrub/tree belonging to the family Euphorbiaceae [10, 11]. Jatrophacurcus is a drought-resistant perennial, growing well in marginal/poor soil. It is easy to establish, grows relatively quickly and lives, producing seeds for 50 years. Cultivated in Central and South America, Jatrophacurcaswas distributed by Portuguese seafarers in Southeast Asia, India and Africa [12]. Propagated by cuttings, is widely planted as a hedge to protect fields from browsed animals. The plant and its seeds are non-edible to animal and humans; toxicity of seeds is mainly due to the presence of curcine and deterpine [11, 13].

The existing distribution of Jatrophacurcas shows that introduction has been most successful in drier regions of the tropics. It grows on well-drained soils with good aeration and is well adapted to marginal soils with low nutrient content [11].

Jatropha plant produces seeds with an oil content of 37% [14]. The advantage of Jatropha oil is that the oil can be combusted as fuel without being refined. Besides, it burns with clear smoke-free flame, tested successfully as fuel for simple diesel engine. The by-products are press cake a good organic fertilizer, oil contains also insecticide.

The potential use of extracted oil from Jatrophacurcas as transesterified oil (biodiesel) or as a blend with diesel have been studied [10]. The calorific value and cetane number of Jatrophacurcas oil are comparable to diesel, but the density and viscosity are much higher.

Since the density of oil is high, the engine performance, emissions and combustion parameters can be reached by optimizing the injector opening pressure, injection time, injection rate and enhancing the swirl level of the operated engine [16]. High viscosity of the Jatrophacurcas oil is not advantageous for the compression ignition engine. Pramanik (2003) has studied the performance of the engine using blends and Jatropha oil in a single cylinder (compression ignition) engine and made comparison with the performance obtained with diesel. Adequate thermal efficiencies of the engine were obtained with blends containing up to 50 % volume of Jatropha oil. 40–50 % of Jatropha oil can be replaced without any engine modification and preheating of the blends [16].

In the oil industry, different processes must be done before oil extraction occurs. When Jatrophacurcas fruits arrive for oil extraction different processes are conducted before: (a) dehulling, separating hull from nut, (b) deshelling, separating shell from kernel, (c) drying and then (d) oil extraction.

### 1.2.1Properties of Jatropha Oil

Following to Yee et al,

> *On the basis that the measured acid value is 22.7 mKOH/moil and saponification value is 194.7 mKOH/moil, average molecular weight of CJCO was calculated as 872.0 g/mol. The saponification value of CJCO was found to be small, indicating high concentration of triglycerides, and therefore CJCO can be a suitable feedstock for the production of FAME (biodiesel). Nevertheless, the high content of free fatty acids (11.4% w/w) shows that conventional biodiesel production technology using homogeneous base catalytic system is not suitable for CJCO* [17].

## 1.3 RUBBER SEED OIL

In the present investigation, rubber Seed oil, a non-edible type of vegetable oil, has been considered as a potential alternative fuel. The rubber tree (Hevea brasiliensis) is a perennial plantation crop, indigenous to South America and cultivated as an industrial crop since its introduction to Southeast Asia around 1876. Rubber plantations yield from 100 to 150 Kg/ha rubber seeds. Rubber seeds are composed of about 43% oil [18]. Rubber Seed oil is a semi-dried substance that does not contain any unusual fatty acids, but is a rich source of polyunsaturated fatty acids C18:2 and Physicochemical Characteristics of Malaysian Rubber (Hevea Brasiliensis) Seed oil 438 C18:3 that make up 52% of its total fatty acid composition [19]. Malaysia has around 1.2 million hectare of natural rubber trees planted throughout the country. It is estimated that each hectare of land planted with rubber trees can give an approximate amount of 150 kilogram of oil bearing seeds. This will be a large source for biodiesel in Malaysia. [20]

### 1.3.1 Rubber Seeds Application

Rubber Seed oil has been shown to have many applications for industrial purposes. The seeds are used for the manufacture of fatty acids, paint, alkyd resin, soap making [19], surface coatings, and water-reducible alkyds, as well as in the production of biodiesel and for use in fuel compression ignition engines [20].

### 2.3.2 Rubber Seed oil Extraction

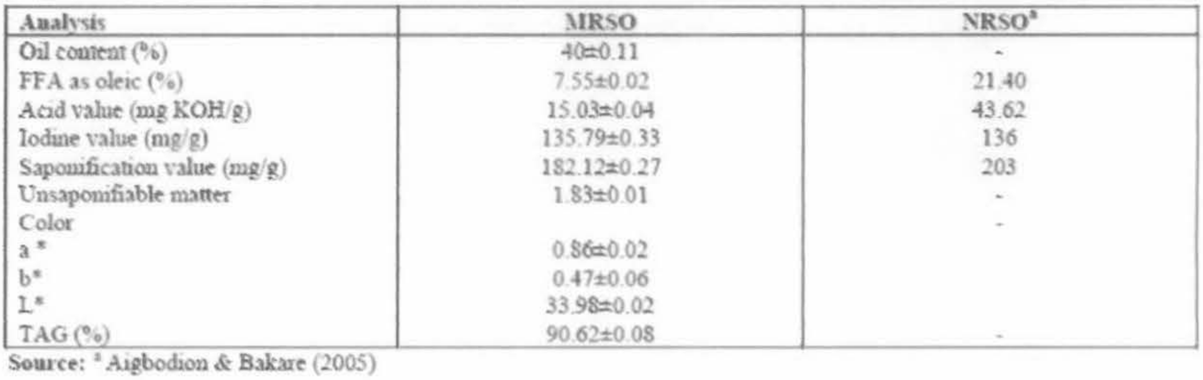
Based on the research of Bashar et al. [21], the methodology of oil extraction are as followed. Rubber seeds were obtained from the Rubber Research Institute, Sungai Buloh, Malaysia. Damaged seeds were discarded, then seeds in good condition were cleaned, shelled and dried at 105°C for 30 min. Seeds were ground using a grinder prior to oil extraction. All chemicals used in the study were analytical grade and used without further purification. The extraction of rubber seeds oil was carried out by soxhlet extraction. The rubber seed powder was extracted using hexane as a solvent for 6 hours.

### 2.3.3 Malaysian Rubber Seeds Oil (MRSO) Properties

The following table presents the physicochemical properties of MRSO. Both physical and chemical characteristics of the oil were as good as those of commercial vegetable oil. MRSO was found to contain a relatively high percentage of total lipids content (40±1.56%) compared to that of seeds such as perah Seed oil (38.59%) and date Seed oil (10.19%). Its % FFA (as oleic) of 7.55±0.02% and its acid value of 15.03±0.04 were high since the RSO had not been neutralized.

MRSO shows a high iodine value (135.79±0.33) due to its high content of unsaturated fatty acids (Table 2). Its iodine level is comparable to that of other Seed oils such as palm oil (iodine value 52), perah Seed oil (106), cotton Seed oil (99-119) and corn Seed oil (103-128) (Gunstone et al., 1994). As a result, the saponification value of RSO was Physicochemical Characteristics of Malaysian Rubber (Hevea Brasiliensis) Seed oil 440 182.12±0.27, similar to that of typical Seed oils such as sunflower, corn, and safflower oils whose average saponification value range from 175 to 250. This finding suggests that RSO has high potential for use in the production of liquid soap and shampoos. [21]

Table 2.1: Difference of Malaysian and Nigerian Rubber Seed oil



| Analysis | MRSO | NRSO[a] |
|---|---|---|
| Oil content (%) | 40±0.11 | - |
| FFA as oleic (%) | 7.55±0.02 | 21.40 |
| Acid value (mg KOH/g) | 15.03±0.04 | 43.62 |
| Iodine value (mg/g) | 135.79±0.33 | 136 |
| Saponification value (mg/g) | 182.12±0.27 | 203 |
| Unsaponifiable matter | 1.83±0.01 | - |
| Color | | - |
| a * | 0.86±0.02 | |
| b* | 0.47±0.06 | |
| L* | 33.98±0.02 | |
| TAG (%) | 90.62±0.08 | - |

**Source:** [a] Aigbodion & Bakare (2005)

## 2.4 METHANOL

Methanol is an alcohol and is a colourless, neutral, polar and flammable liquid. It is miscible with water, alcohols, esters and most other organic solvents. It is only slightly soluble in fats and oils.

Derived from natural gas, methanol is a hydrocarbon, comprised of carbon, hydrogen and oxygen. Its chemical formula is $CH_3OH$.

Methanol can be produced using catalytic process with natural gas and steam as the feedstock. The natural gas is catalytically converted to carbon oxides and hydrogen. The resulting synthesis gas mixture is circulated under pressure and moderate temperature in the existence of a metallic catalyst and converted to crude methanol. The crude methanol is distilled to yield industrial chemical grade methanol.

Other common names for methanol include methyl alcohol, methyl hydrate, wood spirit, wood alcohol, and methyl hydroxide.

### 2.4.1 Uses of Methanol

The main uses for methanol are the production of chemical products and use as a fuel. It is also being used increasingly for waste water treatment and for producing biodiesel.

Methanol is used in the production of formaldehyde, acetic acid and a variety of other chemical intermediates which form the foundation of a large number of secondary derivatives. These secondary derivatives are used in the manufacture of a broad range of products including plywood, particleboard, foams, resins and plastics.

Much of the remaining methanol demand is in the fuel sector, principally in the production of MTBE, which is blended with gasoline to reduce the amount of harmful exhaust emissions from motor vehicles. Methanol is also being used on a small scale as a direct fuel and it is fuel for fuel cells. [23]

Also, it is used in Biodiesel production. Biodiesel is a clean-burning diesel replacement fuel that is manufactured from renewable, nonpetroleum-based sources such as: vegetable oils such as soy, mustard, canola, rapeseed and palm oils; animal fats such as poultry offal, tallow, and fish oils; and used cooking oils and trap grease from restaurants.

Biodiesel is made by chemically reacting these fats and oils are with an alcohol, typically methanol, to produce an ester, or biodiesel. Although most any alcohol can be used, methanol is preferred because it is relatively inexpensive and allows for the most thorough reaction process. This process is known as transesterification. For each 10 volumes of biodiesel produced, one volume of methanol is used in the process. [24]

## 2.5 GLYCEROL

Glycerol is completely soluble in water and alcohol. It is slightly soluble in ether, ethyl acetate, and dioxane and insoluble in hydrocarbons. Glycerol has useful solvent properties similar to those of water and simple aliphatic alcohol's because of its three-hydroxyl groups.

Glycerol is a useful solvent for many solids, both organic and inorganic which is particularly important for the preparation of pharmaceuticals. The solubility of gases in glycerol, like other liquids is temperature and pressure dependent.[25]

### 2.5.1 Chemical Properties

Glycerol is a reactive molecule that undergoes all the usual reactions of alcohols. The two terminal primary hydroxyl groups are more reactive than the internal secondary hydroxyl group. Under neutral or alkaline conditions, glycerol can be heated to 250°C without formation of acrolein. Reactions with glycerol are therefore best carried out under alkaline or neutral conditions at 180°C, alkaline glycerol begins to dehydrate forming ether-linked polyglycerols. At room temperature glycerol rapidly absorbs water. When dilute it is attacked by microorganism.

On oxidation, glycerol yields variety of product depending upon the reaction conditions. By the use of mild oxidizing agent it is possible to oxidize only one hydroxyl group to yield Glyceraldehyde. These compounds may be considered very simple aldose and simplest ketoses respectively and mixture of two compounds obtained from glycerol as well as glyceraldehyde has been Called glycerose. Nitric acid converts glycerol to glyceric acid $CH_2CHCHOHCOOH$ melting at 134-135°C when pure, but usually obtained as syrupy. It is an oily liquid soluble in water and alcohol, but insoluble in ether.

Some industrially important reaction products of glycerol include; 1) Mono-,di-,and tri esters of inorganic and organic acids, 2) Mono and diglyceride of fatty acids formed by transesterification of triglycerides(from fats), 3) Aliphatic and aromatic esters formed by reactions with alkylatingagents respectively, 4) Polyglycerols formed by the intermolecular alienation of water with alkaline catalyst, 5) Cyclic 1,2- or 1,3-acetals or ketals formed by the reaction with aldehyde or ketons respectively
Glycerin has a role in virtually every industry. The largest single user in alkyl resin industry. Cellophane manufacture in which glycerin is a plasticiser is the next largest. The manufacture of the glycerol nitrate is also important consumer of glycerine

## 2.6FATTY ACID METHYL ESTER (FAME)

FAME is made virgin or used vegetable oils (both edible and non-edible) and animal fats. Fatty acid methyl ester operates in compression ignition engines like petro-diesel. Fatty acid methyl ester can be blended in any ratio with petroleum diesel fuels. It can be stored just like the petroleum diesel fuel. Petrodiesel can be replaced by biodiesel due to its superiority.

## 2.7 CATALYST

Transesterification can be catalyzed by acids, bases or enzymes. Among them, base catalysis is the most popular way and most often used commercially for biodiesel production owing to the high catalytic activity. Also, base catalysts are less corrosive than acidic compounds avoiding the necessity of expensive stainless steel as construction material[27].

The applications of other basic amino-compounds in biodiesel synthesis, including amines and tetramethylammonium hydroxide (TMAH), havebeen demonstrated by Cerce et al. [1]. Despite increasing the mutual solubility between methanol and rapeSeed oils, the Lewis amines such as 4-methylpiperidine (4-MP) and N,Ndimethyltrimethylenediamine (DMTMD) showed only moderate activity in mediating TG transesterification. TMAH, on the other hand, was found to give sensational results. In presence of 3 wt% TMAH, all triglycerides were converted to methyl esters after only 15-17 min. Also, the organic base can allow a fast phase separation at the end of reaction and never arouse soap formation. Even better, methanol and catalyst can be simply recovered by distillation yielding high purity glycerol without the need of time-consuming water washing [1]. Accordingly, a pilot plant using TMAH has been designed with a capacity of approximately 1 ton/h [1].

# CHAPTER 3
# METHODOLOGY

## 3.1 MATERIALS AND APPARATUS

### 3.1.1 Materials:

The materials include Jatropha oil, rubber seed, Methanol, Methyl Ester, Sodium Hydroxide Catalyst and Glycerol.

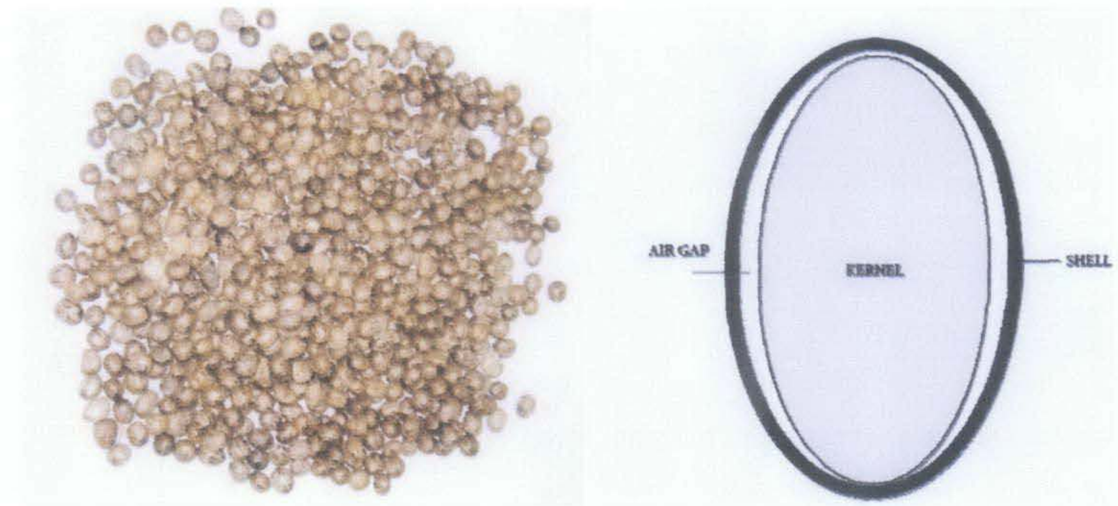


Figure 3.1: Rubber Seeds and its schematic diagram

### 3.1.2 Apparatus:

This apparatus consist of flask, thermometer, water bath with shaker, oven, and pipette.

## 3.2 METHODS

### 3.2.1 Synthesizing Rubber Oil

The rubber seeds are being processed by taken off its shell and the kernels being obtained.

Figure 3.2: Rubber seeds

Figure 3.3: Rubber seed kernals

The kernels are being dried in oven at 105°C for 2 hours. The kernels then are being crushed into smaller pieces using analytical mill equipment with blade size of 2000$\mu$m and stored in an air tight container after the process.

Figure 3.4: 0.25mm seeds

Kernels will be leached by ethanol solvent using conical flask immersed in water bath. The process will be running for 6 hours with the temperature is fixed at 45°C.The kernels are then being filtrated using filter paper to separate solid from solvent. Rotary evaporator is used to separate between oil and ethanol at around 80°C which is higher than the boiling point of ethanol.

Figure 3.5: Rotary Evaporator

### 3.2.2 Fluid Phase Equilibrium

#### 3.2.2.1 Binary LLE

The empty flask is weight on two decimal exactly. Then the first substance was added and the mass of flask with the first substance is weight. Then, the flask was being heated in a water bath, until the designated temperature was achieved. The suggested temperatures for heating are 30°C, 40°C, 50°C, 60°C and 70°C. By accordingly, the second substance was added via a pipette under shaking, drop by drop, until a second phase was observed. The flask is then weighed. The difference between the mass of the flask with the first substance and are added represents the mass of the second substance dosed. Experiments were repeated two times. The weight percentage of the substance dosed is calculated as follows:

$$\text{Percentage of weight} \quad = \quad \frac{A-B}{A-C} \times 100$$

Where, A: mass of the flask with the first and second substance, g; B: mass of the flask with the first substance, g; C: mass of the empty flask, g.

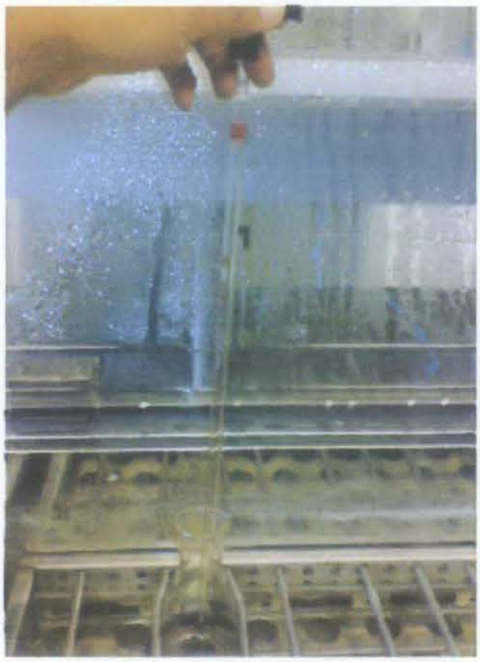


Figure 3.6: Pipetting

The substances suggested to be measured are Jatropha crude oil, rubber Seed oil, methanol, glycerol, fatty acid methyl ester and sodium hydroxide catalyst. All together there will be 28 different pair to be measured.

For the first part of the experiment, all the pairs are measured for 30°C temperature. This is for determining which pairs should be proceed for the higher temperature measurement because not every pairs will form the secondary phase. Some of the pair will be completely soluble in each other, therefore the secondary phase will not be formed.

# CHAPTER 4

# RESULT AND DISCUSSION

## 4.1 Binary LLE

The experiments pairs are listed in table 4.1.

| No. | 1st Substance | 2ndSubstance |
|---|---|---|
| 1) | Jatropha Oil | Methanol |
| 2) | Jatropha Oil | Glycerol |
| 3) | Jatropha Oil | FAME |
| 4) | Jatropha Oil | Catalyst |
| 5) | Rubber Seed oil | Methanol |
| 6) | Rubber Seed oil | Glycerol |
| 7) | Rubber Seed oil | FAME |
| 8) | Rubber Seed oil | Catalyst |
| 9) | Methanol | Glycerol |
| 10) | Methanol | FAME |
| 11) | Methanol | Catalyst |
| 12) | Glycerol | FAME |
| 13) | Glycerol | Catalyst |
| 14) | FAME | Catalyst |

| No. | 1stSubstance | 2ndSubstance |
|---|---|---|
| 15) | Methanol | Jatropha Oil |
| 16) | Glycerol | Jatropha Oil |
| 17) | FAME | Jatropha Oil |
| 18) | Catalyst | Jatropha Oil |
| 19) | Methanol | Rubber Seed oil |
| 20) | Glycerol | Rubber Seed oil |
| 21) | FAME | Rubber Seed oil |
| 22) | Catalyst | Rubber Seed oil |
| 23) | Glycerol | Methanol |
| 24) | FAME | Methanol |
| 25) | Catalyst | Methanol |
| 26) | FAME | Glycerol |
| 27) | Catalyst | Glycerol |
| 28) | Catalyst | FAME |

Table 4.1: Binary LLE Experiment Pairing

For the first part of the experiment, all the pairs are measured for 30°C temperature. This is for determining which pairs should be proceed for the higher temperature measurement because not every pairs will form the secondary phase. The results of the conducted experiments are as follows:

| 1st Substance | 2nd Substance | Solubility Of 2nd substance in 1st substance, (wt. %) |
|---|---|---|
| Jatropha Oil | Methanol | 4.782 |
| Rubber Seed oil | Methanol | 3.428 |
| Jatropha Oil | Glycerol | 0.041 |
| Rubber Seed oil | Glycerol | 0.028 |
| Glycerol | Jatropha Oil | 0.177 |
| Glycerol | Rubber Seed oil | 0.198 |
| Jatropha Oil | Catalyst | Precipitation |
| Rubber Seed oil | Catalyst | Precipitation |
| Catalyst | Rubber Seed oil | Precipitation |
| Catalyst | Jatropha Oil | Precipitation |
| Methanol | Glycerol | Soluble |
| Methanol | Catalyst | Soluble |
| Glycerol | Catalyst | Soluble |
| Glycerol | Methanol | Soluble |
| Catalyst | Methanol | Soluble |
| Catalyst | Glycerol | Soluble |

Table 4.2: Solubility of 1st substance in 2nd substance of the at 30°C conducted experiments

From the 30°C temperature experiment, we can observe that there several pairs which are resulting in completely soluble mixtures and there are some that form precipitations. Therefore the higher temperature experiment for the pair will not be conducted. The discussions on the pairs are as follows;

### 4.1.1 Precipitation

The pairs that fall into this criterion are the Sodium Hydroxide Catalyst diluted into the oils and vice versa. The precipitation is due to the salt formation as the result of the Sodium Hydroxide catalyst which is an alkali solution reacted with oils which are acidic. The reaction is as follows:

$$NaOH + HX \rightarrow NaX + H_2O$$

Where HX is the acid dissolves in the oils and NaX is the salt formed.

Figure 4.1: Precipitate of Jatropha oil diluted in NaOH

Figure 4.2: Precipitate of NaOH diluted in Jatropha oil

Should be sodium tends to form water-soluble compounds, such as halides, sulphates, nitrates, carboxylates and carbonates. The NaX salt which consists of sodium and $X^-$anion will combine in an ionic bond to form a charged NaX molecule. Water consists of a hydrogen atom and an oxygen molecule combined in a covalent bond to form a charged water molecule. This condition will resulting NaX salt dissolves in water. As salt is mixed into water, the charged water molecules break apart the charged salt molecules which are combined in a weaker ionic bond. As the molecules are broken apart, the positive ends of the water molecule surround the negative $X^-$ions and the negative ends of the water molecule surround the positive sodium ions. The sodium and chloride ions mix uniformly with the surrounding water molecules and thus salt dissolves in water, forming a homogenous mixture.

In this case the NaX salt is not mixed with water but with oil. Oil molecules do not contain any charge. Oil is consisting of long chains of hydrogen and carbon atoms linked to each other and do not carry any net charge. As a result, when salt is added to oil, no bonds are broken. Salt and oil simply do not mix. They remain separate as salt molecules and oil molecules.

### 4.1.2 Soluble Mixtures

The pairs which are involved are the methanol diluted in glycerol and vice versa, methanol diluted in catalyst and vice versa, and lastly glycerol diluted in catalyst and vice versa.

The second substance was added to the first substance drop by drop until the mass of the second substance exceeds the first substance. This shows that the pair mixture is completely miscible. The higher temperature will make the solubility rate increased. The mixture will also be totally miscible at higher temperature. Therefore the experiment for the stated pairs at higher temperature will not be conducted.

### 4.1.3 Pair Forming Second Phase

The pairs that forms second layer are the oils diluted in methanol and vice versa and oil diluted in glycerol and vice versa.

#### 4.1.3.1 Pairs of Oils & Methanol

Table 4.3 and Figure 4.1 show the binary phase equilibrium of oils and methanol.

| Temperature, °C | 30 | 40 | 50 | 60 | 70 |
|---|---|---|---|---|---|
| Jatropha Oil, wt.% | 4.782 | 6.012 | 7.532 | 8.027 | 8.753 |
| Rubber Seed oil, wt.% | 3.428 | 4.726 | 5.518 | 6.001 | 6.103 |

Table 4.3: Solubility of methanol in Jatropha oil and Rubber Seed oil

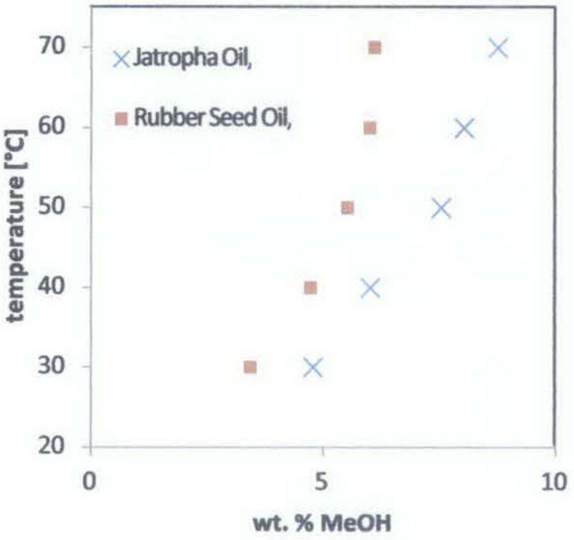


Figure 4.3: Binary phase equilibrium of methanol with Jatropha oil and Rubber Seed oil

The solubility of methanol in Jatropha oil and Rubber Seed oil is shown in Figure 4.3 by a temperature-composition plot. The minimum solubility of methanol in Jatropha oil is 4.782 wt. % at 30°C while 3.428 wt. % in Rubber Seed oil. The maximum solubility of methanol in Jatropha oil in the experiment is 8.753 wt. % at 70°C and 6.103 wt. % in Rubber Seed oil. With the increase in temperature, the weight of methanol dissolved in oil increased. When higher temperature reached, the rate of increment of the weight of Jatropha oil is reducing.

At elevated temperatures, the solubility of methanol in Jatropha Oil is higher than Rubber Seed oil due to the higher density of Rubber Seed oil used.

#### 4.1.3.2 Pair of Glycerol and Jatropha Oil

Table 4.4 to 4.5 and Figure 4.2 shows the binary phase equilibrium of oils and glycerol.

| Temperature, °C | 30 | 40 | 50 | 60 | 70 |
|---|---|---|---|---|---|
| JatrophaOil,wt.% | 0.041 | 1.664 | 2.073 | 2.688 | 3.459 |
| Rubber Seed oil, wt% | 0.028 | 0.901 | 1.571 | 1.963 | 2.201 |

Table 4.4: Solubility of glycerol in Jatropha oil and Rubber Seed oil

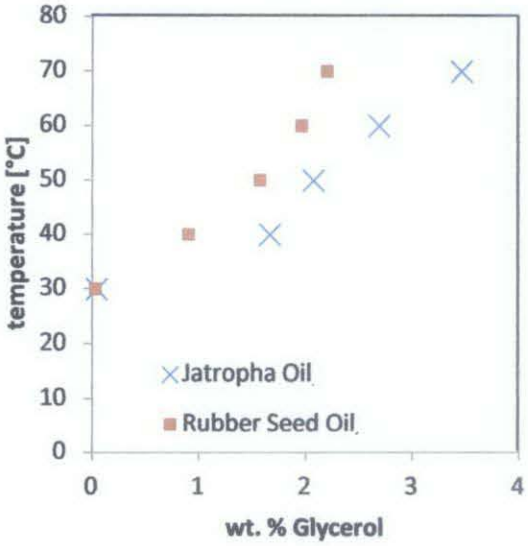


Figure 4.4: Binary phase equilibrium of glycerol with Jatropha oil and Rubber Seed oil

The solubility of glycerol in Jatropha oil and Rubber Seed oil is shown in Figure 4.4 by a temperature-composition plot. The minimum solubility of glycerol inboth of the oils are about the same composition with Jatropha oil is 0.041 wt. % at 30°C while 0.028 wt. % in Rubber Seed oil.

It differs for the maximum solubility. The maximum solubility of glycerol in Jatropha oil is 3.459 wt. % at 70°C and 2.201 wt. % in Rubber Seed oil.

| Temperature, °C | 30 | 40 | 50 | 60 | 70 |
|---|---|---|---|---|---|
| Jatropha Oil, wt.% | 0.177 | 1.149 | 1.872 | 1.901 | 1.989 |
| Rubber Seed oil, wt.% | 0.198 | 1.058 | 1.76 | 1.833 | 1.847 |

Table 4.5: Solubility of Jatropha oil and Rubber Seed oil in glycerol

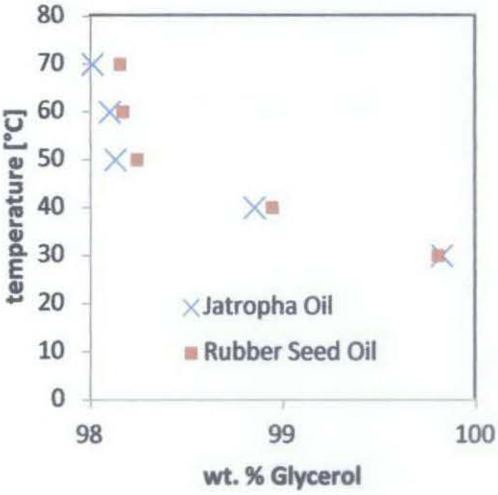


Figure 4.5: Binary phase equilibrium of glycerol with Jatropha oil and Rubber Seed oil

When the oils are diluted in the glycerol, lower solubility trends are observed. The solubility of Jatropha oil and Rubber Seed oil in glycerol is shown in Figure 4.5. The minimum solubility of both oils in glycerol are about the same composition with Jatropha oil is 0.177 wt. % at 30°C while 0.198 wt. % in Rubber Seed oil.

As the temperature raise above 40°C the composition plot is giving about the same data for both oil. Also, the data did not vary much with the maximum solubility of Jatropha oil is 1.989 wt.% and 1.847 wt.% for Rubber Seed oil.

At either reactant of product side, Rubber Seed oil will have lower solubility due to its density.

# CHAPTER 5

# CONCLUSION AND RECOMMENDATION

## 5.1 CONCLUSION

As for the conclusion, this project determined pairs of the reactant and product which are completely miscible in each other, so for the further research on ternary phase behaviour will take it into account.

This project gives a series of data of binary LLE for the reactant and product of biodiesel production. Therefore the results of this project will be beneficial for further researches on producing and extracting biodiesel from its reaction composition.

## 5.2 RECOMMENDATION

It is recommended that the project will be furthered for the Fatty Acid Methyl Ester (FAME) combination and the research on ternary LLE phase.

For better and precise result, the experiments need to be conducted using analytical syringe replacing the pipet for it will have more accurate reading. Also, magnetic stirrer with hot plate replacing the water bath with shaker for more precise temperature reading.

Also, it can be continued in the simulation work and the data can be used to find the best condition for easier product separation.

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