BIODIESEL PRODUCTION VIA TWO-STEPS CATALYZED PROCESS: THE STUDY ON EFFECT OF TEMPERATURE AND CATALYST WEIGHT PERCENT TO THE BIODIESEL YIELD, FFA CONTENT AND ACID VALUE

AMMINATUL FARHAYU BINTI ABDUL TALIB

UNIVERSITY MALAYSIA PAHANG

KOLEJ UNIVERSITI KEJURUTERAAN & TEKNOLOGI MALAYSIA

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Alamat Tetap**: 464-D KG PDG LALANG**   **SHALYDA BINTI MD SHAARANI**
                07000 KUAH, LANGKAWI   Nama Penyelia
                KEDAH DARUL AMAN

Tarikh: _____   Tarikh: _____

"I hereby acknowledge that I had read this technical writing and in my opinion the technical writing is sufficient in terms of scope and quality for the purpose of the granting of Bachelor of Chemical Engineering"

Signature : ....
Name of supervisor: Shalyda Binti Md Shaarani@Md Nawi
Date :

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AMMINATUL FARHAYU BINTI ABDUL TALIB

A report submitted in partial fulfillment of the requirements for the
award of the degree of Bachelor of Technology
(Chemical Engineering and Natural Resource)

Faculty of Chemical Engineering and Natural Resource
University Malaysia Pahang

MARCH 2008

'I declare that this thesis is the result of my own research expect as cited references. The thesis has not been accepted for any degree and is concurrently submitted in candidature of any degree."

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Name of Candidate   : AMMINATUL FARHAYU BINTI ABDUL TALIB

Date   :

En route for beloved father, my late mother, family, friends and those people who'd

giving me support and understanding and the help to finish my journey…

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ABSTRACT

In this study, the effects of temperature and catalyst weight percent to the biodiesel yield, FFA content and acid value were studied. The biodiesel is produced by two-steps catalyzed process. The essential part of the process is the transesterification of waste cooking oil (WCO) with methanol in present of catalyst, to yield methyl ester as the main product and glycerin as the by-product. In the acid treatment or the acid-catalyzed esterification, the temperature is set at 95°C, acid catalyst of 2%w/wH_2SO_4 and methanol to waste cooking oil of 10:1. For the alkali-catalyzed transesterification, the range of temperature is 40°C-80°C, the alkali catalyst weight percent is varied from 0.2 to 1.0%wNaOH/wWCO. The ultrasonic wave and ratio of methanol to waste cooking was fixed at 32MHz and 6:1 respectively. The biodiesel product is then analyzed by titration to check the FFA content and the acid value. The best temperature and alkali catalyst weight percent was found at 70°C and 1.0%wNaOH/wWCO correspondingly. The total reduction of FFA content after acid treatment was 36.92%. The two steps catalyzed process is preferable for raw material that has high content of FFA such as waste cooking oil.

ABSTRAK

Dalam kajian ini, kesan suhu dan peratus berat mangkin terhadap mintak masak terpakai dikaji terhadap hasil, kandungan asid lemak bebas, dan juga nilai asid biodiesel telah dikaji. Biodiesel dihasilkan dengan menggunakan proses dua langkah bermangkin. Secara kasarnya, bahagian penting dalam proses ini adalah transesterifikasi minyak masak terpakai dengan methanol dengan kehadiran mangkin untuk menghasilkan biodiesel sebagai hasil utama dan glycerin sebagai hasil sampingan. Semasa process rawatan asid, suhu telah ditetapkan pada 95°C, mangkin asid 2%w/wH_2SO_4 dan methanol terhadap minyak masak terpakai 10:1. Untuk proses traneseterifikasi bermangkin alkali jarak suhu dipelbagaikan di antara 40°C-80°C, nisbah berat mangkin terhadap minyak masak di antara 0.2 to 1.0%wNaOH/wWCO. Gelombang ultrasonic dan nisbah methanol terhadap minyak masak masing-masing ditetapkan pada 32MHz dan 6:1. Biodiesel yang terhasil diuji dengan menggunakan kaedah pentitratan untuk menguji kandungan asid lemak bebas dan juga tahap kandungan asid. Suhu terbaik yang telah ditemui adalah pada 70°C dan nisbah berat mangkin pada 1.0%wNaOH/wWCO. Jumlah pengurangan asid lemak bebas selepas process rawatan asid adalah 36.92%. Proses dua langkah bermangkin ini lebih bermakna apabila menggunakan bahan asas yang mempunyai kandungan asid lemak bebas yang tinggi seperti minyak masak terpakai.

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LIST OF SYMBOLS

Symbol	Title
P	Pressure
m	Mass
T	Temperature
°C	Degree Celsius
Pa	Pascal
Hz	Hertz
L	Liter
g	Gram
mg	Milligram
m	Meter
cm	Centimeter
%wt	Weight Percent

CHAPTER I

INTRODUCTION

Worldwide economies are struggling to cope with the raising crude oil prices and at the same time need to negotiate with the environmental concern associated with fossil fuel usage. Therefore, countries across the world are now penetrating viable alternative to fossil fuels that are cost-effective and environmental friendly. As the result, biofuels are gaining popularity, especially in transport sectors, across the globe. Consumption of biofuels is aimed to minimize over-dependence of conventional and expensive fossil fuel. Apart from reducing pollution, biofuels usage offers economies benefits such as increased job opportunities, and contributes in strengthening the agriculture sector.

Biodiesel and bioethanol are the primary biofuels currently in used across the world. The demand of biodiesel is rapidly increasing even though bioethanol is them most widely consumed. Rising the environmental pollution and volatile prices of petroleum diesel are supercritical factors that increased the demand for the biodiesel worldwide.

1.1   Biodiesel

Biodiesel is one of the alternative fuels having many advantages. It is derived from the renewable, domestic resource that relieves the reliance on petroleum fuel import. Biodiesel is biodegradable and non-toxic that made it safe to the environment. Compared to the petroleum based diesel, biodiesel have more favorable combustion emission profile, such as low emission of carbon monoxide produced by particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis and reducing the impact of biodiesel combustion on the greenhouse effect. Biodiesel is light to dark yellow liquid, practically immiscible with water, has a high boiling point and low vapor pressure. High flash point which is 150°C makes it less volatile and safer. In brief, these merits of biodiesel make it a good alternative to petroleum-based fuel and have led to its use in many countries, especially in environmentally sensitive areas.

1.2   Transesterification

The transesterification process is the reaction of triglyceride (fat/oil) with alcohol to form esters and glycerol. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst; usually strong base liked potassium hydroxide. The alcohol reacts with fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is alkali-catalyzed by either potassium or sodium hydroxide. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel production; either alkali can be used for the methyl ester. A common product of the transesterification process Rape Methyl Ester (RME) produced from raw rapeseed oil with methanol

Figure 1.1 shows the chemical process for methyl ester biodiesel. The reaction between the fat or oil and the alcohol is reversible reaction and so the alcohol must be added in excess to drive the reaction toward the right and ensure complete conversion.

$$
\begin{array}{ccccccc}
CH_2\text{-}OOC\text{-}R_1 & & & & R_1\text{-}COO\text{-}R' & & CH_2\text{-}OH \\
CH_2\text{-}OOC\text{-}R_2 & + & 3R'OH & \xrightarrow{\text{catalyst}} & R_2\text{-}COO\text{-}R' & + & CH\text{-}OH \\
CH_2\text{-}OOC\text{-}R_3 & & & & R_3\text{-}COO\text{-}R' & & CH_2\text{-}OH \\
\textbf{Glyceride} & & \textbf{Alcohol} & & \textbf{Ester} & & \textbf{Glycerol}
\end{array} \quad (1.1)
$$
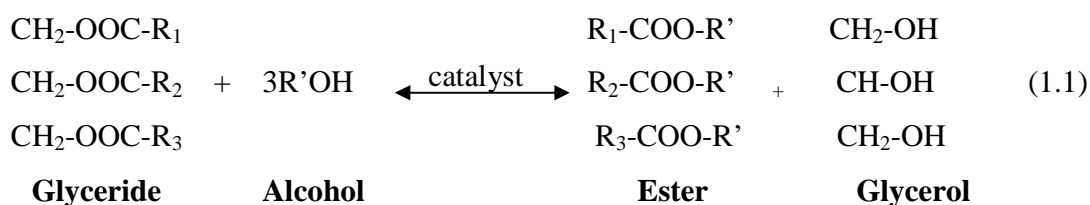
Figure 1.1: Chemical reaction general equation for methyl ester biodiesel production

The products of the reaction are the biodiesel itself and glycerol. A successful transesterification is signified by the separation of the ester and glycerol layers after the reaction time. The heavy co-product, glycerol settles out and may be sold as it is may be purified for use in other industries (Gerpen, 2005).

1.3   Ultrasonic Transesterification

The latest technology used by many researchers to produce biodiesel is ultrasound technology or ultrasonic transesterification (Ji *et al*, 2006). Ultrasonic was proven to be an efficient method for the preparation of biodiesel by transesterification from oil. This method gives the shorter reaction time and less energy consumption than the conventional mechanical stirring method. It can produce almost 99% of biodiesel yield from oil. Ultrasound reduces the processing time from the conventional 1-5 hours processing batch to less than 5 minutes (Ji *et al*, 2006). It can also help to reduce the separation time from 10 to 5 hours. Moreover, the international standards for biodiesel ensures that important factors such as complete reaction, the removal of catalyst, the removal of alcohol, the absence of Free Fatty Acids (FFAs) and low sulfur content are adhere to.

1.4   Alkali-catalyzed Transesterification

Alkali-catalyzed transesterification process is more efficient and is less corrosive than acid-catalyzed process which makes it more applicable to industrial use. Alkali catalysts for transesterification process include metal hydroxides like sodium or potassium hydroxide, carbonates, and metal alkoxides. Increasing the concentration of catalyst in the mixture accelerate the reaction. The condition of activity of this catalyst is under anhydrous condition. However, this cannot be avoided as water is formed during the reaction between hydroxides and alcohols. The yield of alkyl esters is reduced as water hydrolyses the ester, forming soap. Soap forms an emulsion with glycerol making recovery of glycerol difficult (Zhang *et al*, 2002). This commonly catalyst used is sodium hydroxide due to its economical availability.

1.5   Acid-catalyzed Esterification (Pre-treatment Step)

When waste cooking oil (WCO) with more than 10%FFA is used, an acid catalyzed is preferred, but it requires more excess methanol, high pressure and high cost stainless steel equipment (Yong *et al*, 2002). In addition, the yield of product is low when the common sulfuric acid is used. Hence, a combine process with acid-catalyzed pre-treatment is developed to synthesize biodiesel from waste cooking oil. The first step would be the esterification of FFA with methanol by acid catalyst (sulfuric acid). The sulfuric acid is then drained before the homogenous alkali is introduced into the system to complete the transesterification.

To improve the acid catalyst pre-treatment process, the homogenous Lewis acid catalyst is used to synthesize biodiesel from waste cooking oil. However, the temperature used is quite high but the conversion is relatively low. So, the two steps catalyzed are adopted for the production of biodiesel. At the first step, sulfuric acid is introduced to catalyze the esterification reaction in which the FFAs in waste cooking oil

reacted with methanol. The sulfuric acid is insoluble in the oil is centrifuge from the liquid after the methanol recovery and could be reused. At the second step, sodium hydroxide is added to catalyze the transesterification reaction in which Triglyceride (TG) reacted with methanol. Without waste water, reusing the catalyst and low cost reaction tank, these two steps shows the potential application in the biodiesel fuel industry.

1.6 Research Background and Problem Statement

Biodiesel is renewable fuel that can be used to power up the conventional diesel engines with little or no modifications. Biodiesel is composed of mono-alkyl esters of fatty acid chain from animal fat or vegetable oils. Waste vegetable oil will reduce the cost of biodiesel production, and will give the world a way to reuse the total production cost of biodiesel results from the cost raw material (Krawczyk, 1996). This cost is significantly lowered when waste cooking oil is used.

Waste cooking oil presents additional problems compared to virgin oil. These problems will be identified, and reactor configuration will be chosen that will minimize the cost of the reactor. The most obvious problem associated with WCO is that WCO may contain dirt, charred food and other material that would otherwise be present in vegetable oil. These materials should be filtered out of the oil before it enters the reactor.

The most common method of biodiesel production is the transesterification of the oils. Transesterification is affected by the molar ratio of alcohol to triglycerides, the catalyst used, the reaction temperature, reaction time and the FFAs and water content of the oil used. There are three main catalysts that are frequently used to produce biodiesel, alkali-catalyzed, acid-catalyzed or enzyme-catalyzed. However, for some circumstances, when the FFAs contain in the oil is relatively high, two-steps

transesterification is needed. Therefore, the two-step catalyzed transesterification will be studied. The catalyst must be chosen first, because this affects the reaction temperature, time and the molar ratio of alcohol to WCO needed to complete the reaction.

1.7   Objective of the Research

The main objective of this study is to identify the effect of temperature and catalyst ratio to WCO to the yield, FFA content and the acid value of biodiesel, by two-steps catalyzed transesterification assisted by ultrasonic radiation.

1.8   Scope of the Research

To achieve all the objective stated above, the scope of the study is identified and listed as below;

- Raw material preparation
- Acid catalyst preparation
- Acid-catalyzed transesterification
- Alkali catalyst preparation
- Alkali-catalyzed transesterification
- Product purification
- Product analysis

In the raw material preparation step, WCO is first need to be filtered to remove the dirt and small particles might contain in WCO. The WCO is now ready to go through the first step acid-catalyzed transesterification. After the acid catalyst preparation, now the reaction can be run. After reaction is complete, the alkali catalyst is prepared so that

the second step of the experiment which is the alkali-catalyzed transesterification can be started. The product is then let to settle for one night before can be purify and going through the analysis.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction

Diesel-petroleum based has released problems such as toxicity, water, land and air pollution, fire risk, non-biodegradability and limited resources had opened a unique opportunity to produced new environmental acceptable fuel and lubricants derived from natural ester like vegetable oil. Reported that, the world production of   17 major oils and fats are over 100 billion tones and out this 79% are from vegetable oil (Hamm and Hamilton, 2002).

Research, development and application of vegetable based oil in industrial and automotive sectors are rapidly increasing. The attractive part of vegetable oil is they are neutral, non-toxic, biodegradable, and relatively non-polluting and derived from renewable raw material. During the last decade, due to strict government and environment regulation almost of all country in the world, there has been constant demand for environmentally friendly fuel (Rhee, 1996). Most of fuel originates from petroleum stock which is toxic to environment and difficult to dispose. Vegetable oils with high oleic acid content are considered to be potential candidates to substitute conventional mineral oil base fuel oils and synthetic esters.

Although biodiesel cannot entirely replace petroleum-based diesel fuel, there are at least five reasons that justify its development (Gerpen, 2005):

I. It provides a sufficient market for excess production of vegetable oils and fats.

II. It decreased, although will not eliminate, most country's dependencies on imported petroleum.

III. Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that generally CO_2 emissions were reduced by 78% compared with petroleum-based diesel fuel (Shehan *et al*, 1998).

IV. The exhausts emissions of carbon monoxide, unburned hydrocarbons, and particulate emissions from biodiesel are lower that with regular diesel fuel. Unfortunately, most emissions test has shown a slight increased of nitrogen oxides (NO_x).

V. When added to regular diesel fuel in an amount equal to 1-2%, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur diesel fuel, into an acceptable fuel.

In 1997, the production of biodiesel fuel was 550,000 tones in Europe, 10,000 tones in Malaysia and 9000 tones in North America. In 2000, the annual production of biodiesel in Europe was 1,210,000 tones. The production increased 2.2 times in three years (Kann *et al*, 2002).

2.2   **Characteristic of Biodiesel**

Biodiesel is well known as an alternative fuel for diesel engines that is chemically produced by reacting the virgin or used vegetable oil or animal fats with an alcohol such as methanol in order to accelerate the reaction (Leung *et al*, 2006).

Figure 2.1 shows an example of biodiesel. However, it colors cab be varied between golden and dark brown because it depends on the production feedstock. It is practically immiscible with water, has high boiling point and low vapor pressure. Typical methyl ester biodiesel has a flash point of ~150°C (300°F), making it rather non-flammable. Biodiesel has density of ~0.88g/cm^3, less than water. Biodiesel that unpolluted with starting material can be regarded as non-toxic. It also has similar viscosity with petro-diesel that produces from petroleum.

Figure 2.1: Example of biodiesel

Moreover, biodiesel is also clean burning diesel fuel replacement made from natural, renewable source, such as new and used vegetable oils or animal fats. It will run in any diesel engine with a little or no modification and can be mixed with regular diesel fuel in any ratio. Biodiesel is non-toxic and biodegradable.

2.3 Feedstock

All natural fats and oils are esters of fatty acids and glycerol. These are known as Glyceride or Triglyceride (TG). With few exceptions, the carboxylic acid (fatty acid) from which the fats and oils are derived, are all straight-chain compound ranging in size from 3 to 18 carbons.

2.3.1 Waste Cooking Oil

It is estimated that some 20 million tones of oils and fats are used for cooking around the world, with food industries is the major user of the cooking oil. Industrial of cooking or frying requires oils and fats of good quality and nutritive value. Palm oil has this entire requirement as it characteristic with no unpleasant odors, high resistance to oxidation and high content of nutrient from its fatty acids composition (Loh *et al*, 2006).

In cooking, the hot oil serves as the medium of the heat exchanger where heat is transferred to the food being cooked. Eventually, cooking leads to darkening the oil and palm oil no exception. These due to oil degradation where the heat, air and moisture to which oil is exposed to lead to its polymerization, oxidation, and hydrolysis (Gebhardt, 1996). The oil darkens from formation of polar arterials such as phenolic minor component oxidation products and color compounds (Subramanian *et al*, 2000). The indicators to indicate poor oil quality are elevated FFA, high Total Polar Material (TPM), and change of color, high foaming property, low smoke point, low iodine value and increasing n viscosity. These entire characteristic indicates that the oil is no longer acceptable for health reason though need to be exposed (Pantzaris and Ahmad, 1998).

Waste oil used as a direct source of energy must undergo basic treatment to remove water and particulates before it is fit for use as fuel. Currently, the majority of the waste oil is used as fuel by industries such as power generation, road-stone coating

and cement manufacturing. Higher levels of pre-treatment can removed water, sediment, heavy hydrocarbons, metals and additives. The oil product from these processes have similar properties and emission levels to virgin oils, but cost and volume constraints mean that these do not tend to compete directly.

An estimated 50,000 tones of used cooking oil, both vegetable oil and animal fats are disposed year on year in Malaysia without treatment (Loh et al, 2006). This creates negative impact on the environment. This waste can be used if they are purified. Realizing that the used of waste cooking oil has many potential especially to be converted to biodiesel, the industry begun rapidly that give a lot of opportunity to enhance the quality of biodiesel production.

2.3.2   Other Possible Feedstock

The options of the TG choice are many. Among the vegetable oils sources are soybean, canola, palm and rape. Animal fats are products of rendering operations. They include beef tallow, lard, poultry fat, and fish oil. Yellow greases can be mixture of vegetable and animal source (Gerpen *et al*, 2004). Furthermore, there is other less desirable, but also less expensive TG sources such as brown grease and soapstock. The type of biodiesel process used and the yield of fuel the process are affected by the pg the FFAs content. The other contaminant present can also affect the extent of feedstock preparation necessary to use a given reaction chemistry.

FFAs presence with much higher level in animal tallow and recycled (yellow) grease. Yellow grease is approximately limited up to 15% FFAs and is traded commodity that is typically processed into animal and pet food. Trap greases come from trap under kitchen drain and these greases can contain between 50% and 100% FFAs (Gerpen, 2004). Recently there is no market for these greases at this time and most are land-filled. Trap grease is not yet used for biodiesel production and may have

some technical challengers that have not be fully resolved such as difficult to break emulsification (gels), fine silt that will cause equipment wear, high water contents, and very strong color and odor bodies that affect biodiesel and glycerin products.

United State is the largest supplier of soybean oil while Europe is the largest supplier for rapeseed oil. Most of the oils are used in the food production but the do require a several considerable processing before they are considerable as edible. Fully refined oils are also known RBD oil (refined, bleached, and deodorized). Crude soybean oil typically contains 1.5% to 2.5% phosphatides, 1.6% unsapoifiable matter including 0.15% to 0.21% tocopherol (Vitamin E) and 0.3% to 0.7% FFAs. These compounds contribute colors, odors and strong flavors to the oil that are usually undesirable for cooking. Some of the compound also contributes to poor storage stability (Gerpen, 2004).

2.3.3 Environmental Issue

It is illegal to dispose of waste oil down drains although it is biodegradable and far less of problems than mineral oil, it can solidify, blocking drainage systems and pollute sewage systems and waterways. Nowadays, only a small percentage of waste cooking is currently recycled. Conversion to bio-diesel therefore offers a good solution. It produces less environmental damage than ordinary diesel and is less harmful to human health while no internal combustion engine can ever be regarded as clean burning and term long goal must be to use fuel cells powered by hydrogen produced from renewable sources or other clean alternative, in the short term it is important to curb emissions from existing vehicles.

2.4   Feedstock Quality Issues

Generally, the closer a feedstock to contain pure TG, the easier it will be converted to biodiesel and the cost also will be a little higher (Gerpen, 2004). However, using the lower cost of feedstock which contains impure TG, the more difficult and more expensive procedures and equipments are needed to convert the biodiesel. Biodiesel may contain many possible contaminants such as water, FFAs, particles and also phospholipids. There is the potential of this contaminant to effect the quality of the final biodiesel product.

2.4.1   Water

It is important to kept water out of biodiesel production process because it can increase soap production and measurably affect the completeness of the transesterification reaction. Water can be removed by several steps. Heating to break any emulsion between the water and oil and then allowing the water to settle to the bottom can remove water. Other heating process is by heating the oil under pressure and then spraying into a vacuum chamber can bring the water content to a very low level. In addition, centrifuges can also be used to separate water and oil. Water not only impact on the transesterification reaction but also can impact the effective cost of the feedstock (Gerpen, 2004).

2.4.2   Solid

Usually, feedstock used for the biodiesel such as WCO need to be filtered to ensure no particles enter processing scheme. This can be particular problem with recycled product such as waste cooking oil which typically contains fine particles that may require a fine filter (Gerpen, 2004).

2.4.3   Free Fatty Acid

The impact of FFAs on the biodiesel production has been discussed critically elsewhere. FFAs can impact the production of biodiesel by deactivating the catalyst, creating the soap and also releasing water when they are converted into biodiesel. Biodiesel normally produced by alkali catalyst with specification for total glycerol will usually have 0.2%-0.3% FFAs regardless of the initial acid content of the feedstock. The alkali catalyst also serves as a caustic stripper and removes the FFAs by converting them to soap that are removed during washing (Gerpen, 2004).

2.4.4   Sulfur

One of the advantages of biodiesel is that it contains very low levels of sulfur. United States legislation has states that sulfur level for petroleum-based diesel fuel must drop from 500ppm to 15ppm. Most biodiesel is already below this level. However, some sample of biodiesel from yellow grease and animal fats has shown sulfur level as high as 40-50 ppm. The source of this sulfur is not fully understood, but may be originating from food preservatives, proteins, and the hair on the animal hides and in those cases where poultry are being processed, from chicken feet (Gerpen, 2004).

2.5 Transesterification

In the transesterification, TG reacts with an alcohol, generally methanol or ethanol to produced ester and glycerol. Catalyst is added to make it possible. General equation of transesterification has been illustrated in Equation 1.1.

Figure 2.2 shows the overall process of transesterification which is normally series of three consecutive steps which are reversible reactions. In the first steps diglycerides, are obtained from triglycerides. From diglycerides, monoglycerides are then produced. In the last step, from monoglycerides, glycerol is formed. In all these reactions, esters are produced. The excess of alcohol is usually more appropriate to improve the reaction towards the desired final product (Marchetti *et al*, 2007).

Trig ycerides (TG) + R'OH $\underset{k2}{\overset{k1}{\rightleftharpoons}}$ Diglycerides (DG) + R'OOR₁

Diglycerides (DG) + R'OH $\underset{k4}{\overset{k3}{\rightleftharpoons}}$ Monoglycerides (MG) + R''OOR₂ (2.1)

Monog ycerides (MG) + R'OH $\underset{k6}{\overset{k5}{\rightleftharpoons}}$ Glycerol (GL) + R''OOR₃
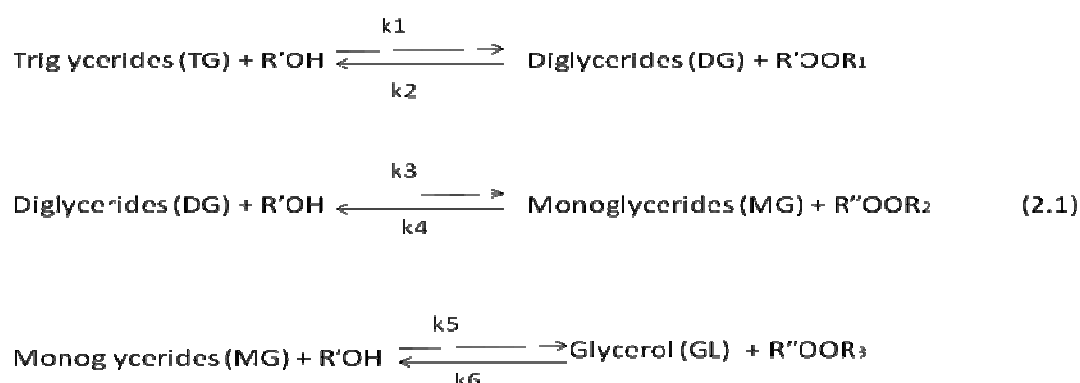
Figure 2.2: Consecutive steps of transesterification

2.5.1 Ultrasonic Transesterification

When the reaction is carried out via ultrasonic wave, transesterification is efficiently activated, with short time of reaction. As the result, a drastic reduction in the quantity of by-product and a short separation time is obtained and at the same time can reduce the energy consumption (Mandar et al, 2007). Biodiesel is primarily produced in the batch processes, in which a basic homogenous catalyst is introduced to catalyze

the reaction. Ultrasound allows for the continuous processing. Besides reducing the reaction time, ultrasonication also reduces the separation time compared to the conventional agitation method. When using the ultrasonication, the amount of excess alcohol required can be reduced. Most commonly, the sonication is performed at an elevated pressure (1 to 3 bar, gauge pressure) using a feed pump. Industrial biodiesel processing does not require much ultrasonic energy. In addition, ultrasonication is an effective means to increase the reaction speed and conversion rate in the commercial processing.

Figure 2.3 shows the typical result of the transesterification of rapeseed oil with potassium hydroxide studied by Carmen Stavarache. The blue line is the control sample, was exposed to intense mechanical mixing while the red line represent the sonicated sample with respect to the volume ratio, catalyst concentration and temperature. The horizontal axis shows the time after mixing or sonication, respectively. The vertical axis shows the volume of glycerin that settled at the bottom. This is the simple means of measuring the reaction speed. In this diagram, the sonicated sample (red line) reacts much faster than the control sample (blue line).
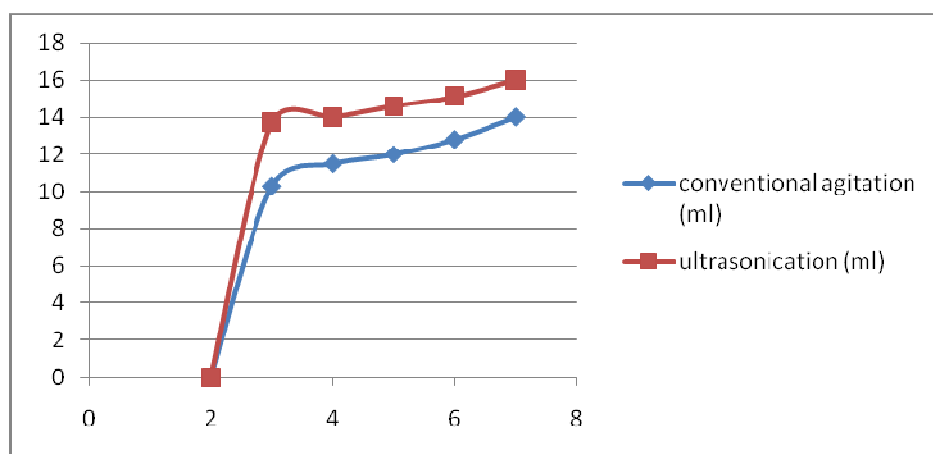
Figure 2.3: Result of rapeseed oil transesterification with potassium hydroxide using conventional agitation and ultrasonication

2.5.2   Ultrasound

Ultrasound is the process of propagation of the compression (rarefaction) waves with frequencies above the range of human hearing (above 15-16 KHz) (Shutilov, 1998). Typical commercial ultrasonic instruments known as "probe system" have a piezoelectric transducer powered by a generator that couples energy into chemical reaction by means of horn or velocity transformer. The converter vibrates in a longitudinal direction and transmits this motion to the horn tip immersed in the solution, causes cavitation

Cavitation implies the opening of holes in liquids. Depending on the circumstances, this holes can be filled either by gases already dissolved in the liquid, in which case the phenomenon is sometimes called as gaseous cavitation or pseudocavitation, or, in the absence of such dissolved gases, by the vapor of the liquid itself (vapor cavitation or true cavitation). It is quite clear that the conditions for the appearance of these two kinds of cavitation can be quite different.

The applications of ultrasound in chemical processing enhance both the mass transfer and chemical reactions, this science called as sonochemistry. It offers the potential for shorter reaction cycles, cheaper reagent and less extreme physical conditions, leading to less expensive and perhaps chemical producing smaller plant. Existing literature on sonochemical reacting system is chemistry-intensive, and applications of this novel mean of reaction in remediation and pollution prevention seems almost unlimited. For example, environmental sonochemistry is a rapidly growing area that deals with the destruction of organic in aqueous solutions. However, some theoretical and engineering aspects are not yet fully understood (Adewuyi, 2001).

The cavitation phenomenon is also accompanied by the emission of visible radiation, which is given the name sonoluminescense. Some researchers take advantage

of this phenomenon doing estimation of the bubbles collapse conditions from the intensity of the light emitted by the system, this area are being explored too.

Another important phenomenon called "acoustic streaming", has been identified when ultrasound is applied to liquid systems. It consists mainly of a hydrodynamic vertical flow near the sound source and its intensity depends on the ability of the medium to absorb the acoustic energy (usually the energy absorbed by the medium generates an increase in temperature). This ability can be modified by the presence of the electrolysis salts.

Other undesired effect of the sonochemical processes are erosion of emitter and reactor surface, creation of noise and acceleration of by-product formation (Loning et al, 2002). For the ultrasound agitations case , ultrasound application generate shockwaves when they collapse by implosion, forcing the oil and methanol to join.

2.6   Acid-catalyzed

This process uses a strong acid such as sulfuric acid to catalyze the esterification of the FFAs and transesterification of the TG. Fortunately, the reaction does not form any soaps because no alkali metal are present. The esterification reaction of the FFAs to alcohol esters are relatively fast, proceeding significantly to completion in one hour at 60°C. However, the transesterification of the TG is very slow, taking several days to complete. Heating to 130°C can greatly accelerate the reaction but the time of the reaction will still be 30-45 minutes. Another problem with acid catalyst is that water production from the following reactions stay in the mixture and ultimately stops the reaction, usually well before reaching completion (Gerpen, 2004). For these reasons, it is determined that alkali-catalyzed reactions are more cost effective and practical.

2.7   Alkali-catalyzed

One limitation to alkali-catalyzed process is its sensitivity to the purity of reactant; especially the alkali system is very sensitive to both water and FFAs. The presence of water, under alkaline condition, may cause ester saponification. Also, FFAs can react with the alkali catalyst to produce soap and water. The resulting soap can causes the formation of emulsions. These circumstances give rise to a consumption of the catalyst and, in addition, cause difficulties in the recuperation and purification of the biodiesel (Encinar *et al*, 2007).

Alkali-catalyzed process is more efficient and less corrosive than acid-catalyzed process which makes it more applicable to industrial use. Alkali catalyst for transesterification process includes metal hydroxides like sodium or potassium hydroxide, carbonates and metal alkoxides. Increasing the concentration of the catalyst in the mixture accelerates the reaction. The condition of activity of this catalyst is under anhydrous conditions. However, this cannot be avoided as water is formed during the reaction between hydroxides and alcohol. The yield of alkyl ester is reducing as water hydrolyses the esters, forming soap. Soap forms an emulsion with glycerol making recovery of glycerol difficult (Zhang *et al*, 2002). The commonly catalyst used is sodium hydroxides due to its economical availability.

2.8   Choice of Alkali Catalyst

The most three regular used alkaline catalyst are sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium methoxide (CH_3ONa).

2.8.1   Amount of Catalyst

The three catalyst (KOH, NaOH, and CH$_3$ONa) exhibit the same trend on the conversion of the TG to esters but different amount of catalyst will be required to achieve the same conversion (Leung *et al*, 2006). Table 2.1 shows the maximum ester content of the biodiesel product was reached at 1.1, 1.3, and 1.5wt% of the catalyst concentration for NaOH, CH$_3$ONa, and KOH respectively. The amount of NaOH used was smaller than those of KOH and CH$_3$ONa for the same mass feedstock oil, since NaOH has the smallest molar mass (40 g/mol), followed by CH$_3$ONa (54 g/mol), and KOH (56 g/mol). However, in term of concentration, CH$_3$ONa was about 10% lesser than NaOH and KOH.

Table 2.1: Comparison of different types of catalyst in the transesterification of WCO (temperature of 70°C, reaction time of 30 minutes, methanol/oil ratio of 7.5:1)

	Concentration of the catalyst (wt%, by weight of crude oil)	Ester content (wt%)	Product yield (wt%)
NaOH	1.1	94	85.3
KOH	1.5	92.5	86
CH$_3$ONa	1.3	92.8	89

As shown in Table 2.2, the biodiesel yield with NaOH and KOH as catalyst were lower than CH$_3$ONa. This happen during the preparation of the catalyst NaOH or KOH is added and dissolved in the anhydrous methanol forming sodium or potassium methoxide together with small amount of water according to the following following equilibrium equation:

$$CH_3OH + NaOH \text{ (or KOH)} \rightarrow CH_3ONA \text{ (or } CH_3OK) + H20 \qquad (2.1)$$
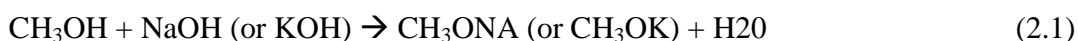
The water in the reaction system predominantly reacts with oils (TG) and the Na$^+$ (or K$^+$) to form sodium (or potassium) soaps. This is the saponification reaction of TGs leading to the loss of TGs and hence reduction in final product yields. On the other

hand, the pure CH_3ONa catalyst only dissociates into CH_3O^- and Na^+ without forming any water as side product in the reaction that will cause a drop in product yield.

2.8.2 Separation of Intermediate Product

The three catalyst mentioned before produced the different physical properties of the final product. Figure 2.4 illustrated the state of final product mixture after let been settled overnight, produced by transesterification WCO by using these three catalysts (Leung *et al*, 2002).
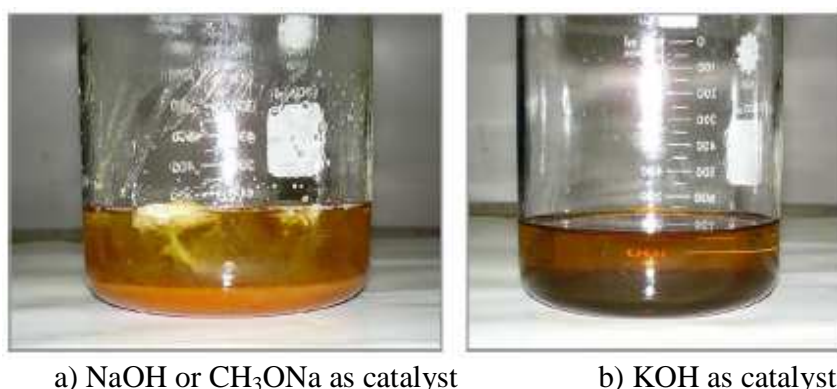
a) NaOH or CH_3ONa as catalyst b) KOH as catalyst
Figure 2.4: State of final product mixture settled overnight with different catalyst

For NaOH and CH_3ONa as catalyst, after settling overnight the product mixture separated into two layer which are crude ester layer in liquid state at the top layer and glycerol layer at the bottom (Figure 2.4a). As a fact, glycerol is a viscous liquid at ambient temperature and pressure. When more and more solid soaps sank to the bottom, a mixture of glycerol and soap in solid state was formed after settling overnight. Thus, the separation of the crude ester layer from the bottom glycerol layer had to be decanted or drawn out from the bottom of the separation unit, and could not flow out directly from the bottom of the separation unit. Different from the two other catalysts, for KOH catalyst, the product mixture separated into two liquid layers after settling overnight, crude ester layer n top and glycerol layer at the bottom (Figure 2.4b).

Due to the fact that potassium soap is softer than sodium soap, its residues which formed during the transesterification reaction, sink onto the glycerol layer at the bottom but suspend in the crude ester layer, thus resulting in a viscous glycerol layer. Therefore, for the separation of the ester layer from the glycerol layer in industrial production, using KOH as catalyst is undoubtedly more convenient and simple in the process as well as apparatus than using NaOH or CH$_3$ONa as catalyst since the glycerol layer in liquid state can be removed easily by direct out-flowing from the bottom of the separation unit (Leong *et al*, 2006). Due to this reason, KOH is commonly used for producing biodiesel using waste recycled oil feedstock.

2.8.3 Cost of Catalyst

Table 2.2 is used to compare the unit price of three catalysts that eventually will be choosing to use in this study. As can be observed, NaOH is much cheaper than the other two catalysts in the market. Comparing the performance and cost of three catalysts, NaOH was found to be more superior to CH$_3$ONa and KOH due to its lower price and smaller amount catalyst concentration neither enhance further conversion no raises the ester content (Leong *et al*, 2006).

Table 2.2: unit prices of catalyst as 2005

	Naoh (purity 99%)	KOH (purity 92%)	CH$_3$ONa (purity 99%)
Price (us$/ton)	400	770	2300

2.9   Acid-Catalyzed Pre-Treatment

When waste cooking oil with more than 10%FFAs is used, an acid catalyzed is preferred, but it requires more excess methanol, high pressure and high cost stainless steel equipments. In addition, the yield of the product is low when the common sulfuric acid is used. Hence, a combine process with acid catalyzed pre-treatment is developed to synthesize biodiesel from waste cooking oil.   The first step would be the esterification of FFAs with methanol by acid catalyst which is acid sulfuric (Yong *et al*, 2002). At the second step, sodium hydroxide is added to catalyze the transesterification reaction in which TG is reacted with methanol. Without waste water, reusing the catalyst and low cost of reaction tank, these to steps shows the potential application in fuel industry.

The esterification pre-treatment step would convert the FFAs to esters (Canaki et al, 2006). Figure 2.7 shows the esterification process. The acid catalyst and methanol should be added, allowed to react, and then settled.

$$
\underset{\text{FFAs}}{\text{HO}-\overset{\overset{\textstyle O}{\|}}{\text{C}}-\text{R}} + \underset{\text{Alcohol}}{\text{CH3OH}} \xrightarrow{\text{Acid catalyst}} \underset{\text{Esters}}{\text{CH3O}-\overset{\overset{\textstyle O}{\|}}{\text{C}}-\text{R}} + \underset{\text{Water}}{\text{H2O}} \qquad (2.2)
$$
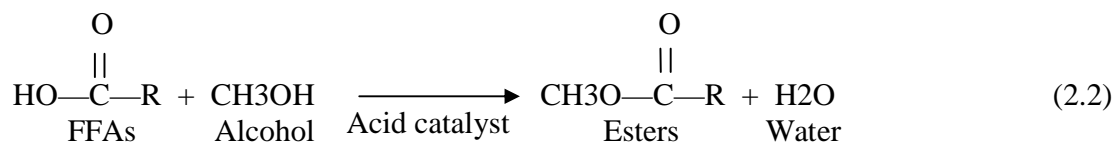
Figure 2.5: Esterification of FFAs to ester using methanol and acid catalyst

The mixture of water and methanol can then be removed. Once the mixture is removed and the oil can go on the transesterification step. It is best to carry this reaction out in at least two stages this way, as water is a by-product of the esterification reaction, and the addition of water causes the reaction to become slow. In addition the presence of water in the oil can make the transesterification reaction turn into a saponification reaction, and unwanted gels and emulsion can form with the biodiesel. After the pre-treatment step, sodium hydroxide catalyst and methanol can be added to the oil and the transesterification reaction can begin.

2.10   Economical By-Product

Luckily, there are some economical aspects that can make biodiesel profitable aside from the sale of fuel. The by-product of biodiesel production, glycerin, has high market value. Glycerin which is formed through the transesterification process has the potential to be worth more than the actual biodiesel fuel. Approximately, 10% of the mixture after transesterification will be glycerin which is leading ingredient is soap. With the increasing amount of glycerin that will become readily available, researchers have been investigating different uses for the product.

CHAPTER III

METHODOLOGY

3.1   Introduction

The overall methodology involved all the steps in achieving the biodiesel. The whole study is divided into four major steps, which are

   I.   Raw material preparation.
  II.   Acid treatment (acid-catalyzed esterification).
III.   Alkali-catalyzed transesterification.
IV.   Product analysis.

The flow system of this study is shown in Figure 3.1

START

Equipment set-up, experimental procedures and safety study

Literature review

Catalyst preparation

Experiments

WCO filtration

FFAs characterization

Acid treatment

Alkali-catalyzed transesterification

Product purification

Product

Product analysis

END
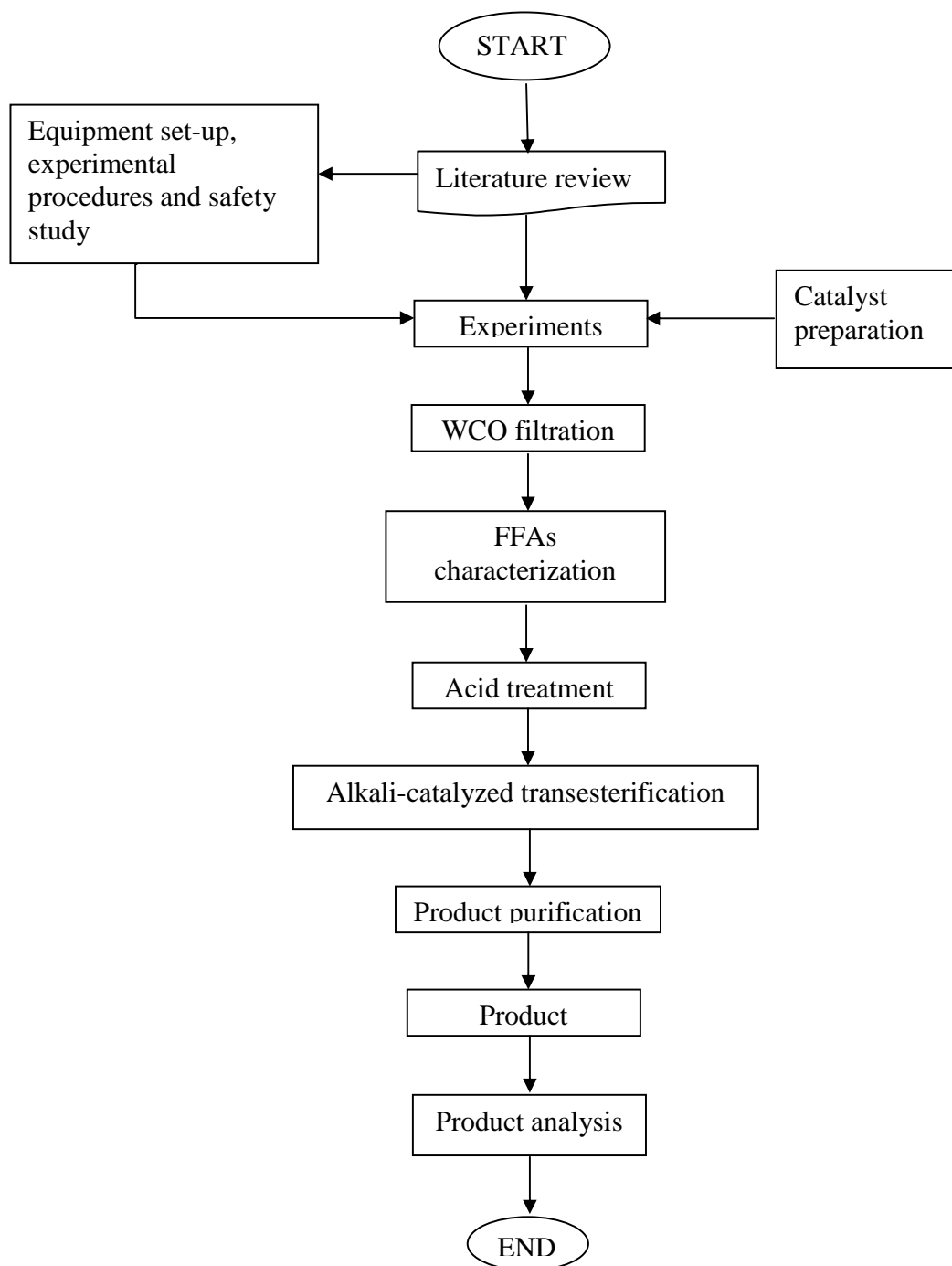
Figure 3.1: Process Flow System

3.2   Equipment

Reactions are carried out in a batch reactor with help of ultrasonic wave to fasten the reaction and reducing the time consuming. For acid esterification step, sample is poured into the reactor at selected temperature.   In the alkali transesterification step, sample at certain amount is placed in the beaker and then put in the ultrasonic batch reactor. Figure 3.2 shows the ultrasonic batch reactor that is used during those experimental works.
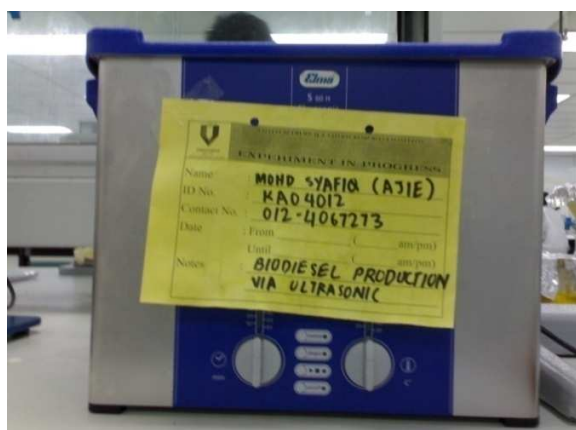
Figure 3.2: Ultrasonic Batch Reactor

3.3   Experimental procedures

3.3.1   Filtering

The raw waste cooking oil is filtered by using filter bed to remove any food particles might contain which might dog up the fuel line. Figure 3.3 shows the filter bed that is used during the experimental works progress.

Figure 3.3: Filter Bed

3.3.2 Material Preparation

- Raw waste cooking oil preparation
  - Raw waste cooking oil is filtered to remove the particles and dirt might contain.
  - FFAs amount in the raw waste cooking oil is determine by titration.

- Acid catalyst preparation
  - 2%wH_2SO_4 / wWCO is prepared.
  - 2% of WCO weight is calculated and taken as H_2SO_4 weight.
  - The calculated weight is then weighed by weighting scale.

- Alkali catalyst preparation
  - Catalyst ratio to waste cooking oil of 0.2, 0.4, 0.6, 0.8 and 1%wtNaOH / wWCO is first calculated.
  - The calculated weight is then will be weighted by weighing scale.

3.3.3 Acid-Catalyzed Esterification

The FFAs is first converted to ester in using an acid catalyst that is acid sulfuric (H_2SO_4). This step is called as pre-treatment step. In the pre-treatment step, WCO at calculated amount is put into the ultrasonic batch reactor and pre-heated at 60°C in order to accelerate the reaction rate. At the same time, methanol and catalyst NaOH are added in a beaker to allow them to mix before added into the WCO in the ultrasonic batch reactor. NaOH does not readily dissolved into methanol, the best way to assure them to mix well. When the particles of NaOH cannot be seen, the methoxide (alcohol and catalyst mixture) is ready to be added. The reaction took placed for 4 hours, at the temperature of 95°C. In this step, molar ratio of methanol to waste cooking oil is 10:1 and the ratio of acid catalyst to waste cooking oil is 2%wtH_2SO_4 / wWCO. Table 3.1 shows the molar ratio and the weight of all the substances needed to run this part of experiment.

Table 3.1: Weight of Substances needed during the acid catalyzed esterification (Refer Appendix A)

Molar ratio of methanol: WCO	10:1
Weight of WCO (g)	100
Weight of methanol (g)	32.04
Catalyst weight percent (wtH_2SO_4 / wWCO)	2%
Catalyst weight (g)	2

3.3.4 Alkali Catalyzed Transesterification

After the acid pre-treatment, esterifies waste cooking oil is gone through the alkali-catalyzed transesterification. In order to speed up the reaction, the oil is pre-heated at 60ºC. Heating with electrical element such as heating plate is usually the easiest way to bring the oil at the required temperature. Methanol and catalyst

In this step, the reactor is initially filled up with water as the medium of the ultrasonic wave. The preferred amount of esterifies waste cooking oil which has been through the acid catalyzed pre-treatment is weighed in a beaker. The oil is placed in the ultrasonic batch reactor with its related equipment and will be heated to a predetermined temperature. The catalyst is added to the ultrasonic batch reactor. The reaction is timed as soon as soon as the catalyst-methanol mixture is added to the reactor and continued for a fixed time. The mixture then transferred into a beaker to allow the glycerol to separate from the crude ester layer by gravity for one night.

The reaction was investigated step by step. The best value of each parameter involved in the process was determined while the rest were kept constant. After each best value was attained, the value was adopted for the investigation of the best value of the next parameter. The alkali-catalyzed transesterification part is divided into two major parts which are:

I.   Phase I

The purpose of phase one is to investigate the effect of temperature on biodiesel yield, FFA content and also the acid value. The fixed and the manipulated variables of this phase is shown in Table 3.2(a) and Table 3.2(b) respectively.

Table 3.2: Fixed and manipulated parameter for alkali catalyzed transesterification (Phase I)

(a): Fixed Parameter

Parameter	Value
Catalyst weight percent (%wtH_2SO_4 / wWCO)	2
Reaction time (hr)	1
Ultrasonic wave (MHz)	32
Settling time	1 night
Agitator speed (rpm)	150

(b) Manipulated Parameter

Sample	Temperature (ºC)
1	40
2	50
3	60
4	70
5	80

II.   Phase II

The purpose of phase two is to investigate the effect of catalyst weight percent on biodiesel yield, FFA content and also the acid value. The fixed and the manipulated variables of this phase is shown in Table 3.3(a) and Table 3.3(b) respectively. The calculated weight of various catalyst weight percent is shown in Table 3.4.

Table 3.3: Fixed and manipulated parameter for alkali catalyzed transesterification (Phase II)

(a): Fixed Parameter

Parameter	Value
Temperature	Best temperature from Phase I
Reaction time (hr)	1
Ultrasonic wave (MHz)	32
Settling time	1 night
Agitator speed (rpm)	150

(b) Manipulated Parameter

Sample	Catalyst weight percent (%wtNaOH / wWCO)
1	0.2
2	0.4
3	0.6
4	0.8
5	1.0

Table 3.4: Weight of alkali Catalyst (Refer Appendix B for the manual calculation)

WCO(g)	%wt NaOH/ wWCO	Weight NaOH (g)
100	0.2	0.2
100	0.4	0.4
100	0.6	0.6
100	0.8	0.8
100	1	1

3.3.5   Gravity Settling

The product of reaction were allowed to settled overnight producing two distinct liquid phases which are crude ester phase at the top and glycerol at the bottom. These two phases is separated to collect the crude ester layer which is the main product of the study. Figure 3.4 shows the layers formed after an overnight gravity settling. During settling, the catalyst residues were kept in the mixture and experience a long settling time together with the mixture so that a better conversion was obtained due to this extended reaction time. The reaction is completely stopped when washing process is finished due to the complete removal of catalyst residue in the product mixture. Therefore, in order to compare the product yield under different reaction conditions, the product mixtures were allowed to settle at for the same period and washed with the same washing time.

Figure 3.4: Layers formed after an overnight gravity settling

3.3.6   Methanol Recovery

After the settling time, the glycerol layer and the methyl ester layer is separated. The methyl ester layer (the upper part) is put in the rotary evaporator to remove the remaining methanol in the methyl ester. The temperature of the rotary evaporator was set at 65-67°C, above than the methanol boiling point which is 64.5°C. Figure 3.5 shows the process of methanol recovery.

Figure 3.5: Methanol recovery

3.3.7   Washing

After methanol recovery, the methyl ester will be washed with warm deionized water for several times until wash water becomes clear. The methyl ester or biodiesel needs to be washed so that it can remove the residue methanol and soapy deposits. The biodiesel and wash water will be foaming two layers and can be separated. The amount of wash water is equal to the amount of oil, and can be drained throughout the washing process. At this point, the biodiesel is usually a pale yellow color. This can be seen in the Figure 3.6.

Figure 3.6: Biodiesel after 1 hour washed with hot water

3.4   Product Analysis

Temperature is the first parameter studied. The effect of reaction temperature on biodiesel methyl ester formation of the waste cooking oil was investigated with its temperature ranging from 40 to 80°C. The operation condition of the whole experiment was fixed at: catalyst weight percent of 1%wtNaOH / wWCO, reaction time of 1 hour, and mol ratio of methanol to oil of 6:1.

To determine the effect of catalyst weight percent, the transesterification reaction was carried out in the best condition obtained from the previous phase. The experiments was conducted at the best temperature investigated from the first phase, reaction time of 1 hour, and mol ratio of methanol to oil of 6:1 and the catalyst weight percent ranging from 0.2 to 1%wtNaOH / wWCO.

3.4.1 Biodiesel Methyl Ester Yield

Product yield is defined as the weight percentage of the final product (purified oil) relative to the weight of oil at the start. Equation 3.1 shows the relationship between before and after react oil:

$$\text{product yield} = \frac{\text{weight of biodiesel}}{\text{weight of raw WCO}} \qquad (3.1)$$

Graph of product yield versus temperature is illustrated for the study purposed. The best temperature is then determined.

3.4.2 FFA Content and Acid Value of Biodiesel Methyl Ester

The FFA content in the biodiesel methyl ester is determined by titration. % of FFA is expressed as equivalent oleic acid which is assumed to be an average of fatty acid. In this titration, propan-2-ol is used to dissolve the 10ml of sample oil. Universal indicator, phenolphthalein, is used to indicate the pH of the mixture. The amount of 0.099 M NaOH is required to neutralize the dissolved oil is determined. Figure 3.7 shows the flow of the titration process and procedures.

10g of oil is exactly measured using graduated

$$\downarrow$$

Dissolve the measured oil into 50ml of propan-2-

$$\downarrow$$

5 to 6 drops of phenolphthalein is added to observe the

$$\downarrow$$

NaOH solution is added drop by drop until the mixture turned into pink or light purple.

$$\downarrow$$

The number of milliliters (ml) of NaOH is note down.
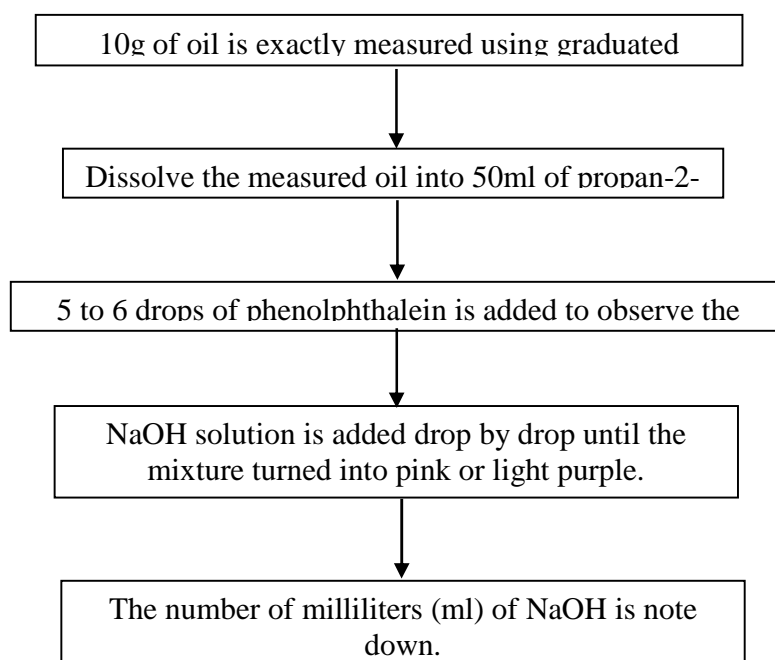
Figure 3.7: Flow of the titration process and its procedures

The FFA content and the acid value is calculated by using Equation 3.2 and 3.3

$$FFA = \frac{25.6 \times N \times (A-B)}{\text{weight sample}}$$
$$= \frac{mgNaOH}{g} \qquad (3.2)$$

Where; N = NaOH molarity

(A-B) = volume of NaOH used to neutralize the dissolved oil

$$Acid\ value = \frac{56.1 \times N \times (A-B)}{\text{weight sample}}$$
$$= \frac{mgNaOH}{g} \qquad (3.3)$$

Where; N = NaOH molarity

(A-B) = volume of NaOH used to neutralize the dissolved oil

3.4.3 Preparation of Sodium Hydroxide 0.099M

Figure 3.8 and 3.10 illustrate the procedure of preparing the NaOH 0.099M and the procedures of standardizing the NaOH 0.099M.

```
┌─────────────────────────────────────┐
│   4g of sodium NaOH is weighed.      │
└─────────────────────────────────────┘
                  │
                  ▼
┌─────────────────────────────────────────┐
│ 1L distilled water is added in a volumetric flask. │
└─────────────────────────────────────────┘
                  │
                  ▼
┌─────────────────────────────────────────────────────┐
│ 4g NaOH is added into the volumetric flask contain 1L of │
│    distilled water and stirred until both are well mixed. │
└─────────────────────────────────────────────────────┘
```
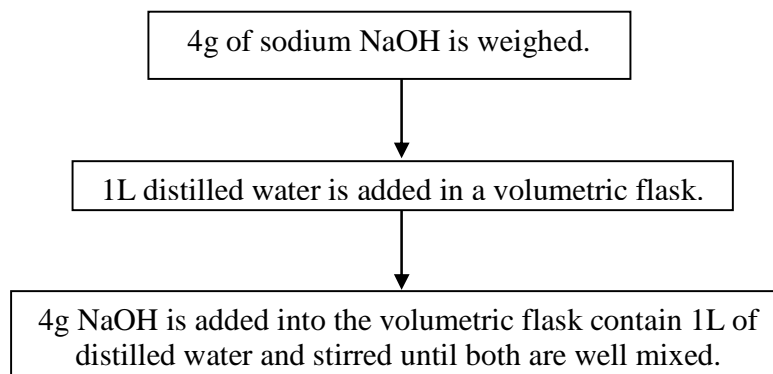
Figure 3.8: Procedure of preparing the 0.099M NaOH
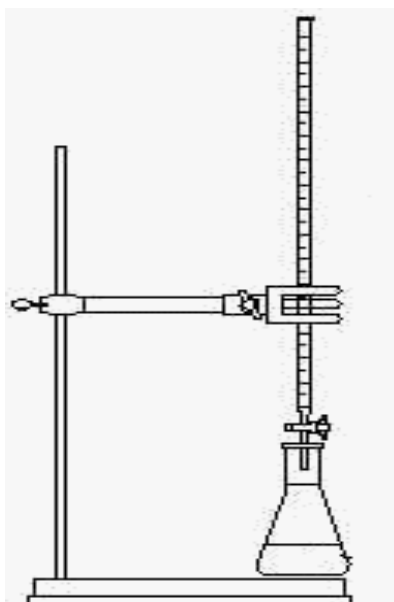
Figure 3.9: Apparatus set up for titration

```
┌──────────────────────────────────────────────────────────┐
│   Potassium hydrogen phthalate is dried at 120ºC for 2    │
└──────────────────────────────────────────────────────────┘
                            │
                            ▼
        ┌──────────────────────────────────────────┐
        │   4g of Potassium hydrogen phthalate is   │
        │   weighed and put into a conical flask.   │
        └──────────────────────────────────────────┘
                            │
                            ▼
    ┌──────────────────────────────────────────────────┐
    │  50ml water and 5 drop of phenolphthalein is added │
    └──────────────────────────────────────────────────┘
                            │
                            ▼
    ┌──────────────────────────────────────────────────┐
    │  The conical flask that contain that mixture is    │
    │  placed on hot plate and stirred until mixture is  │
    │  well mixed.                                       │
    └──────────────────────────────────────────────────┘
                            │
                            ▼
    ┌──────────────────────────────────────────────────┐
    │  The conical flask that contain that mixture is    │
    │  placed on hot plate and stirred until mixture is  │
    │  well mixed.                                       │
    └──────────────────────────────────────────────────┘
                            │
                            ▼
    ┌──────────────────────────────────────────────────┐
    │  The conical flask that contain that mixture is    │
    │  placed on hot plate and stirred until mixture is  │
    │  well mixed.                                       │
    └──────────────────────────────────────────────────┘
```

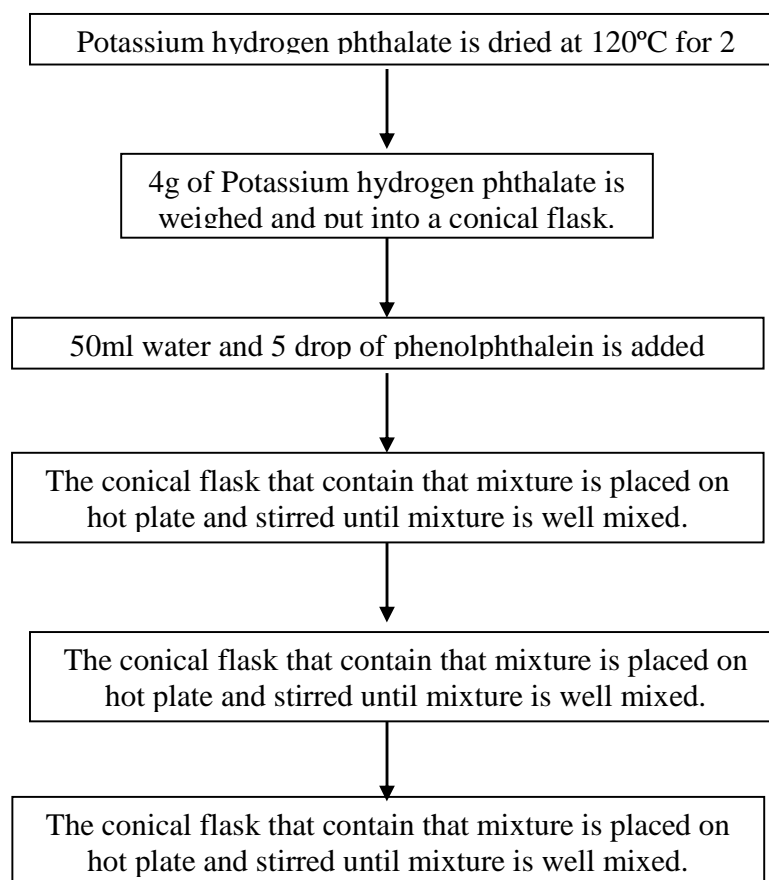**Figure 3.10:** Procedures of standardizing the NaOH 0.099M

The molarity of the NaOH is then calculated by Equation 3.4

$$\text{molarity of NaOH} = \frac{M \times 1000}{V \times 204.2} \qquad\qquad (3.4)$$

Where;   m = mass of phthalate taken, in gram

      V= volume of NaOH in ml

CHAPTER IV

RESULT AND DISCUSSION

4.1   Introduction

This study is carried out to investigate the effect of temperature and catalyst weight percent to the biodiesel yield, FFA content and also the acid value by two-step catalyzed transesterification of waste cooking oil, assisted by the ultrasonic radiation.

4.1.1   Biodiesel Yield

The mass of the biodiesel yield is determined by weighing the after washed methyl ester. The percent yield is calculated by using the equation 3.1; the biodiesel yield is calculated and recorded.

$$\text{Product yield} = \frac{\text{weight of biodiesel}}{\text{weight of raw WCO}} \times 100$$

(A-B) = volume of NaOH used to neutralize the dissolved oil

4.1.2 FFA content

FFA content in the biodiesel is checked by titration. The volume of NaOH used to neutralize the biodiesel is noted. The FFA content is calculated by using Equation 3.2.

$$FFA = \frac{25.6 \times N \times (A - B)}{\text{weight sample}}$$
$$= \frac{mgNaOH}{g}$$

Where;   N = NaOH molarity = 0.0099 M

4.1.3 Acid Value

Acid value is checked by titration. The volume of NaOH used to neutralize the biodiesel is noted. The value of acid value in the biodiesel is calculated by using the Equation 3.3

$$\text{Acid value} = \frac{56.1 \times N \times (A - B)}{\text{weight sample}}$$
$$= \frac{mgNaOH}{g}$$

Where;   N = NaOH molarity = 0.0099 M
                    (A-B) = volume of NaOH used to neutralize the dissolved oil

4.2   FFA Reduction during Acid Esterification

The comparison of the FFA content in the waste cooking oil before and after acid esterification has been observed. Result in table 4.1 shows that after acid esterification, 36.92% of the FFA has been deducted. The acid catalyzed process has esterified the excess FFA to methyl ester that lead to the reduction of the FFA content in the sample.

Table 4.1: FFA content in waste cooking oil before and after acid esterification

Material	FFA content (mgNaOH/g)
Raw waste cooking oil	2.0467
After acid esterification	1.291

4.3   Effect of Temperature (Phase I)

The collected data from the experiment is filled in Table 4.2. These collected data is then plotted in graphs for easy understanding. In this stage, the raw waste cooking oil used to be transesterified was 200g. Table 4.2 shows the quantity in grams of the waste cooking oil that have been converted to fatty acid methyl ester-biodiesel.

Table 4.2: Result of Phase I

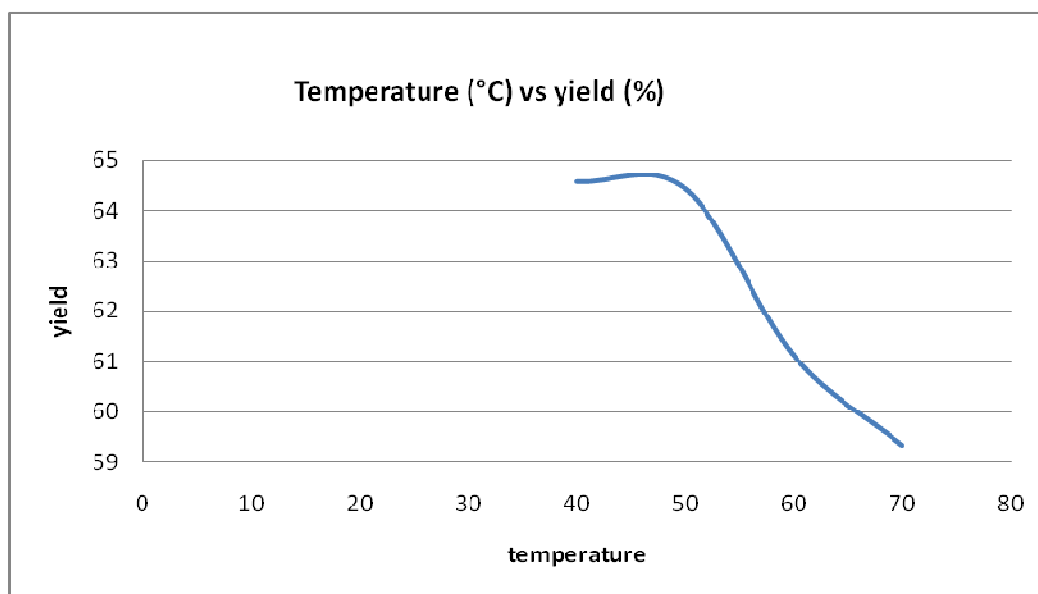| Sample	Temperature (°C)	Biodiesel (g)	Yield (%)	FFA value (mg NaOH/g)	Acid value (mg NaOH/g)
1	40	129.115	64.56	0.2275	0.4986
2	50	128.849	64.42	0.2027	0.4440
3	60	122.211	61.11	0.152	0.3332
4	70	118.244	59.33	0.1266	0.2774
5	80	N/A	N/A	N/A	N/A

Figure 4.1: Graph temperature versus biodiesel yield of Phase I

Figure 4.1 shows the graph of temperature versus biodiesel yield of Phase I (the effect of temperature). The graph shows that, as the temperature is increased, the biodiesel yield also faced the same situation. These situations happened because; higher temperature could accelerate the saponification of the triglyceride, and had gave the negative impact on the product yield and had lead to a drastic decreased in viscosity of waste cooking oil that is favorable to increase the solubility of the oil in the methanol and improved the contact between oil and methanol molecules, thereby reaching a better conversion of triglycerides (Leung *et al*, 2006).
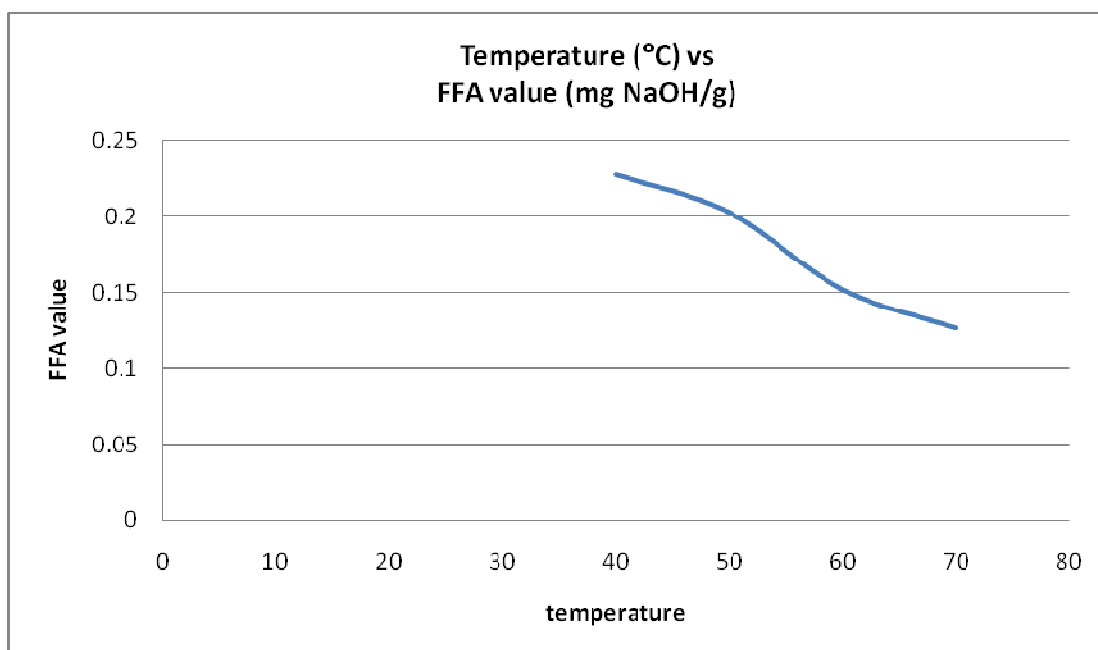
Temperature (°C) vs
FFA value (mg NaOH/g)

Figure 4.2: Graph temperature versus FFA content of Phase I

Figure 4.2 illustrated the relationship between temperature and FFA content in the biodiesel methyl ester which had been conducted in the first Phase I of the experimental work. In the Phase I, temperature is manipulated. From the figure, t is obviously seen that, as the temperature increased, the value of FFA content in the biodiesel methyl ester is constantly decreased. The increasing of temperature accelerates the side saponification reaction of triglycerides (Leung *et al*, 2006). This means, at higher temperature the impurities or the excess FFA in the oil is tend to form the soap and settled at bottom layer leave the high purity of biodiesel at the upper layer. The temperature with the lower FFA content, 70°C is taken as the best temperature to continue the second Phase II
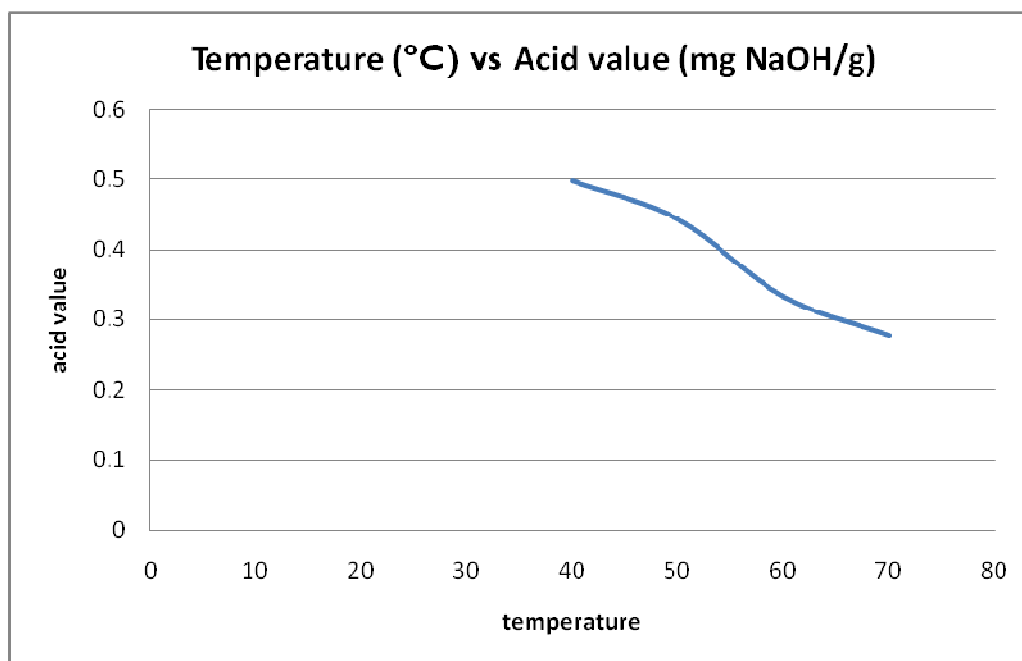
Figure 4.3: Graph of temperature versus acid value of Phase I

Figure 4.3 illustrated the relationship between temperature and acid value in the biodiesel methyl ester which had been conducted in the first Phase I of the experimental work where the temperature is manipulated to investigate the effect temperature to the acid value. From the Figure 4.6, it is apparently seen that, as the temperature increased, the value of acid value in the biodiesel methyl ester is frequently decreased. This condition is happened because of the increasing of water production as the acceleration of the production of the side saponification reaction, which prevented further reaction (Shashikant *et al*, 2005). High production of water as the by product of saponification had diluted the acidic concentration that caused the decreasing of the acid value when the temperature is increased. Again, at temperature of 70ºC, the biodiesel is produce at the lowest value of acid value.

From all the result observed in this phase, reaction temperature of 70ºC is taken as the most suitable temperature for this study. The FFA content and the acid value at this temperature was the lowest. Even though the yield of biodiesel produced was not

higher, but the final product has at least the higher purity of the product as the contaminant is removed with the glycerol. This temperature is used to continue the second phase alkali transesterification.

4.4   Effect of Catalyst Concentration (Phase II)

The collected data from the experiment is filled in Table 4.3. These collected data is then plotted in graphs for easy understanding. In this stage, the raw waste cooking oil used to be transesterified was 100g. Table 4.3 shows the quantity in grams of the waste cooking oil that have been converted to fatty acid methyl ester-biodiesel

Table 4.3: Result of Phase II

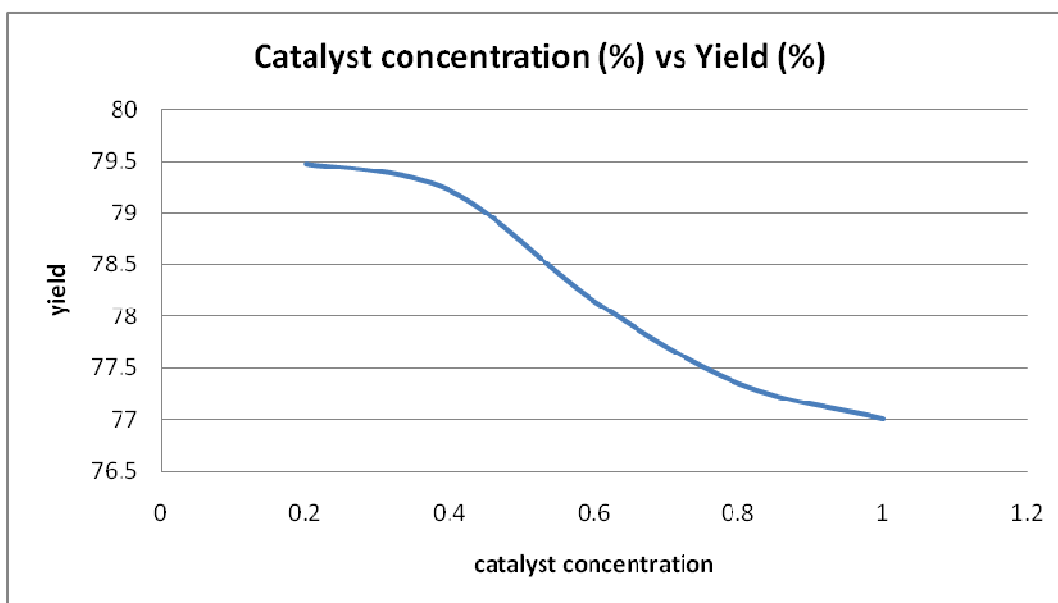| Sample	Catalyst weight percent (%)	WCO (g)	Biodiesel (g)	Yield (%)	FFA value (mg NaOH/g)	Acid value (mg NaOH/g)
6	0.2	100	79.476	79.476	0.2275	0.6664
7	0.4	100	79.215	79.219	0.2027	0.5552
8	0.6	100	78.147	78.147	0.1520	0.3885
9	0.8	100	77.351	77.351	0.1266	0.3331
10	1.0	100	77.009	77.009	N/A	0.2774

Figure 4.4: Graph temperature versus biodiesel yield of Phase II

Figure 4.4 shows the relationship between the biodiesel yield and the catalyst weight percent. From the graph, as the catalyst weight percent in increased from 0.2 to 1.0 wt%, the yield of biodiesel dropped from 79% to 77%, a reduction of 2% yield. Large amount of soap were observed during the experiment of excess NaOH catalyst were added, which was responsible for the yield reduction. This is because; addition of excess alkaline catalyst (NaOH) caused more triglycerides participating in the saponification reaction with NaOH producing more soap, thereby reducing the aster layer. The reaction happened very fast that lead the soap formation. The same trend was observed by D.Y.C Leung, 2006.
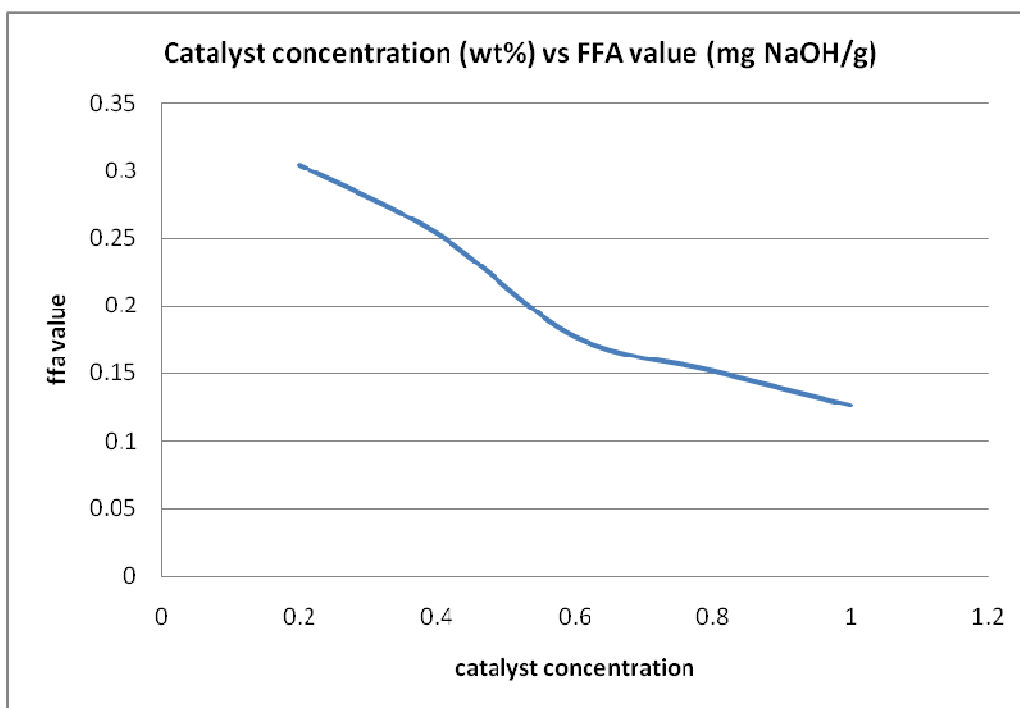
Figure 4.5: Graph of temperature versus FFA content of Phase II

From Figure 4.5, it is shown that the FFA value of the biodiesel methyl ester is constantly decreasing when the higher catalyst weight percent is used to catalyze the process. The same concept when higher temperature is used is applied in this case. The higher the catalyst concentration is used, the more effective the reaction and the higher the acceleration of the side saponification reaction of the triglyceride. When the amount of catalyst in increase, the more FFA is reacted to formed soap and settled as bottom layer leave the high purity biodiesel methyl ester at the top layer. The value of catalyst weight percent that produce biodiesel methyl ester with lowest FFA content is said as the best value of the catalyst weight percent to catalyze the reaction (Leung, 2006).
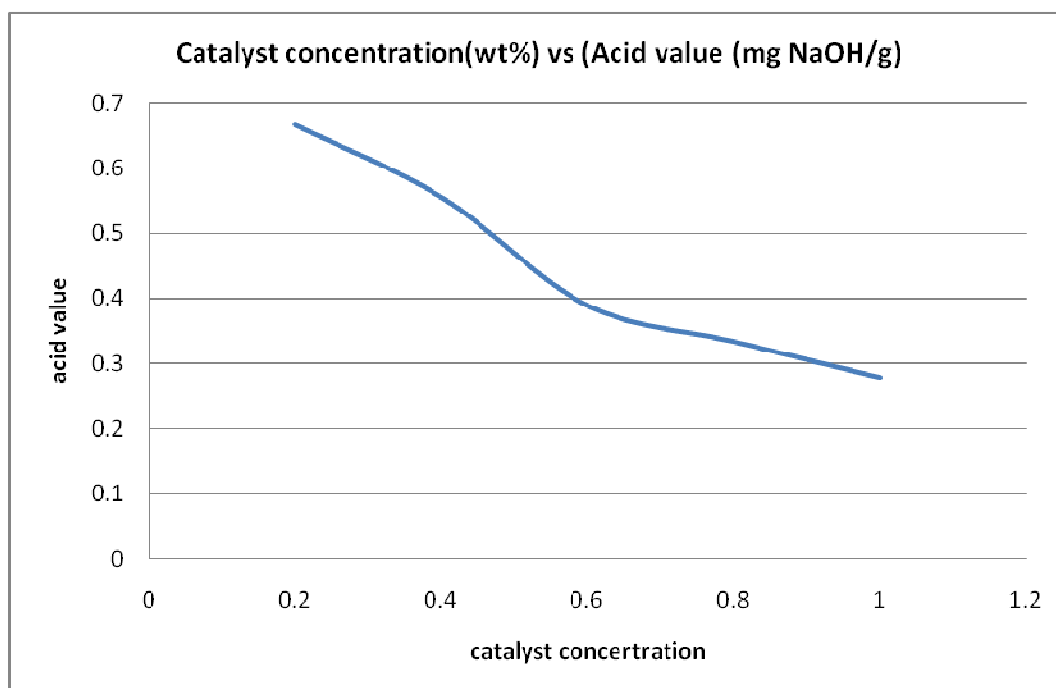
Figure 4.6: Graph of catalyst weight percent versus acid value

In order to determined the best catalyst weight percent should be used to produce the biodiesel methyl ester with low acid value, the best temperature (70°C) from the Phase I investigation is taken as the reaction temperature while the catalyst weight percent is varied in range of 0.2 to 1.0wt%. Figure 4.6 shows that as the catalyst weight percent used to catalyze the reaction is increased, the acid value of the biodiesel methyl ester product is constantly decreased. The same concept when higher temperature is used is applied in this case. The higher the catalyst concentration is used, the more effective the reaction and the higher the acceleration of the side saponification reaction of the triglyceride. So that, the more water is produced that diluted the acidic condition in the biodiesel methyl ester. The value of catalyst weight percent that produce biodiesel methyl ester with lowest acid is said as the best value of the catalyst weight percent to catalyze the reaction.

Figure 4.7: Frozen sample at highest temperature reaction of 80ºC

For both phases of experiment, further increase of temperature or catalyst weight percent neither enhances further conversion nor raises the ester content (Leung *et al,* 2006). At temperature of 80ºC, there was no product yield. This due to the high temperature use to run the experiment that accelerates the reaction to happened at very high rate. The sample turned out to produce soap and Figure 4.7 shows the frozen sample. The sample was frozen just after the reaction time is stopped. However, as the product yield is decreasing, the product selectivity is increasing due to the removal of lots of the contaminant in the biodiesel methyl ester production during the saponification process. The maximum product was produce at temperature of 40ºC and 0.2wt% of NaOH. However this condition is yet cannot be claim as the best reaction condition as the FFA content and the acid value in the biodiesel methyl ester are the highest. In biodiesel production, the quality of the product is the most crucial part that needs to be considered.

CHAPTER IV

CONCLUSION AND RECOMMENDATION

Increased concern over the global warming and high demand of energy consumption are fueling the demand for alternative fuel such biodiesel. Varieties of oil can be used to produce biodiesel such as palm oil, soybean oil, sunflower oil, waste cooking oil or even the animal fats. However as far as the cost of the raw material is concerned, choosing the waste cooking oil as the raw material has effectively proven to reduced the cost. The process was run with the help of the ultrasonic to reduce the time consuming of the biodiesel production. The higher conversion was achieved when short time residence time employed. The two steps process to produce biodiesel was the better procedure for waste cooking oil with high FFA content towards achieving the high yield and quality of the product.

This study is divided into two parts which are the acid-catalyzed esterification and alkali-catalyzed transesterification. At the second part, the study was divided into two phase; Phase I and Phase II. Each phase are conducted to investigate the effect of temperature and catalyst weight percent to the yield, FFA content and the acid value of the biodiesel methyl ester product. The response of this study was investigated step by step. The best value of each parameter involved was determined while the rest kept constant.

Higher temperature proved to have positive influence on increasing the rate of transesterification. However, higher temperature also induces a negative impact on the ester yield due to acceleration of the saponification of triglyceride. In the Phase I, the best temperature was investigated to be at 70°C. At this point the biodiesel yield was 59.33%. Even though the value shows slightly lower that other temperature, but at this point the FFA content and the acid value is in the lowest value which is good for the biodiesel production.

In addition, the used of the ultrasonic wave in this study helps a lot. The induced asymmetric cavitational bubbles collapse at the oil – methanol boundary creates tiny drops of each liquid into other; leading into an enhanced mass transfer between the phases thus accelerates the reaction. The transesterification under ultrasonic irradiation is mainly influenced by the superiority of the emulsion created by the collapse of the bubbles in contrast to mechanical stirring.

As the conclusion, the objective of the study was successfully achieved. The best values of temperature and catalyst concentration for this study are 70ºC and 1wt% respectively.

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APPENDICES

APPENDIX A: Acid Esterification

Acid catalyst preparation

WCO (g)	8000
%wt NaOH/ wWCO	2
Weight NaOH (g)	$$w = \frac{2}{100} \times 100 = 2$$

Weight of methanol

	Methanol	WCO
Molar ratio (mol)	10	1
Molecular weight (g/mol)	32.04	1000
Mass (mol x MW) (g)	320.04	1000
Scale down ($\div$ 10) (g)	32.04	100

APPENDIX B: Alkali Transesterification

Alkali catalyst weight

WCO(g)	%wt NaOH/ wWCO	Weight NaOH (g)
100	0.2	$w = \dfrac{0.2}{100} \times 100 = 0.2$
100	0.4	$w = \dfrac{0.4}{100} \times 100 = 0.4$
100	0.6	$w = \dfrac{0.6}{100} \times 100 = 0.6$
100	0.8	$w = \dfrac{0.8}{100} \times 100 = 0.8$
100	1	$w = \dfrac{1}{100} \times 100 = 0.1$

APPENDIX C: Biodiesel Yield

The product yield is calculated by using Equation 3.1

$$\text{Product yield} = \frac{\text{weight of biodiesel}}{\text{weight of raw WCO}} \times 100 \qquad (3.1)$$

Phase I

Sample	Temperature (°C)	WCO (g)	Biodiesel (g)	Yield (%)
1	40	200	129.115	$\text{yield} = \frac{\text{weight of biodiesel}}{\text{weight of raw WCO}} \times 100$ $= \frac{129.115}{200} \times 100$ $= 64.56\%$
2	50	200	128.849	$\text{yield} = \frac{\text{weight of biodiesel}}{\text{weight of raw WCO}} \times 100$ $= \frac{128.843}{200} \times 100$ $= 64.42\%$
3	60	200	122.211	$\text{yield} = \frac{\text{weight of biodiesel}}{\text{weight of raw WCO}} \times 100$ $= \frac{122.211}{200} \times 100$ $= 61.11\%$
4	70	200	118.244	$\text{yield} = \frac{\text{weight of biodiesel}}{\text{weight of raw WCO}} \times 100$ $= \frac{118.669}{200} \times 100$ $= 59.33\%$
5	80	200	N/A	N/A

Phase II

Sample	Catalyst weight percent (%)	WCO (g)	Biodiesel (g)	Yield (%)
6	0.2	100	79.476	$yield = \dfrac{weight\ of\ biodiesel}{weight\ of\ raw\ WCO} \times 100$ $= \dfrac{79.476}{100} \times 100$ $= 79.476\%$
7	0.4	100	79.215	$yield = \dfrac{weight\ of\ biodiesel}{weight\ of\ raw\ WCO} \times 100$ $= \dfrac{79.215}{100} \times 100$ $= 79.219\%$
8	0.6	100	78.147	$yield = \dfrac{weight\ of\ biodiesel}{weight\ of\ raw\ WCO} \times 100$ $= \dfrac{78.147}{100} \times 100$ $= 78.147\%$
9	0.8	100	77.351	$yield = \dfrac{weight\ of\ biodiesel}{weight\ of\ raw\ WCO} \times 100$ $= \dfrac{77.351}{100} \times 100$ $= 77.351\%$
10	1	100	77.009	$yield = \dfrac{weight\ of\ biodiesel}{weight\ of\ raw\ WCO} \times 100$ $= \dfrac{77.009}{100} \times 100$ $= 77.009\%$

APPENDIX D: FFA Content

$$FFA = \frac{25.6 \times N \times (A - B)}{weight\ sample}$$

$$= \frac{mgNaOH}{g} \qquad (3.2)$$

Where;　　　　　N = NaOH molarity

　　　　　(A-B) = volume of NaOH used to neutralize the dissolved oil

Raw waste cooking oil

Sample	Sample weight (g)	Volume of NaOH (ml)	FFA value (mg NaOH/g)
Raw waste cooking oil	10.01	4.5	$FFA = \frac{25.6 \times 0.099 \times (4.5)}{10.01}$ $= 1.139 \frac{mgNaOH}{g}$

Phase I

Sample	T (ºC)	Sample weight (g)	Volume of NaOH (ml)	FFA value (mg NaOH/g)
1	40	10.025	0.9	$FFA = \dfrac{25.6 \times 0.099 \times 0.9}{10.01}$ $= 0.2275$
2	50	10.005	0.8	$FFA = \dfrac{25.6 \times 0.099 \times 0.8}{10.01}$ $= 0.2027$
3	60	10.002	0.6	$FFA = \dfrac{25.6 \times 0.099 \times 0.6}{10.01}$ $= 0.1520$
4	70	10.008	0.5	$FFA = \dfrac{25.6 \times 0.099 \times 0.5}{10.01}$ $= 0.1266$
5	80	N/A	N/A	N/A

Phase II

Sample	Catalyst weight percent (%)	Sample weight (g)	Volume of NaOH (ml)	FFA value (mg NaOH/g)
6	0.2	10.001	1.2	$FFA = \dfrac{25.6 \times 0.099 \times 1.2}{10.01}$ $= 0.3041$
7	0.4	10.003	1.0	$FFA = \dfrac{25.6 \times 0.099 \times 1.0}{10.01}$ $= 0.2534$
8	0.6	10.008	0.7	$FFA = \dfrac{25.6 \times 0.099 \times 0.7}{10.01}$ $= 0.1773$
9	0.8	10.002	0.6	$FFA = \dfrac{25.6 \times 0.099 \times 0.6}{10.01}$ $= 0.1520$
10	1.0	10.008	0.5	$FFA = \dfrac{25.6 \times 0.099 \times 0.5}{10.01}$ $= 0.1266$

APPENDIX E: Acid Value

Acid value is calculated by using the Equation 3.3

$$\text{Acid value} = \frac{56.1 \times N \times (A - B)}{\text{weight sample}}$$

$$= \frac{mgNaOH}{g}$$

Where;   N = NaOH molarity =0.0099 M
   (A-B) = volume of NaOH used to neutralize the dissolved oil

I.   FFA content of the raw waste cooking oil

Sample	Sample weight (g)	Volume of NaOH (ml)	FFA value (mg NaOH/g)
Raw waste cooking oil	10.01	4.5	$\text{Acid value} = \frac{56.1 \times 0.099 \times 4.5}{10.01}$ $= 2.4968 \frac{mgNaOH}{g}$

Phase I

Sample	T (ºC)	Sample weight (g)	Volume of NaOH (ml)	Acid value (mg NaOH/g)
1	40	10.025	0.9	$= \dfrac{56.1 \times 0.099 \times 0.9}{10.025}$ $= 0.4986$
2	50	10.005	0.8	$= \dfrac{56.1 \times 0.099 \times 0.9}{10.025}$ $= 0.4440$
3	60	10.002	0.6	$= \dfrac{56.1 \times 0.099 \times 0.9}{10.025}$ $= 0.3332$
4	70	10.008	0.5	$= \dfrac{56.1 \times 0.099 \times 0.9}{10.025}$ $= 0.2774$
5	80	N/A	N/A	N/A

Phase II

Sample	Catalyst weight percent (%)	Sample weight (g)	Volume of NaOH (ml)	Acid value (mg NaOH/g)
6	0.2	10.001	1.2	$= \dfrac{56.1 \times 0.099 \times 1.2}{10.001}$ $= 0.6664$
7	0.4	10.003	1.0	$= \dfrac{56.1 \times 0.099 \times 1.0}{10.003}$ $= 0.5552$
8	0.6	10.008	0.7	$= \dfrac{56.1 \times 0.099 \times 0.7}{10.008}$ $= 0.3885$
9	0.8	10.002	0.6	$= \dfrac{56.1 \times 0.099 \times 0.6}{10.002}$ $= 0.3331$
10	1.0	10.008	0.5	$= \dfrac{56.1 \times 0.099 \times 0.5}{10.025}$ $= 0.2774$