

**EQUILIBRIA OF THE TRIGLYCERIDES + FAEE +
ETHANOL SYSTEM AND EXTRACTION OF TWO
IMMISCIBLE LIQUID**

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EQUILIBRIA OF THE TRIGLYCERIDES + FAEE + ETHANOL SYSTEM AND EXTRACTION OF TWO IMMISCIBLE LIQUID

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
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**Faculty of Chemical & Natural Resources Engineering
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JUNE 2015

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Dedication

For those who love chemistry and engineering

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First and foremost, I would like to dedicate the most sincere gratitude to my supervisor, Dr. Mohd Sabri bin Mahmud due to his patience, guidance, ideas and also critics have made this research possible. I also want to express my thanks to Mrs. Adibah for her cooperation and guidance during the experiment runs in the laboratory and also searching for related information for this experiment.

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ABSTRACT

The goal of this project is to construct McCabe Thiele chart and ternary diagram for ethyl oleate and triolein under various alcohol compositions. Low grade oils are practically used as a biodiesel feedstock to overcome the high costs of biodiesel production. However, existing processes involved with extra cost of the feedstock pretreatment. This study is to provide extraction characteristic for a separating reactor of biodiesel synthesis for pure raw material before using the low grade feedstock as a benchmark. Liquid-liquid extraction (LLE) is the mechanism used as the alternative method to improve the reactivity of immobilized enzymatic process. In this study, standard sample ethyl oleate and triolein were prepared to plot the calibration curve. Calibration curve was needed to determine the concentration of all components in the system. To prepare the sample, ethyl oleate was mixed with n-heptane with different concentration in 1 ml vial. The same procedure was repeated for triolein sample preparation. Then, the compositions of ethyl oleate and triolein were determined from gas chromatography. The data from GC analysis were used to plot the calibration curve. The work was continued with the preparation of fatty acid ethyl ester (FAEE) through the transesterification reaction of vegetable oils with ethanol by using potassium hydroxide (KOH) and was mixed in conical flasks with triglycerides from palm oil and ethanol. In equilibrium analysis study, two liquid phases clearly separated. One phase is enriched triglycerides at the bottom and enriched ethanol at the top of the layer. After the equilibrium was achieved, a sample was taken from both phases for concentration measurements by using gas chromatography. The GC analysis was carried and the data needed was tabulated in order to determine the peak area and retention time to plot the calibration curve. Next, the concentrations of all samples were determined from the calibration curve to construct McCabe-Thiele charts. From this graph, the composition of triglycerides and FAEE were determined to identify whether extraction process is possible or not and to determine the composition of FAEE and triglycerides whether it rich in solvent phase or solution phase. By referred to the trend of McCabe-Thiele chart for FAEE and triglycerides, the extraction was not possible and stripping would occur in this process since the solvent ratio used is not high enough to achieve effective removal of FAEE from the solution using solvent extraction. In other hand, McCabe-Thiele chart for triglycerides shows addition of FAEE shifted the equilibrium towards the operating line. This may imply that FAEE helps increase concentration of triglycerides in ethanol. For ternary diagram, the result was confirmed that the biodiesel has greater solubility in the triglycerides-enriched phase at constant temperature. From the McCabe-Thiele charts, it was concluded that volume ratio for the solvent must be greater than 1:1 in order to ensure the extraction process can be attained and the increment of FAEE concentration was reduced the solubility of solute (triglycerides) in the solution. Lastly, from the ternary diagram, the compositions that create two immiscible liquid system was successfully obtained and the result shows that biodiesel has greater solubility in the triglycerides-enriched phase in the system containing ethanol at constant temperature.

Key words: Liquid-liquid extraction (LLE), gas chromatography analysis, McCabe-Thiele charts and ternary diagram.

ABSTRAK

Objektif projek ini adalah untuk membina gambar rajah segi tiga dan carta McCabe-Thiele untuk triolein dan etil oleate di bawah etanol komposisi. Bahan mentah berkualiti rendah biasanya digunakan untuk menghasilkan biodiesel bagi mengatasi kos yang tinggi untuk menghasilkan biodiesel. Walau bagaimanapun, proses ini memerlukan penambahan kos untuk pra-rawatan bahan mentah. Kajian ini adalah untuk menyediakan ciri-ciri pengekstrakan di dalam biodiesel sintesis reactor pemisah untuk bahan mentah sebelum menggunakan bahan mentah berkualiti rendah sebagai penanda aras. Cecair-cecair pengekstrakan adalah salah satu kaedah alternatif yang digunakan untuk meningkatkan kadar tindak balas proses enzim bergerak. Dalam kajian ini, sampel piawaian etil oleate dan triolein telah disediakan untuk memplot lengkung kalibrasi. Kalibrasi lengkung diperlukan untuk menentukan komposisi setiap komponen di dalam sistem. Bagi menyediakan sampel, etil oleate dicampurkan dengan n-heptane dengan kepekatan yang berbeza di dalam 1ml botol. Kemudian, komposisi etil oleate dan triolein telah ditentukan menggunakan kromatografi gas. Data daripada analisis kromatografi gas telah digunakan untuk memplot lengkung kalibrasi. Kerja ini diteruskan dengan penyediaan asid lemak etil ester (FAEE) melalui tindak balas transesterifikasi minyak sayuran dengan etanol dengan menggunakan kalium hidroksida (KOH) dan dicampurkan ke dalam termos kon dengan trigliserida daripada minyak sawit dan etanol. Dalam kajian analisis keseimbangan, campuran yang terpisah kepada dua lapisan dapat dilihat dengan jelas. Satu fasa adalah kaya dengan trigliserida pada lapisan bawah dan satu fasa lagi diperkaya dengan etanol pada lapisan atas. Selepas keseimbangan telah dicapai, sampel diambil dari kedua-dua fasa untuk membuat ukuran kepekatan dengan menggunakan kromatografi gas. Analisis GC telah dijalankan dan data yang diperlukan diambil untuk menentukan luas kawasan puncak dan masa yang diambil untuk pengekstrakan agar dapat digunakan untuk memplot lengkung kalibrasi. Seterusnya, kepekatan bagi semua sampel telah ditentukan menggunakan lengkung kalibrasi. Daripada graf ini, komposisi trigliserida dan FAEE ditentukan untuk menentukan sama ada ia proses pengekstrakan dapat dihasilkan atau tidak dan untuk menentukan sama ada FAEE dan trigliserida lebih banyak di dalam fasa pelarut atau fasa campuran. Merujuk kepada carta McCabe-Thiele untuk FAEE dan trigliserida, pengekstrakan tidak terjadi dan proses perlucutan terjadi dalam proses ini memandangkan nisbah bahan pelarut yang digunakan tidak cukup tinggi untuk mencapai penyingkiran bahan larut daripada campuran menggunakan bahan pelarut. Pada sudut lain, carta McCabe-Thiele bagi trigliserida menunjukkan penambahan FAEE mengakibatkan keseimbangan teralih ke arah garisan operasi. Situasi ini menggambarkan FAEE membantu meningkatkan kepekatan trigliserida di dalam lapisan etanol. Untuk gambar rajah segi tiga, keputusan telah mengesahkan bahawa biodiesel mempunyai kelarutan yang lebih tinggi di dalam fasa trigliserida pada suhu yang tidak berubah. Daripada carta McCabe-Thiele, satu kesimpulan dapat dibuat iaitu nisbah isipadu mesti melebihi 1:1 agar proses pengekstrakan dapat dicapai dan penambahan kepekatan FAEE mengurangkan kadar kelarutan bahan larut di dalam campuran. Akhir sekali, daripada gambar rajah segi tiga, komposisi yang menghasilkan system dua lapisan cecair yang tidak bercampur dapat dicapai dan biodiesel mempunyai kadar kelarutan yang lebih tinggi di dalam lapisan yang mengandungi lebih banyak trigliserida di dalam sistem yang mengandungi etanol pada suhu tetap.

Kata kunci: pengekstrakan cecair-cecair (LLE), analisis kromatografi gas, carta McCabe-Thiele dan gambar rajah pertigaan.

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LIST OF ABBREVIATIONS

<i>EO</i>	ethyl oleate
<i>EtOH</i>	ethanol
<i>FAAE</i>	fatty acid alkyl ester
<i>FAEE</i>	fatty acid ethyl ester
<i>Gl</i>	glycerol
<i>GC</i>	gas chromatography
<i>KOH</i>	potassium hydroxide
<i>LLE</i>	liquid-liquid equilibrium
<i>NaOH</i>	sodium hydroxide
<i>TG</i>	triglyceride
<i>TO</i>	triolein

1 INTRODUCTION

This chapter will give the ideas about the significant of the research formulation. This first chapter will cover up the subtopic of background of study or information, problem statement, research objectives, scope of proposed research, expected outcomes and significance of the proposed research.

1.1 Background of Study

Biodiesel fuel is one of the alternative fuels for petroleum-derived diesel. Low grade oils are practically used to overcome the high costs of biodiesel production. Biodiesel is currently synthesized via liquid base catalysed trans-esterification of triglyceride components with alcohols, alongside glycerol as a potentially valuable by-product. The potential alcohols are methanol and ethanol. Methanol is the most favourable due to relatively-low cost and more favourable properties in the process. On the other alcohol, ethanol is relatively less toxic - and can be obtained from biomass, making biodiesel production completely renewable (Oliveira et.al, 2011). In this study, ethanol was employed because it shows more excellent fuel properties although it is expensive.

Extractive reaction was used as the method to run the experiment as it is one of the alternatives for more cost effectiveness of the biodiesel production by using low grade oils. This process consists of chemical reaction and liquid-liquid extraction in the same unit achieving such synergistic effect, that the increase of selectivity, conversion, productivity, and purity of final product (Rinaldi et.al, 2007). Liquid-liquid extraction (LLE) is a separation process that takes advantage of the relative solubility of solutes in immiscible solvents (Thomopoulos, 1971). Liquid phases emerged during the biodiesel synthesis reaction change dynamically. Initially, two immiscible liquids appear: rich triglyceride and rich alcohol. Then, depending to the initial amount of excess ethanol or excess triglycerides, the transition phases would be two or single due to the virtual solvent characteristics of FAEE during the biodiesel reaction. The fatty acid esters and glycerol, obtained after the complete trans-esterification reaction are again immiscible. To increase the immiscibility of two liquid phases another solvent which is hydrated ethanol was added. Ethanol was used as solvent because it is a promising technique for refining edible oils, including palm oil, without significant losses of natural antioxidants

(Knothe, 2009). When the extraction system was employed, the denser phase is rich in triglycerides settles at the bottom of the less dense phase which contains ethanol.

Components used in this work were analysed by using gas chromatography that included biodiesel, triglycerides and ethanol to form the ternary diagram for each component. In order to carry a sample through the chromatograph, a carrier gas was used. The choice of carrier gas was dictated both by the nature of the sample and by the type of detector to be used (Med, 1968).

The determination of liquid-liquid equilibrium data (LLE) for the system was important to delineate compositions of component in different phases in the region below bimodal curves. To overcome the lack of phase equilibria information concerning systems from the trans-esterification reaction with ethanol, in this work, liquid-liquid equilibria data, tie-lines and phase boundaries, was measured for the ternary system triglycerides + FAEE + ethanol at temperature 40°C. For the tie-line determination, compositions in the two phase region were selected keeping the molar relation between ethanol and triglycerides constant and changing the FAEE proportion. According to the phase rule, at a fixed temperature and pressure, only one component can independently change its composition. The mixture composition is determined identifying in the bimodal curves measured, the point which represents the composition of the specified component (Oliveira et.al, 2011).

1.2 Motivation and Problem Statement

Biodiesel is nowadays seen as one of the most worthy alternatives to conventional fossil fuels. It is generally accepted that the available fossil fuel reserves will only last for a few more decades. In addition, most of the accessible petroleum fuel comes from politically unstable countries raising the uncertainty of its availability and price (Hallock, 2004). The use of renewable energy sources of biodiesel can also decrease greenhouse gases and emissions of other air contaminants contributing to reduce the global warming problem (Shahid & Jamal, 2008). Nowadays, a major challenge to face in the field of biodiesel production is how to overcome the high costs associated to conventional feedstock (Morales et.al,2011). One way to overcome drawback is using low grade feedstock, so that most of the efforts applied in biodiesel research are focused on looking for new raw materials fulfilling the requirements. The low grade feedstock is

also used in biodiesel production in order to overcome the high costs of production associated to conventional feedstock.

Therefore, this study is one alternative to improve current process not economical for low grade feedstock and to provide equilibrium data for biodiesel synthesis system using low grade feedstock, for intensified reactor such as liquid-liquid reactor. Currently, most of the researchers have been done the researches on the liquid-liquid equilibria in order to provide equilibrium data for biodiesel synthesis system using low grade feedstock. For example, they use phase equilibrium of ternary systems with biodiesel, glycerol, and alcohol to provide the equilibrium data (Negi et.al, 2006).

1.3 Research Objective

The objective of this research is to construct the McCabe-Thiele and the ternary diagram of triolein and ethyl oleate under various alcohol compositions.

1.4 Scope of Research

Scope of study is very crucial and one of the important parts in this research. The scopes of this study are:

1. Ethanol was used as a solvent for this process since it is more excellent fuel compared to methanol.
2. Palm oil was used as the easy resource of triglycerides.
3. Biodiesel (FAEE) was produced through trans-esterification reaction.
4. Analysis of components was conducted by using gas chromatography.

2 LITERATURE REVIEW

2.1 Overview

This paper presents details about the biodiesel production process, type of low grade feedstock that have been used in biodiesel production, liquid-liquid extraction process, analysis of biodiesel feedstock by using GC, McCabe Thiele study and ternary diagram system from previous work. The purpose of this chapter is to get understanding deeply about the analysis method to improve current process not economical for low grade feedstock and the method to provide equilibrium data for biodiesel synthesis system using low grade feedstock.

2.2 Biodiesel Feedstock

Biodiesel is an alternative fuel for diesel engines that more renewable, non-toxic and biodegradable. It can also be used directly in most diesel engines without requiring extensive engine modifications (Gerpen et.al, 2004). Biodiesel consists of a mixture of fatty acid alkyl esters (FAAEs) obtained from a variety of feedstock by transesterification (Canoira et.al, 2008). Biodiesel feedstock can be classified into two categories, which are edible feedstock that consists of coconut oil and Aleuritas moluccana (candle nut); besides non-edible feedstock consists of animal tallow, waste oil and algae. These materials contain triglycerides, free fatty acids, and other contaminants depending on the degree of pre-treatment they have received prior to delivery. There are several types of edible oil and non-edible oil that has been used in biodiesel production, for example, algae oil, babassu oil, beef tallow, borage oil, soybean oil, canola oil, castor oil, fish oil, corn oil, coconut oil and many others (Sanford et.al, 2009).

2.2.1 Edible Oil

Different physical and chemical properties of feedstock like fatty acid composition, free fatty acid content, moisture and impurities influenced biodiesel production process as well as the properties of the product. There are many types of feedstock involve as a path way to produce biodiesel. Many researchers investigate the production of biodiesel using vegetables oils, animal fats or waste cooking oil. The choice of raw material

depends on the local crops availability such as palm biodiesel dominantly used in Asia, while soybean used in United States and canola biodiesel is dominantly used in Europe. In Europe, rapeseed oil has become the primary feedstock for biodiesel. Globally, there are over 350 oil-bearing crops identified as potential sources for biodiesel production. Table 2.1 below shows some world production of vegetable oil in 2008 and 2009.

Table 2.1: The world production of vegetable oil in year 2008 and 2009 (Guerrero-Lemus & Martinez-Duart, 2010)

<i>Oils</i>	<i>Million Tons</i>
Palm oil (fruit)	43.20
Soy oil	38.11
Rapeseed oil	19.38
Sunflower oil	11.45
Cotton oil	4.94
Palm oil (seed)	5.10
Peanut oil	4.93
Coconut oil	3.62
Olive oil	2.97

Palm oil (*Elaeisguineensis*) industry is one of the major contributors to the Malaysia economic growths. The oil palm is native to West Africa, and is extensively cultivated in Malaysia, Indonesia, and Central Africa. Palm oil is an important and versatile vegetable oil which is used as a raw material for both food and non-food industries (Man et.al, 2013).

Coconut oil is edible oil extracted from the kernel of matured coconuts harvested from the coconut. It has various applications in food, medicine, and industry. Coconut oil has been tested for use as a feedstock for biodiesel to be used as a diesel engine fuel. Furthermore, it can be applied to power generators and transport using diesel engines. Since straight coconut oil has a high gelling temperature around 22–25 °C, high viscosity and minimum combustion chamber temperature of 500 °C (932 °F) (to avoid polymerization of the fuel), coconut oil is transesterified to make biodiesel. Coconut oil has been produced on a large scale in the east and south coastal areas. At

present, coconut oil with high FFA is available at a low price and does not have major applications. Thus, this oil has a high potential as the feedstock to reduce the biodiesel production cost. From these points of view, it led to the study of biodiesel production from coconut oil with high FFA content by two-step process, acid-catalysed esterification followed by alkali catalysed transesterification. The viscosity of coconut was lower than those of other biodiesels, such as soybean (4.08 mm²/s), rapeseed (4.5 mm²/s), and rubber seed (5.81 mm²/s) (Nakpong & Wootthikanokkhan, 2010). This was due to coconut triglyceride consisted of 57.7% short chain fatty acids comprising mainly of lauric and myristic acids containing 12 and 14 carbon atoms, respectively.

Aleurites moluccana, the candle nut is a flowering tree in the spurge family Euphorbiaceae also known as Candleberry or 'buah keras'. Candle nut trees grow to a height of 15–25 m, with wide spreading or pendulous branches. The leaves are pale green in color with an acute apex, 10–20 cm long. The nut is round, 4–6 cm in diameter; the seed inside has a very hard seed coat and a high oil content, which allows its use as a candle (Silitonga et.al, 2013) research on "Overview Properties of Biodiesel Diesel Blends from Edible and Non – Edible Feedstock" describe about aleuritas moluccana or the other name is candle nut. Candle nut is one of the world's largest domesticated multipurpose trees. It is originated from Malaysia, Indonesia, Philippines and South Pacific islands including Hawaii. The candle nut trees can grow very well in tropical climates with ample rainfall and also adaptable to dry climates. The productivity of candle nut fruit yields vary from 4mt/ha to 20mt/ha and oil yield is around 3100kg/ha every year. Candle nut seed consists around 30% of oil and 15% of free fatty acid with high iodine number. The oil derived from the seeds provided material for lighting, cooking, resin, pharmaceuticals and cosmetics production (Atabani et.al, 2009).

2.2.2 Non-Edible Oil

Animal fat tallow, lard, chicken fat, and the by-products of the production of Omega-3 fatty acids from fish oil are increasingly used as biodiesel fuel feedstock. Material selected from the rendering of meat products and occasionally plant materials that have a range of uses depending on the purity. Its main use is in the manufacture of soap but it can be a feedstock for the manufacture of biodiesel. Although it would not be resourceful to raise animals simply for their fat, the use of the by-product as feedstock for biodiesel fuel adds value to the livestock industry. However, producing biodiesel

fuel with animal fat would substitute only a little percentage of petroleum diesel usage. Currently, a 5-million dollar plant is being built in the USA, with the intention of making 3 million gallons of biodiesel fuel from some of the estimated 1 billion kg of chicken fat produced annually at the local Tyson poultry plant. Some small-scale biodiesel factories are using waste fish oil as biodiesel fuel feedstock. In Vietnamese case study, plant aims to produce 13 tons/day of biodiesel from catfish from 81 tons of fish waste. The worldwide production of vegetable oil and animal fat as raw material for biodiesel fuel is not sufficient to substitute for the liquid fossil fuel use.

Waste oil is known as any oil based on edible, non-edible, petroleum or synthetic oils, through use or handling it becomes unsuitable for its original purpose due to the presence of impurities or its original properties had been vanished. Waste cooking oil (WCO) is not suitable for human consumption but it is one of the good feedstock for biodiesel production. There are huge amount of waste lipids generated from restaurants, food processing industries, fast food shops and house holds in daily live. Disposal of WCO becomes a serious environmental problem in many of the countries around the world. This environmental problem could be solved by proper utilization and management of WCO as a diesel fuel. Due to the high cost of crude and refined vegetable oils for the production of biodiesel, WCO available from restaurants and households are attracting attention as an alternative feedstock for biodiesel production. Its usage significantly decreases the cost of biodiesel production. However, the quality of WCO may cause concern because its physical and chemical properties depend on the contents of fresh cooking oil and WCO may contain lots of undesired impurity, such as water, free fatty acids (Liang et.al, 2013)

2.3 Low Grade Oil Properties

For this research, palm oil was chosen as a feedstock since it is low cost and considered as an excellent feedstock for biodiesel production. In addition, palm oil is high availability in Malaysia as it forms the economic backbone of our country. From palm oil, most common fatty acid found is oleic acid. Triglyceride obtained from oleic acid is called as triolein. Triolein is a symmetrical triglyceride derived from the glycerol and three units of the unsaturated fatty acids oleic acids.

The palm oil consists of 50% saturated and 50% unsaturated fatty acids, and the major triglycerides (TG), according to equivalent carbon number (ECN), were C50 (42.58%) and C52 (40.46%). The major TG of the olein fraction are C50 (42.04%) and C52 (45.66%) with an iodine value (IV) of about 56. The stearin fraction consists of C48 (22.3%), C50 (40%), and C52 (29%) TG with IV is about 44. TG of palm oil consist of trisaturated (10.2%), disaturated (48%), monosaturated (34.6%), and triunsaturated (6.8%) (Man et.al, 2013).

As a general rule of process synthesis, the closer a feedstock is to containing pure triglycerides, the easier it will be to convert it to biodiesel, and the higher will be its cost. The lower the cost of the feedstock, the more difficult and more expensive it is to convert to biodiesel. Biodiesel feedstock will contain many possible contaminants such as water, solids, free fatty acids, particles, and phospholipids that are potential to impact the quality of the final biodiesel product particularly the saponification value. Table 2.2 shows the maximum tolerance of impurities and physical properties of low grade oil in biodiesel production.

Table 2.2: Maximum Tolerance of Impurities and Physical Properties of Low Grade Oil in Malaysia (Gerpen et al., 2004)

Constituent	Limitations
Triglycerides,%	95
Water	$\leq 1\%$
Red Colour (5 $\frac{1}{4}$ " Lovibond Cell)	Orange red
Moisture & Impurities, %	0.15 – 3.0
Peroxide Value, PV (meq/kg)	1.0– 5.0
Anisidine Value, AV	2 – 6
β – carotene content, ppm	500 – 700
Iron (Fe), ppm	4-10

Tocopherols, ppm	600 – 1000
Solid	5 μ m
Free Fatty Acids (FFAs),%	2-5
Phosphorus	\leq 10 ppm
Sulfur	40-50 ppm
Iodine Value	\leq 120 gI ₂ /100g

In biodiesel production process, it is important to remove water in order to avoid the soap formation which can also affect to the completeness of the transesterification reaction. Most processes can only tolerate up to 1% water in biodiesel production (Gerpen et al., 2004).

Similarly, FFAs can impact the production process by deactivating the catalyst, creating soap, and by releasing water when they are converted to esters. Biodiesel will usually have 0.2- 0.3% FFAs regardless of the initial acid content of the feedstock (Gerpen et al., 2004). Phosphorus content in biodiesel is only limit to 10 ppm. Fortunately, even if the oil is not degummed to remove this material, the usual biodiesel production process removes the phosphorus and it is either transferred to the glycerol fraction or removed by water washing. There does not seem to be any effect of the initial phosphorus content of the feedstock on the final phosphorus content of the biodiesel (Gerpen et al., 2004).

One of the advantages of biodiesel is that it contains very low levels of sulfur. For example, sulfur levels for petroleum must drop to 15 ppm from 500 ppm by 2006. The limitation of sulfur content in biodiesel is between 40 to 50 ppm. Most biodiesel is already containing sulfur in between this range (Gerpen et al., 2004). The iodine value is a very crude but commonly used indicator of the level of saturation of oil. The limitation for iodine value is \leq 120 gI₂/100g. The adjustment of iodine value would help to expand the feedstock source and to fulfill the biodiesel production (Gerpen et al., 2004).

2.4 Major Feedstock

Since biodiesel is a mono-alkyl fatty acid ester, the primary alcohol is the other major feedstock that used to form ester. The most commonly used primary alcohol in biodiesel production is methanol, although other alcohols, such as ethanol, isopropanol, and butyl, can be used. A key quality factor for the primary alcohol is the water content. Water interferes with transesterification reactions and can result in poor yields and high levels of soap, free fatty acids, and triglycerides in the final fuel (Gerpen et al., 2004).

However, alcohols of higher molar mass, which is ethanol is less toxic, have higher boiling points and energy densities, making ethanol interesting options as a feedstock (Santasalo-Aarnio et.al, 2011). Other issues such as cost of the alcohol and the amount of alcohol needed for the reaction influence the choice of alcohol. Since the reaction to form the esters is on a molar basis and alcohol is purchased on a volume basis, their properties make a significant difference in raw material price. It takes three moles of alcohol to react completely with one mole of triglyceride.

Today, one gallon of methanol costs \$0.61. That gallon contains 93.56 gram-moles of methanol; at a cost of \$ 0.00652 per gram- mole. By contrast, a gallon of ethanol, at the current price of \$ 1.45 per gallon for fuel-grade ethanol, costs \$ 0.02237 per gram-mole, or 3.4 times more (Gerpen et al., 2004). Therefore, methanol is the most commonly used alcohol as a feedstock for trans-esterification reaction due to lower cost and more favourable properties in the process. However, in this study, ethanol is employed because it is more excellent fuel compared to methanol although it is expensive.

2.5 Catalyst Involved

Most processes for making biodiesel use a catalyst to initiate the transesterification reaction. The catalyst was required because the alcohol is sparingly soluble in the oil phase. The catalyst promotes an increase in solubility to allow the reaction to proceed at a reasonable rate. The most common catalysts used are strong mineral bases such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) (Gerpen et al., 2004). Both catalysts can be used to produce high quality biodiesel because they both can react with the triglycerides to break them apart so that alcohol can bond with the fatty acids and make biodiesel. However, there are some differences

between NaOH and KOH. Table 2.3 below shows the comparison between NaOH and KOH.

Table 2.3: Comparison between NaOH and KOH

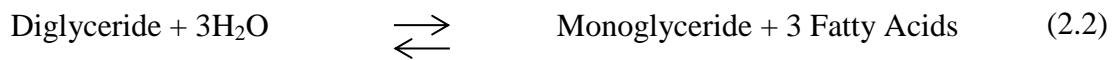
	Sodium Hydroxide (NaOH)	Potassium Hydroxide (KOH)
Reactivity with oil	React better	Doesn't react well
Dissolving in alcohol	Dissolves slowly	Dissolves extremely
Amounts required	Less NaOH in grams per batch	More KOH in grams per batch
Costs	\$ 1.27/lb	\$ 2.50/lb
Effects on Glycerin	Layer of glycerin much thicker	Layer of glycerin nice and liquid

The reactivity of NaOH with oil is slightly better than KOH. One of the biggest differences of using NaOH and KOH can be seen in the glycerin layer. Glycerin from NaOH reacted oil tends to be much thicker. Glycerin from KOH reacted biodiesel on the other hand is nice and liquid.

In order to make biodiesel, KOH in grams per batch is needed more compared to NaOH. In instance, 2175 grams of NaOH is required for 50 gallons of oil with a 5% free fatty acid content. However, it will take roughly 3030 grams of KOH for the same oil. On average, KOH costs more than NaOH. Cost for NaOH is only \$1.27/lb while for KOH is \$2.50/lb. Therefore, not only more amount of KOH is required, but it is also high cost of KOH is needed for biodiesel production. Potassium Hydroxide (KOH) however, will begin dissolving almost on contact with alcohol and dissolves extremely fast compared to Sodium Hydroxide (NaOH). From the previous work, it is found that a pound of KOH can be dissolved in under 15 minutes in gallons of alcohol while NaOH take 30 to 40 minutes to dissolve in alcohol. The chances of KOH dissolving quickly are greatly increased which means they can get that batch of biodiesel going quicker. Therefore, for this reason, KOH is tend to be used for this research although it is more expensive compared to NaOH.

2.6 Process for Producing Biodiesel

One of the most commercially used methods to produce biodiesel is transesterification and the process involves a reaction between ester (triglyceride) and alcohol to form new ester and alcohol. Three reversible reactions take place consecutively in the transesterification of triglyceride to fatty acid alkyl esters in which diglycerides and monoglycerides are major intermediate products. The chemical reaction involved is as following steps:



The alcohol used in transesterification process is methanol or ethanol. The parameters that affect on the rate of transesterification reaction are reaction temperature, alcohol to oil molar ratio, catalyst concentration and type of catalyst. The transesterification reaction required three moles of alcohol to have a complete reaction therefore the used of alcohol in excess could prevent a backward reaction.

However, if the temperature achieves the boiling point of alcohol, a lot of alcohol's bubbles are formed hence prevent the mass transfer on the phase's interface (Zabeti et.al, 2009). Base catalysts, acid catalysts and enzymes are three categories of catalysts which have been studied for biodiesel production. Enzymatic base production of biodiesel has attracted many attentions in past few years since enzymes tolerate FFA and water contents in the oil to prevent soap formation and thus purification of biodiesel and glycerol is easier. However, enzymes are expensive to be used in a commercial production of biodiesel. Figure 2.1 below shows the transesterification process between vegetable oil and alcohol with catalyst to produce fatty acid alkyl ester and glycerol.

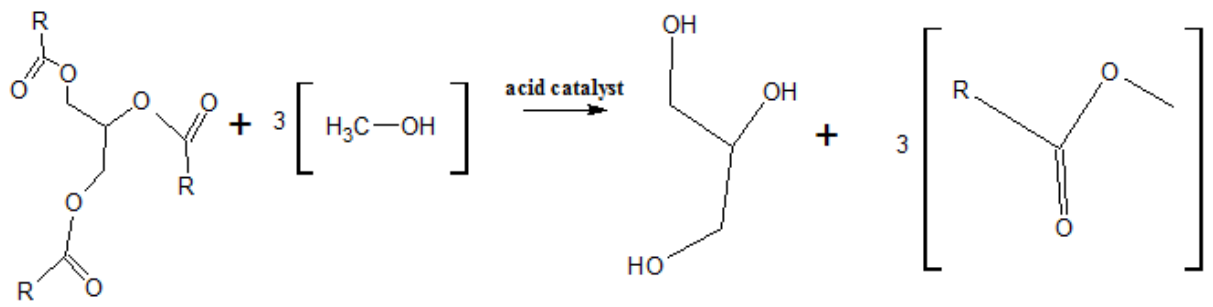


Figure 2.1: The transesterification equation between vegetable oil and alcohol with catalyst to produce fatty acid alkyl ester and glycerol

2.7 Liquid-Liquid Extraction

Extraction is a liquid-liquid operation which is a process of transferring a solute from one liquid phase to another immiscible or partially miscible liquid in contact with the first. The two phases are chemically quite different, which leads to a separation of the components according to their distribution or partition between the two phases, normally one organic and one water. This is different from distillation, in which the liquid is partially vaporized to create another (vapor) phase, but the two phases are similar chemically. The process is shown in the Figure 2.2 below.

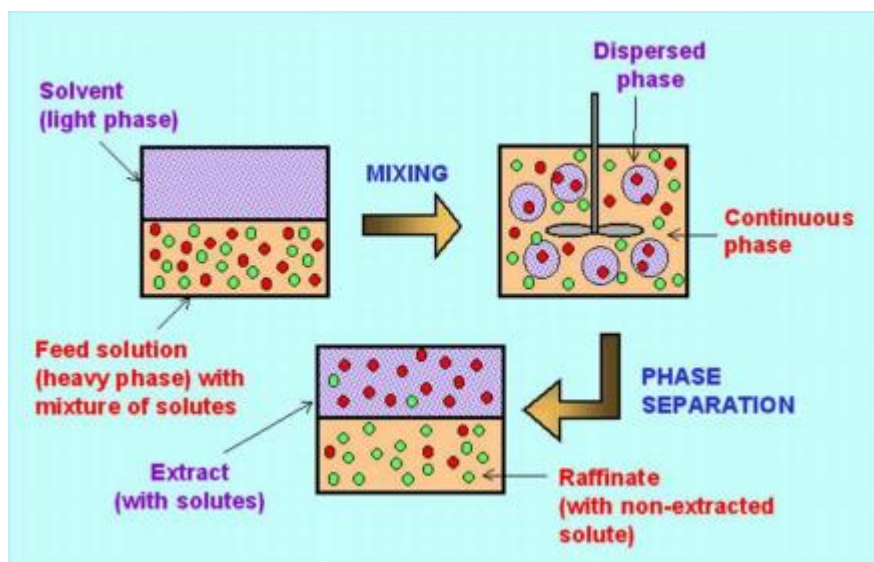


Figure 2.2: Liquid-Liquid Extraction Process

Separation process takes advantage of the relative solubility of solutes in immiscible solvents. A partial separation occurs when the components of the original mixture have different relative solubility in the selected solvent phase (Thomopoulos

et.al, 1971). Biodiesel synthesis by liquid–liquid extraction by means of an appropriate solvent is receiving attention because of the low energy and reagent consumption, avoiding pollution and submitting the oil to softer treatments. Moreover, such process reduces the loss of neutral oil and may preserve the nutraceutical compounds (Kim et.al, 1985). In addition, the compound that attempting to extract, must be soluble in the organic solvent, but insoluble in the water layer.

Once the two layers were mixed, the layer was separated by pouring off the less dense layer into a conical flask. A conical flask was used to make the separation of two liquids in liquid-liquid extraction. The two layers were mixed together vigorously to provide maximum surface contact between the two immiscible layers so that substances can be pulled or extracted from one into the other. Thorough mixing is very important because the two solutions must be in contact with each other to allow the solute to be extracted into the second layer.

2.8 Analysis Methods by Using Gas Chromatography

Gas Chromatography (GC) was used for the measurements. GC is a common type of chromatography used in analytical chemistry for separating and analysing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture. In some situations, GC may help in identifying a compound (Pavia et.al, 2006).

In order to carry a sample through the chromatograph, a carrier gas was required. The choice of carrier gas is dictated both by the nature of the sample and by the type of detector to be used (Med, 1968). The carrier gas is comprised of an inert gas, such as helium, argon, and nitrogen. The carrier gas system contains a molecular sieve to remove water and other impurities. Operating pressures for the carrier gas vary between 10 and 60 lb/in² (0.7-4.2 kg/cm²) and accurate needle valve are required to control its flow.

The analytical process takes place in the chromatograph column, which is merely a length of tube containing a packing material, known as the stationary phase (Med, 1968). The length of the column depends on the retention time required - the longer the column, the longer the retention time (Podbielniak et.al, 1970).

To distinguish analyte peaks in chromatograms, the carrier gas pressure and oven temperature is programmed simultaneously in both methods. The moderate nonpolar layer on internal surface of the column permits peaks to be distinguished.

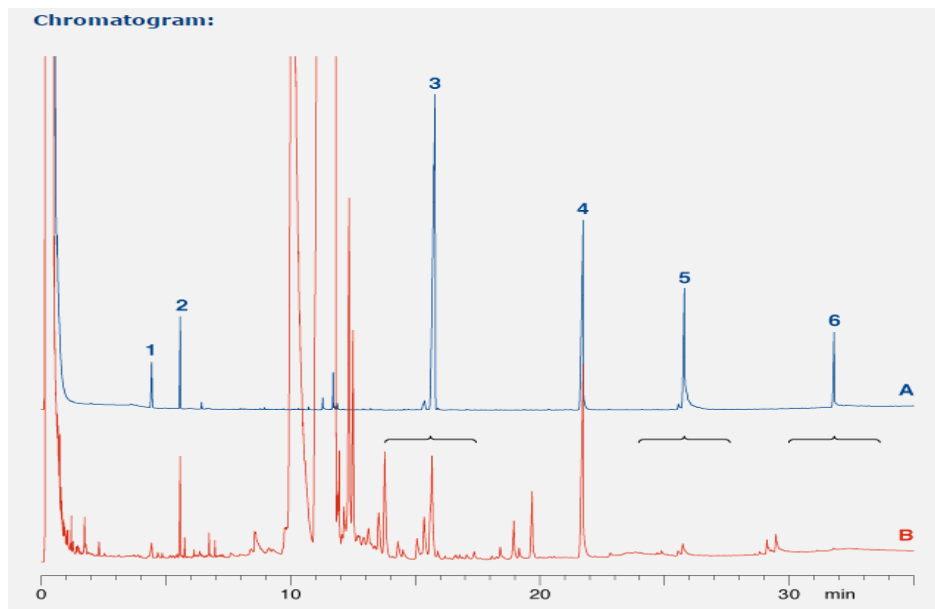


Figure 2.3: Analysis of Glycerides and Glycerol from Biodiesel using GC

Figure 2.3 above illustrated the example of the analysis by using GC. The sample pre-treatment is standard in n-heptane and biodiesel and the carrier gas used is hydrogen. The samples were quantified using the OPTIMA Biodiesel G, 10 m x 0.25 mm ID column. Injection volume that used for this previous work is 2 μ l and the injection temperature was started from 15 $^{\circ}$ C to 350 $^{\circ}$ C. Peak 1 and peak 6 represent the peak for glycerol and triolein respectively (GC Department, 2010).

Quantification of sample components is more accurately achieved by measurements of peak areas which do not vary much with fluctuations of temperatures and carrier gas flow and are not dependent upon injection technique. The measurement of peak height is accurate if the peaks are tall and narrowly based (Hamilton, 1962). The retention time of sample components and the peak characteristics will remain constant if variable such as carrier gas flow and pressure, injection technique, oven temperature and detector sensitivity are not altered.

2.9 Previous work on Ternary Diagram Systems

For ternary diagram systems, three component systems were required which are solute, solution and solvent component. In ternary diagram, solute, solution and solvent were represented by biodiesel (FAEE), triglycerides and ethanol respectively. Several factors such as ternary diagram methods, solubility and compositions of component were considered to plot the ternary phase diagrams.

2.9.1 Ternary Diagram Methods

Ternary phase diagrams are those having three component systems. To construct a ternary diagram it is necessary to know the three binary systems for the three components. The actual ternary diagram may be represented as a three dimensional form or more commonly as a two dimensional projection of the liquids surface onto the base of the triangle created when the three binary diagrams are joined together.

All compositions on ternary diagrams are expressed in terms of the three end member components which define the system. The external variables that must be considered in ternary constitution are temperature, pressure, composition X, and composition Y (Campbell, 2012). Composition X is the composition of each constituent in mole fraction or percent. Basically, the composition of points which lie inside the area of the triangle can be determined by using either two line method or triangular grid method.

(a) Two Line Method

In this method, only two lines are drawn, through the point of interest, parallel to any sides of the triangle. The intersection of these two lines with the third side divides this side into three line segments. The lengths of the individual line segments are proportional to the relative amounts of the three components. Two lines are drawn through composition parallel to any two sides of the triangle.

(b) Triangular Grid Method

In this method, a 10% triangular grid is constructed on the diagram. To determine the composition of a point within the triangular area of the diagram a series of three lines are drawn through the point of interest, with each line parallel to a side of the triangle.

With these line in place the percentage of each component in the composition of the point can readily determined. The proportion of any point within the triangle can be represented by grid lines drawn through the point of interest, parallel to each side of the triangle as shown in Figure 2.4 below.

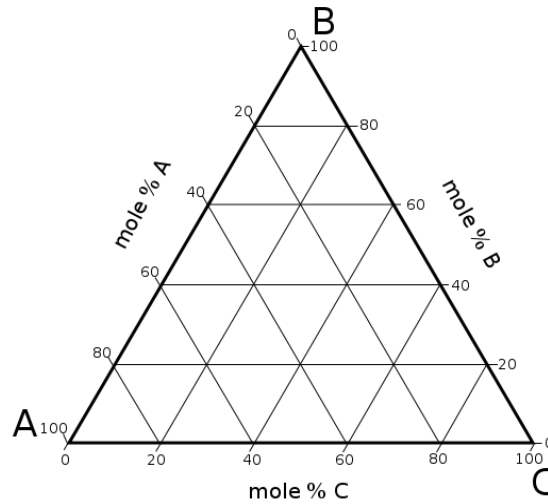


Figure 2.4: Triangular Grid of Ternary Diagram

From this ternary diagram, the mole percentage of A can be represented by grid lines parallel to the BC edge, while to determine the mole percentage of B, it can be represented by grid lines parallel to the AC edge. Lastly, the percentage of C can be represented by grid lines parallel to the AB edge.

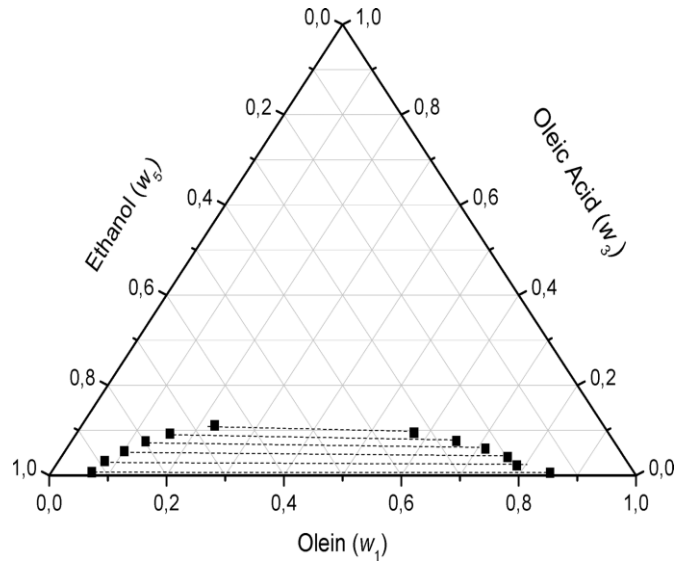


Figure 2.5: Liquid -liquid Equilibrium for the Ternary System Containing Palm Olein + Commercial Oleic Acid + Ethanol at 298.15K (Silva et.al, 2011)

Usually, triangular grid method is tend to be used compared to two line method as shown in Figure 2.5 above for liquid-liquid equilibrium for the ternary system containing palm olein + commercial oleic acid + ethanol at 298.15K. Therefore, triangular grid method is chosen to be used to plot the ternary diagram in this work.

2.9.2 Solubility in Ternary Diagram

A ternary diagram is actually a collection of solubility limit curves. The phase fields in equilibrium diagrams depend on the particular systems being depicted. Phase equilibrium refers to the set of conditions where more than one phase may exist. It can be reflected by constancy with time in the phase characteristics of a system. Equilibrium phase diagrams represent the relationships between temperature and the compositions and the quantities of phases at equilibrium. Pressure is assumed to be constant (1 atm.) in most applications. Set of solubility curves that represents locus of temperatures which all compositions are liquid are called *liquidus* (Kailas, 2012).

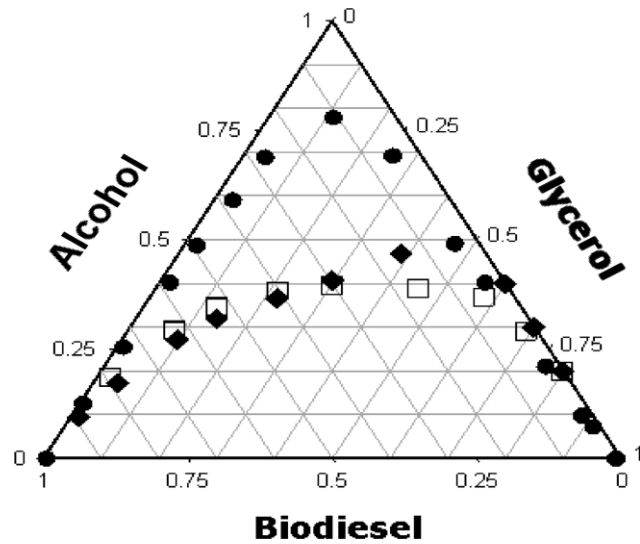


Figure 2.6: Phase diagram of castor oil biodiesel + glycerol + methanol; + ethanol at 298.15 K. b, *Jatropha curcas* biodiesel at 298.15 K (Franca et.al, 2009)

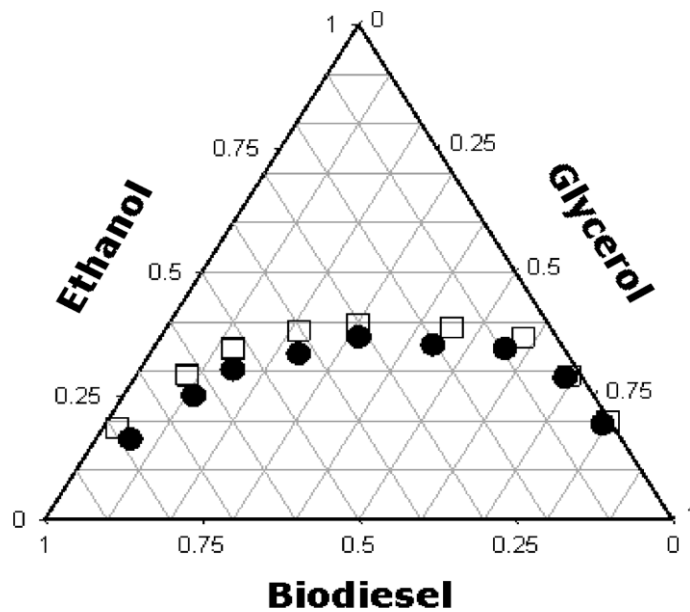


Figure 2.7: Phase diagram of biodiesel + glycerol + ethanol at 0, 298.15 K (Franc et al., 2009).

From the previous study, it can be observed that biodiesel has greater solubility in the glycerol-enriched phase in the system containing ethanol at constant temperature as shown in Figure 2.6 above. For second study, the systems was compared at different temperature as shown in Figure 2.7, it can be observed that the solubility increases with temperature. Despite these variations, they are not significant enough to determine

phase behaviour of the systems. The alcohol concentration is the main factor that affects biodiesel product solubility (Franc et al., 2009).

2.9.3 Tie Line in Ternary Diagram

The percentages of the two components in each phase enable the composition of that phase represented by a point on triangular coordinates. The points for equilibrium pairs of phases are the ends of the tie line for that system. When these are all plotted, the phase diagram can be completed by drawing the bimodal curve through the points. The gross composition of each system can be calculated from the weights of the three components used and also plotted on the diagram. Each such point should lie on the corresponding tie line (Clarke, 1974).

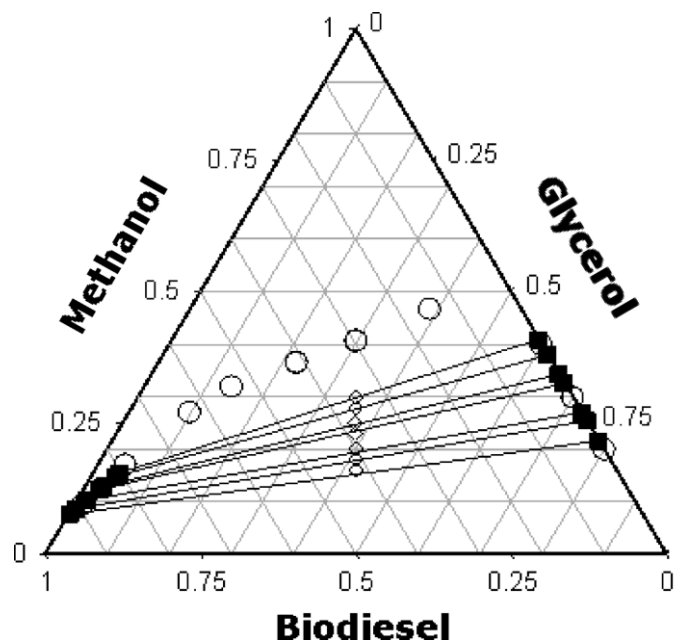


Figure 2.8: Tie lines for the system biodiesel + glycerol + methanol at 298.15 (Othmer & Tobias, 1942).

From the previous study of tie lines for the system biodiesel + glycerol + methanol at 298.15 K as shown in Figure 2.8 above, it can be seen that the composition of equilibrium phases cross global composition.

2.9.4 Compositions on Ternary Diagram

All compositions on ternary diagrams were expressed in terms of the three end-member components which define the system. The mixture of two or more phases may permit

interaction between different phases. Usually, a liquid solution is a single phase, even as a liquid mixture for example, mixture of oil and water forms two phases as there is no mixing at the molecular level. A single-phase system is termed as homogeneous, and systems composed of two or more phases are termed as mixtures or heterogeneous (Kailas, 2012).

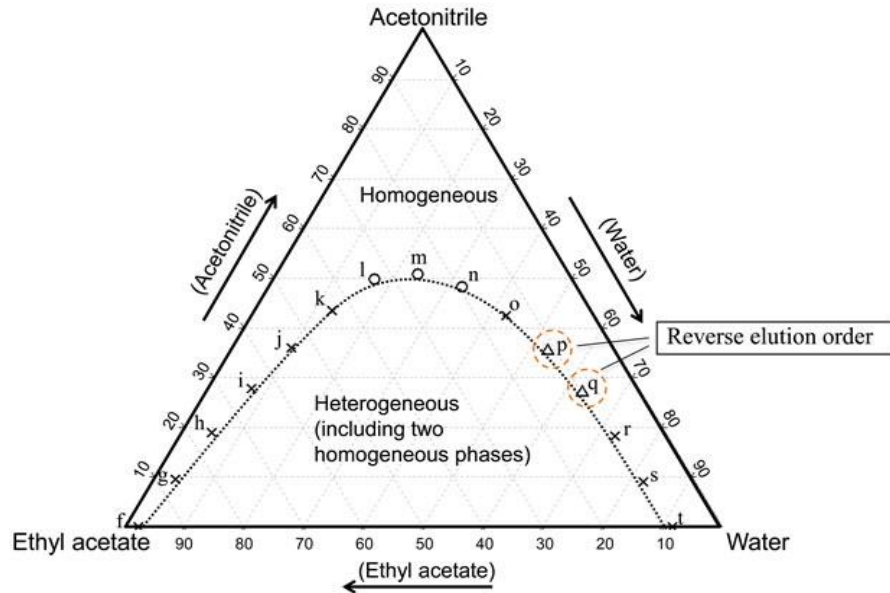


Figure 2.9: Phase diagram for water-acetonitrile-ethyl acetate mixture (Tanigawa et.al, 2012).

The phase diagram in Figure 2.9 above shows that each component ratio of the solvents formed a homogeneous (one homogeneous phase) or heterogeneous (two homogeneous phases) solution. The dotted curve in the diagram indicates the boundary between homogeneous and heterogeneous phases (Tanigawa et al., 2012). The aim for this research is to delineate compositions of component in different phases. Therefore, the compositions of component will hopefully delineate in the region below binodal curves.

3 MATERIALS AND METHODS

3.1 Materials Description

3.1.1 Chemicals

In this research, oil was used as the source of triglycerides, obtained from refined palm oil supplied from Saji brand with 100% purity. Another five chemicals were used in this work to determine the LLE data. All chemicals used were supplied from Sigma Aldrich. Potassium Hydroxide (KOH) was used as the catalyst in biodiesel production with purity 2wt%. Ethanol was of absolute grade with purity 99%. Another chemical also purchased from Sigma Aldrich. Other components include n-Heptane (99%) as a dilute sample for gas chromatography analysis and triolein (100%) and ethyl oleate (100%) were used as a standard sample. Table 3.1 below shows the summarization chemicals used characteristic and its function for this research.

Table 3.1: Characteristics of chemical used and its functions

Chemical	Brand	Purity	Purpose
Cooking palm oil	Saji	100%	Component in LLE and feedstock to provide FAEE
Absolute Ethanol	Sigma Aldrich	100%	Component in LLE
n-Heptane (Analytical)	Sigma Aldrich	99%	Use as a dilute sample for gas chromatography analysis
Potassium Hydroxide (KOH)	Sigma Aldrich	2wt%	Use in biodiesel production as a catalyst
Ethyl Oleate	Sigma Aldrich	100%	Standard sample
Triolein	Sigma Aldrich	100%	Standard sample

3.1.2 Apparatus

The apparatus listed below were used to conduct the experiment:

- i. 50 mL conical flask
- ii. Stopper
- iii. 1000 mL beaker
- iv. Micropipette
- v. 1 mL vial
- vi. Round bottom conical flask
- vii. Condenser
- viii. Separating funnel

3.1.3 Equipment

(a) Gas chromatography (GC)

Gas Chromatography (GC) was used in this work to obtain concentration measurements of ethyl oleate (EO), triolein (TO) and ethanol (Gl). GC also was used to determine the compositions of FAEE, triglycerides and ethanol in the samples of the phases to form the ternary diagram for each component. N-heptane was chosen as a dilute sample for gas chromatography. The composition for each component in this research was determined by GC using the Restex MXT Biodiesel TG column (15m x 0.32 mm x 10 μ m). Figure 3.1 and Figure 3.2 below shows the image for GC and the schematic diagram of GC respectively.



Figure 3.1: Gas Chromatography

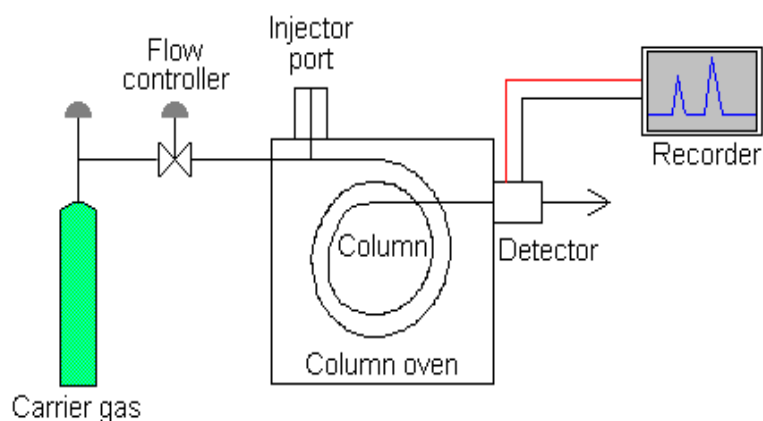


Figure 3.2: Schematic Diagram of a Gas Chromatograph

(b) Hot Plate Magnetic Stirrer

A hot plate magnetic stirrer or magnetic mixer was used in the experiment to stir the mixture of triglycerides, FAEE and ethanol vigorously. Hot plate magnetic stirrer is a laboratory device that employs a rotating magnetic field to cause a stir bar immersed in a liquid to spin very quickly, thus stirring it. The rotating field may be created either by a rotating magnet or a set of stationary electromagnets, placed beneath the vessel with the liquid. The mixture of three components was placed in the conical flask. Since glass does not affect a magnetic field appreciably, magnetic stir bars can work well in conical flask. On the other hand, the limited size of the bar means that magnetic stirrers can only be used for relatively small which is under 4 litres experiments. The

experiment was allowed a small amount of mixture since it is conducted by using 50ml conical flask. Therefore, it is suitable to use the hot plate magnetic stirrer to mix well the mixtures. Figure 3.3 below shows the image for hot plate magnetic stirrer.



Figure 3.3: Hot plate magnetic stirrer

3.2 Method Description

Before the experiment was started, the standard samples triolein and ethyl oleate were prepared by mixed with dilute sample (n-heptane) at concentrations 200 000 ppm in 1 ml vial. Then, another different concentrations within the range of 200 ppm to 100 000 ppm were prepared in 1 ml vial by using dilution method by taking the needed amount from 200 000 ppm sample preparation. The volume needed for triolein preparation at 200 000 ppm was calculated simultaneously by using these formulas:

$$V_{TO} + V_{nH} = 1\text{ml} \quad (3.1)$$

$$V_{TO} = \frac{m_{TO}}{\rho_{TO}} = n_{TO} MW_{TO} \quad (3.2)$$

$$V_{nH} = \frac{m_{nH}}{\rho_{nH}} = n_{nH} MW_{nH} \quad (3.3)$$

Where,

V = volume

m = mass

ρ = density

MW = molecular weight

Same formula and calculation method was used to calculate the volume needed for ethyl oleate preparation at 200 000 ppm. The calculation of volume needed for preparation of triolein sample at 200 000 ppm is shown in Appendix A-1. From the calculation, 0.56 ml of triolein was needed to mix with 0.44 ml n-heptane in 1 ml vial and 0.41 ml of ethyl oleate was needed to mix with 0.59 ml of n-heptane in 1 ml vial.

Then, formula below was used to determine the volume needed from sample at 200 000 ppm to be dilute with n-heptane in order to prepared another samples at different concentrations.

$$M_1V_1 = M_2V_2 \quad (3.4)$$

Where,

M_1 = concentration (200 000 ppm)

V_1 = volume needed

M_2 = concentration (200 ppm to 100 000 ppm)

V_2 = volume (1 ml)

The calculations of volume needed from sample at 200 000 ppm and n-heptane required to prepare standard sample at different concentration is shown in Appendix A-2. The summarization of the calculation was tabulated in Table 3.2 below.

Table 3.2: Data of volume needed for standard samples preparation.

Concentration (ppm)	Volume needed from sample at 200 000 ppm (ml)	Volume of n-Heptane (ml)
100 000	0.500	0.500
50 000	0.250	0.750
25 000	0.125	0.875
10 000	0.050	0.950
2000	0.010	0.990
200	0.001	0.999

After the samples were prepared, the compositions of the samples were accordingly analysed by GC using Restek MXT-Biodiesel TG column. The area under peak for every concentration from chromatogram was then calculated in order to plot the calibration curve. It is necessary to normalise the measured peak area against peak area of a standard solute. The normalised area, A_i^* may thus be defined as,

$$A_i^* = \frac{A_i}{A_{ref}} \quad (3.6)$$

Where, A_i^* = normalised area of component i ,

A_i = absolute area of component i ,

A_{ref} = reference area of component in standard solution.

This work was continued with the preparation of fatty acid ethyl ester (FAEE) which used as the source of fatty acids. The reaction for biodiesel production is the transesterification reaction. In this reaction, the mixture of oil and ethanol following 1:6 molar ratios was employed. Potassium hydroxide (KOH) was used as the catalyst for biodiesel production. The production of biodiesel was conducted with the following conditions:

Table 3.3: Conditions for FAEE production by transesterification reaction

Molar ratio oil/alcohol	1:6
Catalyst	1.05g of 2 wt % KOH
Reaction temperature	298.15 K
Speed of hot plate magnetic stirrer	300 rpm

The FAEE was prepared in 1000 ml round bottom conical flask. The volume needed for ethanol and triglycerides required for this reaction was calculated by using the formula below:

$$V_{etOH} + V_{TG} = 1000 \text{ ml} \quad (3.6)$$

$$R_{TG:etOH} = 1/6 \quad (3.7)$$

$$R_{TG:etOH} = \frac{n_{TG}}{n_{etOH}} = \frac{(\rho_{TG})(V_{TG})(MW_{etOH})}{(\rho_{etOH})(V_{etOH})(MW_{TG})} \quad (3.8)$$

$$\frac{V_{TG}}{V_{etOH}} = \frac{(RTG: etOH)(\rho_{etOH})(MW_{TG})}{(\rho_{TG})(MW_{etOH})} \quad (3.9)$$

From the calculations, the volume of ethanol and triglycerides needed for FAEE preparation is 261.62 ml and 738.38 ml respectively. The calculation is shown in Appendix A-3.

In equilibrium study, FAEE, triglycerides and ethanol were mixed together at different mass ratios. The ratios used are (1:1:0), (0.35:0.35:0.3), (0.3:0.3:0.4), (0.25:0.25:0.5) and (0.2:0.2:0.6) for triglycerides, ethanol and FAEE respectively. In this study, one phase was enriched triglycerides and the other was enriched ethanol. With the systems in equilibrium, the concentrations of both phases were measured by using gas chromatography. The concentration data were used to plot the ternary diagrams and McCabe-Thiele chart, and the results were compared with those obtained from the literature.

3.3 Experimental Procedure

3.3.1 FAEE Preparation

First step, 261.62 mL of ethanol was poured into the round bottom conical flask. Next, 15 g of 2 wt% of potassium hydroxide (KOH) was added to ensure the reaction can be occur. Then, 738.38 mL of palm oil was measured in 1000 ml beaker, then, it was poured into the conical flask of dissolved KOH and ethanol. The stopper was replaced on conical flask and the mixtures were stirred and heated by using hot plate magnetic stirrer with 300rpm speed at temperature 40°C. A condenser was assembled on top of the conical flask to condensate the mixture. The mixtures was left for one day to ensure complete reaction occur. Then, the separation of the biodiesel and the glycerine were produced. Biodiesel was produced at the top and the glycerine was produced at the bottom of layer. Next, the separating funnel was used to separate these two liquids. The mixture was washed for three times by using dilute water to remove the impurities. Figure 3.4 below shows the setup for FAEE preparation.

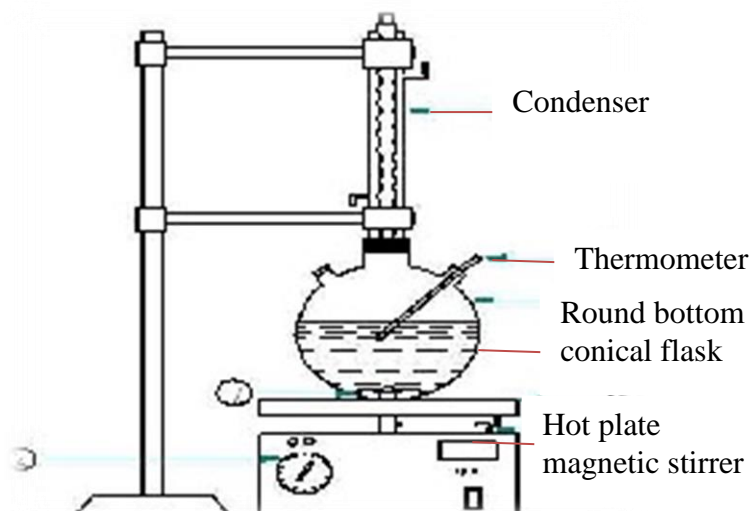
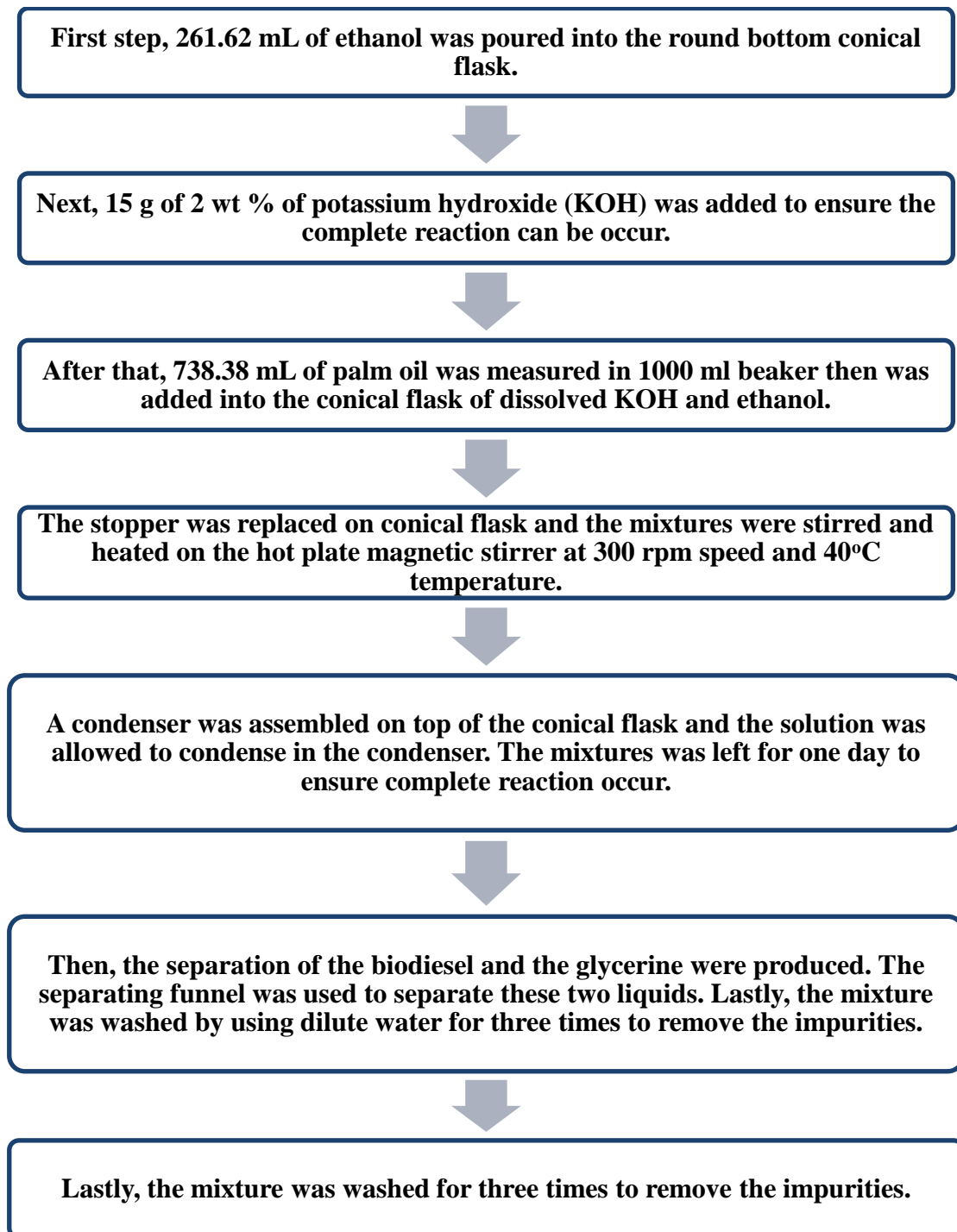


Figure 3.4: Setup for FAEE preparation

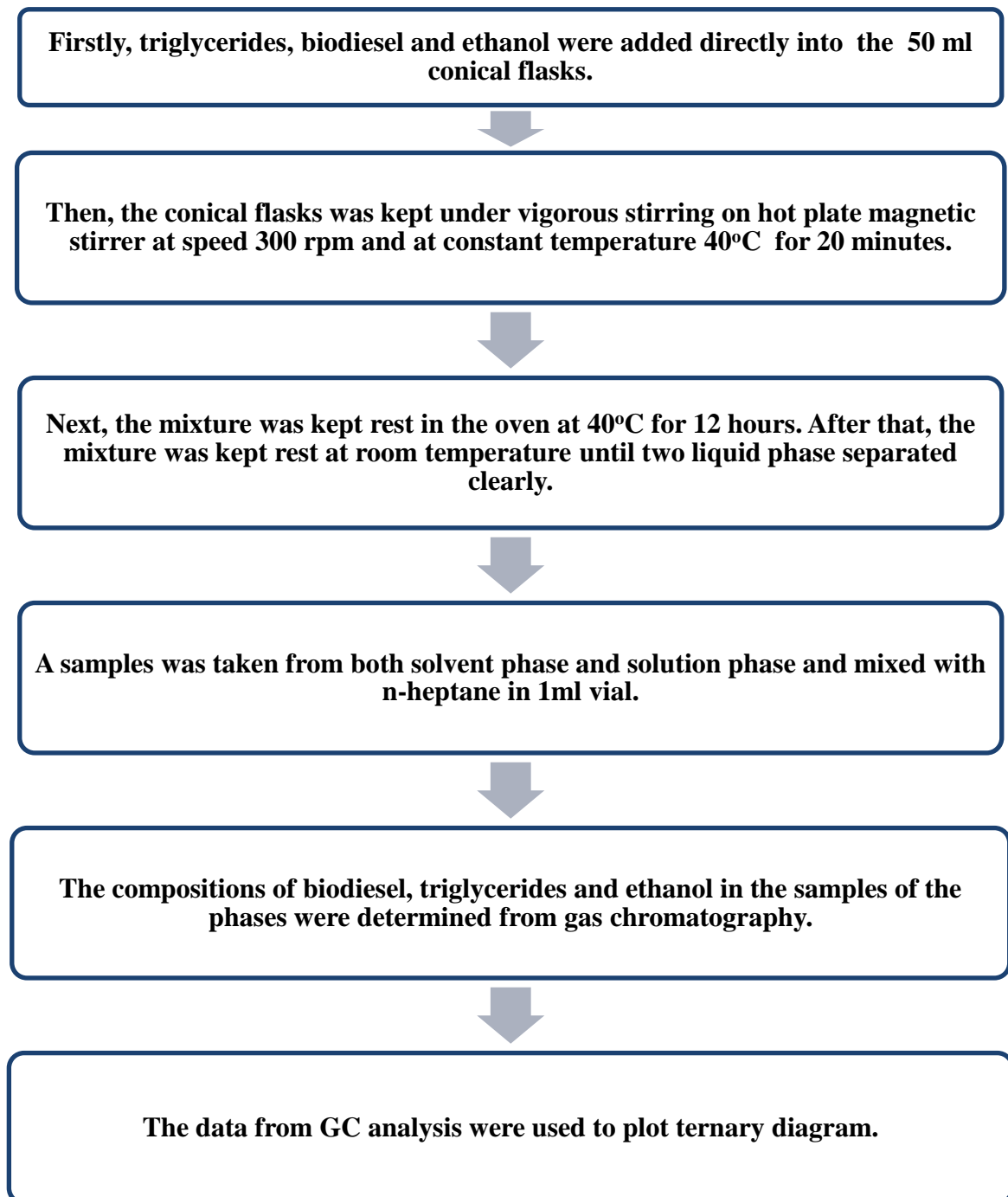
3.3.2 Experiment of Equilibria of the Triglycerides + FAEE + Ethanol System

Conical flask with a volume 50 mL and hot plate magnetic stirrer were used to perform liquid-liquid extraction (LLE) measures at atmospheric pressure. The ternary mixture of triglycerides, biodiesel and ethanol were added directly into conical flask. To promote contact between the phases, the conical flask was kept under vigorous stirring by hot plate magnetic stirrer with speed 300 rpm at constant temperature 40°C for 20 minutes. After that, the ternary mixture was kept rest in the oven at 40°C. After a period time which is about 12 hours, the ternary mixtures were kept rest at room temperature until two liquid phases clearly separated. One phase was enriched solvent (ethanol) and the other enriched solution (biodiesel and triglycerides). When the equilibrium was achieved, a sample was taken from both the solvent- enriched phase at the top of layer and the solution enriched phase at the bottom layer. The samples were mixed with n-heptane in 1ml vial. To determine the compositions for each phase, the sample was run by using gas chromatography. Then, the compositions of biodiesel, triglycerides and ethanol in the samples of the phases were determined from the GC analysis to construct the ternary diagram and McCabe-Thiele chart. The procedure of samples preparation was shown in Appendix B-1.

3.3.3 Flow Diagram of F AEE Preparation



3.3.4 Flow Diagram of Experiment



4 RESULTS AND DISCUSSION

4.1 Overview

This chapter provided the results that obtained through this research that divide in certain subtopic which are GC analysis for standard sample, the result for calibration curve for standard sample and determination of concentration for ethyl oleate and triolein in solvent phase and solution phase in order to plot the McCabe-Thiele extraction graph. Besides, Liquid-liquid Equilibrium data for each sample which are ethanol, FAEE and triglycerides also tabulated in order to plot the ternary diagram.

4.2 GC Analysis for Standard Sample

In this work, a known volume of standard ethyl oleate and triolein was injected by using GC. The various components of the mixture are separated as they progress along the column and reach the end of the column at different times (retention time). Prior to analyzing composition of samples from an experiment, it is necessary to identify retention time and peak area for each component to be analyzed. These data was needed in order to determine the composition of the samples. The data obtained from GC analysis for standard ethyl oleate and triolein were tabulated in the Table 4.1 (a) and Table 4.1(b) respectively.

Table 4.1(a): Data from GC analysis for standard ethyl oleate

Sample Concentration (ppm)	Retention Time (min)	Area (pA*s)	Area (%)	Peak Height (pA)
2000	10.687	2515.14	1.216	4.519
10000	10.454	14918.8	6.863	1280.767
25000	10.279	32602.4	14.678	1997.639
50000	10.158	52808.6	22.657	2545.035
100000	10.146	52833.7	21.388	2630.816
200000	9.828	110622	42.893	3563.863

Table 4.1(b): Data from GC analysis for standard triolein

Sample Concentration (ppm)	Retention Time (min)	Area (pA*s)	Area (%)	Peak Height (pA)
200	24.3	2323.22144	0.81173	310.6716
2000	24.447	3289.27417	1.35973	504.7486
10000	24.384	3872.22754	1.38237	480.78632
25000	24.436	4583.9668	1.55199	588.25964
50000	24.493	5546.30908	2.75579	554.25262
100000	24.513	6412.19287	2.75579	554.25262

4.3 Calibration Curve for Standard Sample

Calibration curve is a curve relating the areas of the peaks on chromatograms to the mixture composition. Knowledge of the retention times which is the time at which the peak was observed from the GC analysis for individual components used to identify components corresponding to different peaks in multi-component mixtures. The concentration of the standard ethyl oleate and triolein was lie within the range from 200ppm to 100000 ppm. The data needed to plot the calibration curve for standard sample is tabulated in Table 4.2 below.

Table 4.2: Calibration Curve Data for Standard Sample

Area pA*S \ Concentration (ppm)	Ethyl Oleate	Triolein
200	-	267.45898
2000	2515.14	931.71472
10000	14918.8	1833.39502
25000	32602.4	2940.69556
50000	52808.6	4583.9668
100000	52833.7	6412.19287

However, not all the tabulated data above were used to plot the calibration curve, since some errors associated with measurement of the absolute value of the peak area at the bigger concentration are quite large. This is because the absolute peak areas may vary significantly from measurement to measurement due to variation of the total amount of the mixture injected into the GC. On the other hand, the relative peak areas yield high degree of reproducibility so that the error bars are not even visible on the plot. Therefore, the relative area of the peaks is a more reliable measure of the sample composition and it should be used in analysis of samples collected during the experiment.

To avoid the error, the calibration curve must have R-squared value on chart above than 95%. Therefore, the high concentration was removed from the graph when the R-squared value below than 95%. For standard ethyl oleate, the graph was plotted for concentration between 2000ppm to 50000ppm and for standard triolein, the graph was plotted between 200ppm to 50000ppm. Figure 4.1(a) and Figure 4.1(b) below shows the calibration curve for standard ethyl oleate and triolein respectively.

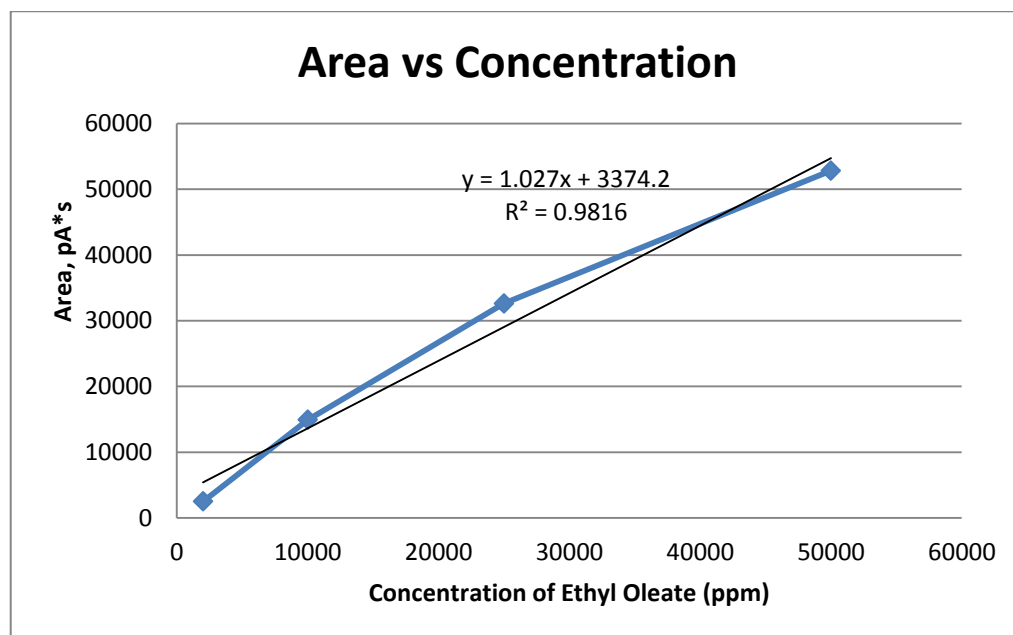


Figure 4.1 (a): Calibration curve for Ethyl Oleate

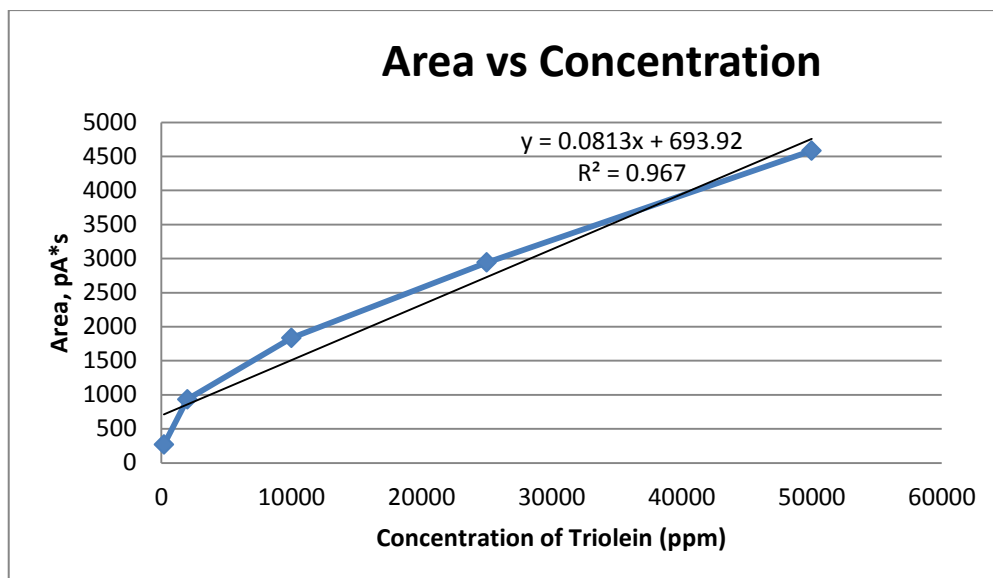


Figure 4.1(b): Calibration curve for Triolein

For this analysis, a plot of peak area vs. concentration for both standard ethyl oleate and triolein show a linear relationship. The obtained calibration curves are then used for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration.

4.4 McCabe-Thiele Chart

A McCabe-Thiele method is needed to identify the composition for separation of a binary mixture of FA EE and ethanol, and also binary mixture of triglycerides and ethanol whether FAEE and triglycerides is rich in solvent phase or in solution phase. The composition of the solute can be determined by constructing a McCabe-Thiele chart.

The chart was constructed by determining concentration of samples for extraction or stripping via experiments. The equilibrium isotherm was obtained by mixing solvent and solution at different phase ratios until equilibrium was reached. In this research, two charts were plotted which are for FAEE sample and triglycerides sample. By referring to the GC analysis, the time to reach equilibrium for FAEE is 10 minutes while for triglycerides is 23 minutes.

The phase was analysed and the concentration for the samples was determined by using calibration curve. Usually, interpolation method is used to find the concentration of the samples from calibration curve. However, since the average of peak

area for the samples obtained from the GC analysis were quite small, therefore, an extrapolation was made from the calibration curve by assuming its linearity in order to get the concentration value. Then, the FAEE and triglycerides content in the solvent and solution phase was calculated and tabulated in the Table 4.3 (a) and Table 4.3(b) respectively.

Table 4.3 (a): Concentration of FAEE in the solvent and solution phases

Concentration FAEE in Solution (ppm)	Concentration FAEE in Solvent (ppm)
10926.37	10794.13
8173.4	8058.98
6450.48	6355.66
5295.55	5322.55

Table 4.3(b): Concentration of TG in the solvent and solution phases

Concentration of TG in Solution (ppm)	Concentration TG in Solution (ppm)
80103.83	8522.83
58479.47	20720.06
45491.96	20527.96
35848.73	22346.13
34225.46	23053.61

The equilibrium isotherm for extraction was obtained by plotting the concentration of solute in solvent against the concentration of solute in solution in a chart. The equilibrium isotherm obtained is specific for this particular system. Changes in concentrations of FAEE, triglycerides or ethanol will lead to another equilibrium curve. Figure 4.2 below shows the McCabe-Thiele chart for FAEE with ethanol.

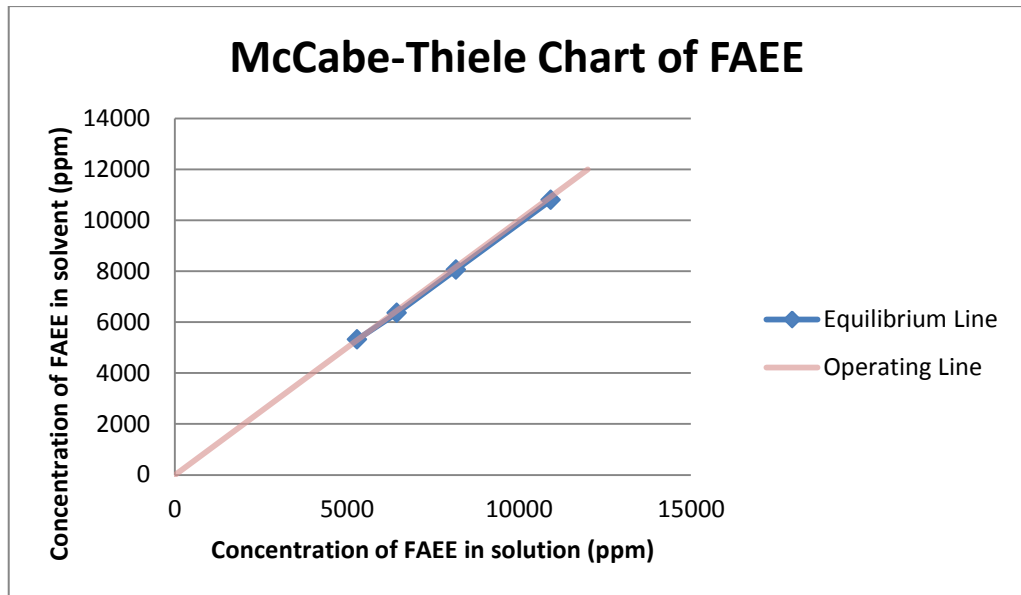


Figure 4.2: McCabe-Thiele Chart for FAEE

After the equilibrium isotherm has been plotted into the chart, based on this method, an operating line is drawn by using free coordinates which based on the mass fraction of ethanol and oil (1:1). Based on the literature, the equilibrium relation is not a straight line in the mole fraction or mass fraction coordinates while the operating line in the solute-free coordinates is a straight line. Therefore it is advantage to use solute-free coordinates because the operating line will always be straight (Seader & Henley, 2006). The operating line should go from a point on the equilibrium isotherm corresponding to the FAEE content in the solvent phase to the value on the x-axis corresponding to the FAEE concentration in the solution phase.

From the graph, it can be seen that the equilibrium line is linear and quit near to the operating line and it is located below the operating line which means that the extraction of FAEE from the solution by using ethanol solvent was failed. This may be due to the solvent ratio used is not high enough to achieve effective removal of FAEE from the solution using solvent extraction. Therefore, mass ratio for the solvent must be high enough in order to ensure the extraction process can be occurred. The extraction process occurred can be proved if the equilibrium line is achieved above the operating line.

The driving force for mass transfer becomes zero whenever the operating line intersects or touches the equilibrium curve. This limiting condition represents the minimum solvent rate to recover a specified quantity of solute or the solvent rate

required to remove the maximum amount of solute (Seader & Henley, 2006). From the graph, the intersection of the equilibrium line and operating line occurs at the bottom. This condition defines the minimum solvent rate to recover a specified quantity of solute.

A McCabe-Thiele chart is constructed in a similar way to plot the McCabe-Thiele chart for triglycerides with ethanol. The chart for triglycerides is shown in Figure 4.3 below.

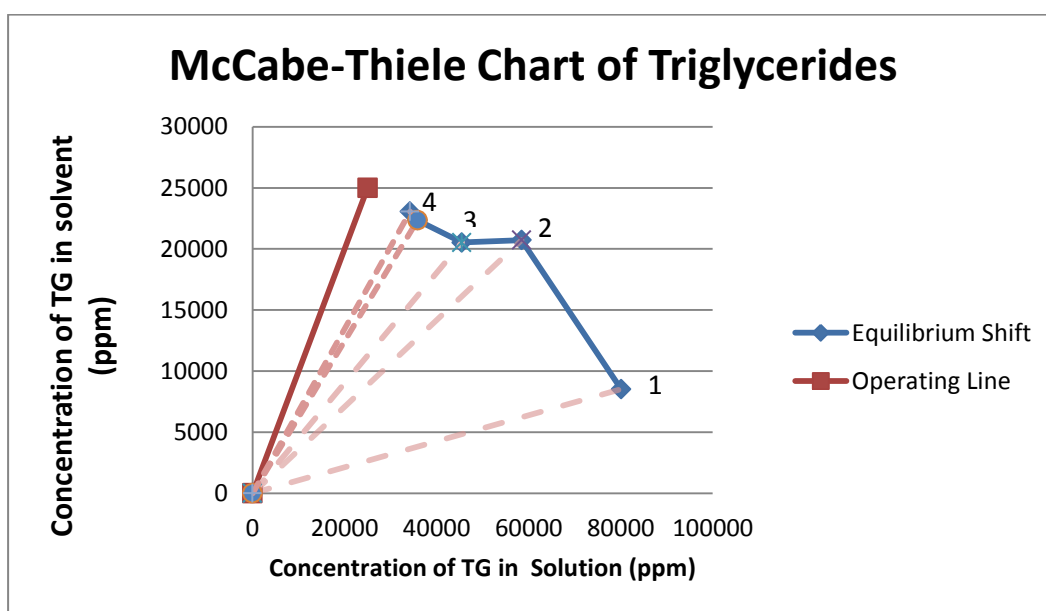


Figure 4.3: McCabe-Thiele Chart for Triglycerides

The graph shows that the equilibrium line is below the operating line, which means the stripping would occur in this process. Addition of FAEE shifted the equilibrium towards the operating line. If virtual equilibrium lines are drawn from the origin as depicted by dotted line, the steepness of the lines would clearly increase suggesting that the stripping affinity of triglycerides from ethanol solvent becomes lesser when FAEE concentration was increased. This may imply that FAEE helps increase concentration of triglycerides in ethanol.

4.5 Ternary Diagram

The experimental procedure used in this work allows determination of liquid-liquid equilibrium data from percentage of peak area analysis in order to determine the compositions of the components, whether it is rich in FAEE phase or in ethanol phase. Table 4.4 presents the area fractions of each component in the FAEE and ethanol phase.

Table 4.4: Ethanol + FAEE + Triglycerides System, Liquid-Liquid Equilibria at 313K.

Solution Layer (Area %)/Total of Area (%)			Solvent Layer (Area %)/Total of Area (%)		
Ethanol	FAEE	Triglycerides	Ethanol	FAEE	Triglycerides
0.0136	0.0648	0.9216	0.3546	0.5390	0.1064
0.0971	0.3091	0.5938	0.6992	0.2605	0.0403
0.1103	0.4033	0.4864	0.5358	0.3843	0.0800
0.1329	0.4775	0.3896	0.4472	0.4558	0.0970
0.1255	0.5663	0.3082	0.1445	0.5597	0.2957

The percentage areas of the three components in each phase that obtain from the GC analysis enable the composition of that phase represented by a point on triangular coordinates. As can be seen from Figure 4.4, the tie lines were plotted by joining the points for equilibrium pairs of phases in this system. The phase diagram was completed by drawing the bimodal curve through the points.

The system shows that each component ratio of the solvents formed either a homogeneous (one homogeneous phase) or heterogeneous (two homogeneous phases) solution. The two homogeneous phases were located below bimodal curve. For this process, some error occurs at initial mix composed of 50% triglycerides and 50% ethanol. This is may be due to the mistake during taking the sample from both layers.

From the graph, it can be observed that biodiesel has greater solubility in the triglycerides-enriched phase at constant temperature. Despite these variations, they are not significant enough to determine phase behaviour of the systems. The alcohol concentration is the main factor that affects biodiesel product solubility in creating two-immiscible liquid phase environment (Franc et al., 2009). Figure 4.4 below shows the ternary diagram for FAEE + triglycerides + ethanol system.

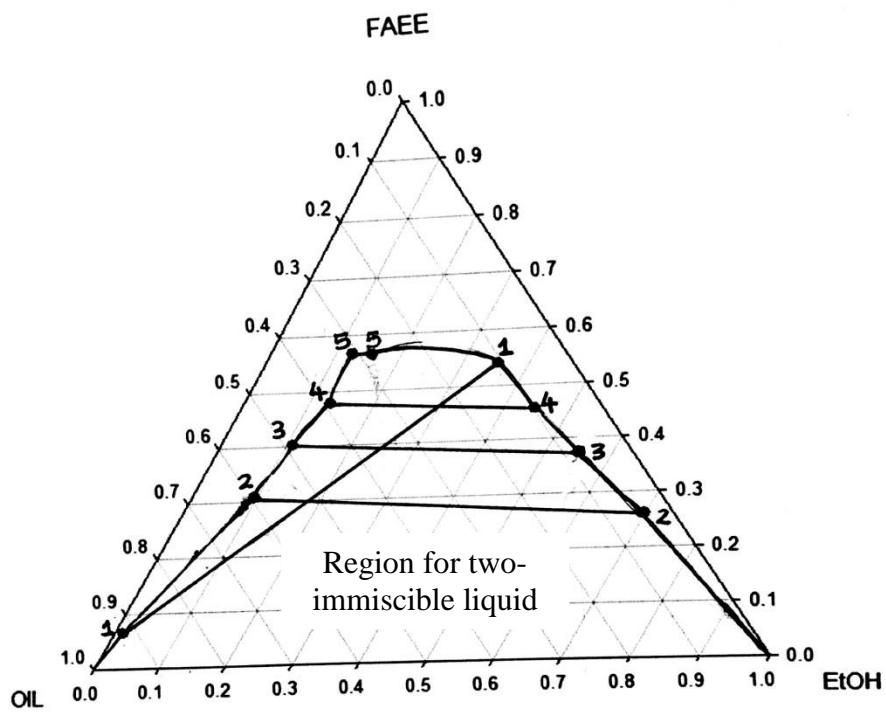


Figure 4.4: Ternary Diagram for the system FAEE + triglycerides + ethanol at 313K

5 CONCLUSION

5.1 Conclusion

The Data to plot McCabe-Thiele chart for triolein and ethyl oleate and Liquid-liquid equilibrium data for system containing triglycerides + ethanol + FAEE were experimentally determined at 313.15K. From the McCabe-Thiele graph for ethyl oleate, it can be concluded that the extraction of FAEE from the solution by using ethanol solvent was not possible because the solvent ratio used is not high enough to achieve effective removal of FAEE from the solution using solvent extraction. Therefore, volume ratio for the solvent must be greater than 1:1 in order to ensure the extraction process can be attained. For McCabe-Thiele chart of triglycerides, the results confirm that the solubility of solute (triglycerides) in solution is higher than the solubility of the solute in solvent. Increment of FAEE concentration however reduced the solubility of solute (triglycerides) in the solution. Lastly, from the ternary diagram, the compositions that create two immiscible liquid system was successfully obtained and the result shows that biodiesel has greater solubility in the triglycerides-enriched phase in the system containing ethanol at constant temperature.

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APPENDICES

Appendix A-1

Calculation of volume needed for triolein preparation with concentration 200 000 ppm is as shown below:

$$\begin{aligned}\frac{200\ 000\ ppm}{1\ 000\ 000} &= 0.2 \\ \frac{n_{TO}}{n_{nH} + n_{TO}} &= 0.2 \\ n_{TO} &= 0.25\ n_{nH}\end{aligned}\tag{1}$$

Equation (1) is substitute into Equation (3.2),

$$V_{TO} = \frac{0.25\ n_{nH}MW_{TO}}{\rho_{TO}}\tag{2}$$

Equation (2) and Equation (3.3) is substitute into Equation (3.1),

$$\frac{0.25\ n_{nH}MW_{TO}}{\rho_{TO}} + \frac{n_{nH}MW_{nH}}{\rho_{nH}} = 1$$

The value of molecular weight and density of triolein and n-heptane is substitute into the equation,

$$\frac{0.25\ n_{nH}(885.432)}{0.95} + \frac{n_{nH}(100.21)}{0.684} = 1$$

$$n_{nH}(233.01 + 146.51) = 1$$

$$n_{nH} = 0.003$$

$$n_{TO} = 0.25 (0.003) = 0.0007$$

Equation (3.3) is used to calculate the volume of n-heptane needed,

$$V_{nH} = \frac{(0.003)(100.21)}{0.684} = 0.44\ ml$$

By using Equation (3.1),

$$V_{TO} = 1 - 0.44 = 0.56\ ml$$

Same calculation steps was used to calculate the volume of ethyl oleate and n-heptane needed for ethyl oleate sample preparation.

Appendix A-2

Volume of sample at 200 000 ppm needed to dilute with n-heptane is calculated by using Equation (3.4) as shown below:

For concentration 100 000 ppm,

$$\begin{aligned}M_1V_1 &= M_2V_2 \\(200\ 000)V_1 &= (100\ 000)(1) \\V_1 &= 0.5\ ml\end{aligned}$$

Same calculation steps is repeated for concentration 50 000 ppm, 25 000 ppm, 10 000 ppm, 2000 ppm and 200 ppm. The value of M_1 and V_2 is kept constant.

Appendix A-3

The volume of triglycerides and ethanol is calculated by using Equation (3.6) and Equation (3.9) as shown below,

$$\begin{aligned}\frac{V_{TG}}{V_{etOH}} &= \frac{\left(\frac{1}{6}\right)\left(0.78\frac{g}{ml}\right)(890\ g/mol)}{\left(0.89\frac{g}{ml}\right)(46.06\ g/mol)} = 2.822 \\V_{etOH} + 2.822V_{etOH} &= 1000\ ml \\V_{etOH} &= 261.62\ ml \\V_{TG} &= 1000\ ml - 261.62\ ml = 738.38\ ml\end{aligned}$$

Appendix B-1

Step of samples preparation.



Figure B-1.1: Preparation of FAEE by transesterification reaction



Figure B-1.2: Preparation of FAEE + triglycerides + ethanol at different ratio

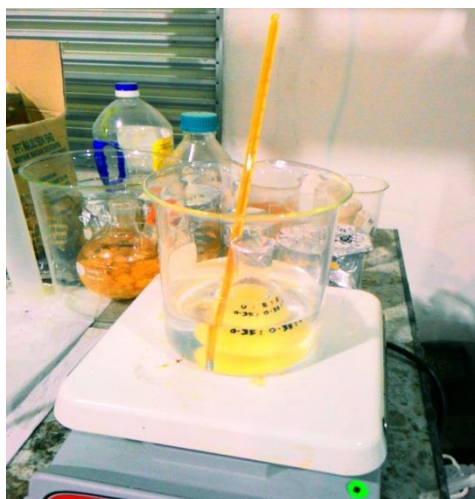


Figure B-1.3: The sample was stirred on hot plate magnetic stirrer



Figure B-1.4: Two separated layer were observed clearly



Figure B-1.5: Sample from upper and lower phase were mixed with n-heptane in 1 ml vial and GC analysis was conducted