

**PREPARATION OF BIODIESEL FROM WASTE COOKING OIL VIA TWO
STEP BATCH CATALYZED PROCESS WITH THE AID OF ACID
SULFURIC AND SODIUM HYDROXIDE AS THE CATALYST**

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UNIVERSITI MALAYSIA PAHANG

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JUDUL **PREPARATION OF BIODIESEL FROM WASTE COOKING OIL VIA TWO STEP BATCH CATALYZED PROCESS WITH THE AID OF ACID SULFURIC AND SODIUM HYDROXIDE AS THE CATALYST**

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A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor in Chemical Engineering

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MAY 2008

I declare that this thesis entitled “Preparation of biodiesel from waste cooking oil via two step batch catalyzed process” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently in candidature of any other degree.

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*Special dedication to:
For my beloved family.*

Wan Abd Ghani Bin Wan Salim

Siti Rokiah Bt Omar

Wan Ahmad Kamal Bin Wan Abd Ghani

Wan Julia Bt Wan Abd Ghani

Wan Julina Bt Wan Abd Ghani

Wan Jasreen Bt Wan Abd Ghani

Thank you for everything.....

I love all of you so much....

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ABSTRACT

With environmental and energy source concerns on the rise, using agricultural fats and biological sources as fuel in diesel engines has captured increasing attention. Biodiesel has many advantages relative to petroleum. It has several processes that can be used in producing biodiesel but transesterification is the most commonly used in industry. In transesterification, it involved reaction between tryglycerides from waste cooking oil and methanol to produce biodiesel. The catalysts used in this experiment were acid sulfuric and sodium hydroxide catalyst. Two step catalyzed was chosen to be used in preparation biodiesel from waste cooking oil because the free fatty acid content was high in waste cooking oil. For the first step, the molar ratio used was 10:1 with the presence of 2 wt% of H_2SO_4 as catalyst with the temperature was 95°C and 4 hours of reaction time. For the second step, the molar ratio used was 6:1 with the presence of 0.2, 0.4, 0.6, 0.8 and 1wt% of NaOH as catalyst with the temperature were 40,50,60,70, 80°C and 1 hour of reaction time. Then, the biodiesel have to analyse by titration method to check free fatty acid and acid value content. It is proved that, this method can remove both free fatty acid and acid value up to 95%. This study also has indicated that the main factors that affect the reaction are reaction temperature and catalyst concentration.

ABSTRAK

Kesedaran tentang kepentingan alam sekitar telah membawa kepada penggunaan enjin diesel dari sumber semulajadi. Biodiesel boleh dihasilkan dari pelbagai cara. Dalam proses transesterifikasi, ia melibatkan tindakbalas antara *tryglycerides* dari minyak masak terpakai dan alkohol seperti metanol untuk menghasilkan biodiesel. Mangkin yang digunakan dalam eksperimen ini adalah asid sulfurik dan natrium hidroksida. Dua langkah mangkin telah dipilih untuk digunakan dalam pembuatan biodiesel dari minyak terpakai kerana kandungan bebas asid lemak adalah lebih tinggi dalam minyak masak terpakai. Bagi langkah pertama, nisbah molar yang digunakan adalah 10:1 dengan kehadiran 2 wt% H_2SO_4 sebagai mangkin dan suhunya adalah $95^{\circ}C$ serta tempoh tindakbalas adalah 4 jam. Bagi langkah kedua, nisbah molar yang digunakan adalah 6:1 dengan kehadiran 0.2, 0.4, 0.6, 0.8 and 1wt% of NaOH sebagai mangkin dan suhunya adalah $40,50,60,70,80^{\circ}C$ serta tempoh tindakbalas adalah 1 jam. Selepas pembuatan biodiesel, analisis seperti kandungan bebas lemak dan nilai asid diperlukan. Melalui analisis yang dijalankan, telah terbukti bahawa kaedah ini dapat menyingkirkan kandungan bebas lemak dan nilai asid lebih dari 95%. Kajian ini juga menunjukkan bahawa dua faktor penting yang mempengaruhi tindakbalas adalah suhu tindakbalas dan kepekatan mangkin yang digunakan.

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LIST OF SYMBOLS

g	-	gram
mL	-	mililitre
L	-	Litre
°C	-	degree Celcius
%	-	percent
μl	-	microlitre
w/w	-	weight per weight

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CHAPTER 1

INTRODUCTION

Bioenergy, derived from sustainable agricultural practices and resources, has received increased consideration as a renewable substitute for fossil fuels. According to the World Energy Outlook by 2030 world energy consumption under the "Business as Usual" will increase by about 1.8% per year between 2000 and 2030. Bioenergy production being a compound issue that depends on many varying factors can play a significant role in improving rural productivity, energy supply, the environment, economic development and sustainability.

Bioenergy resources such as biofuels comprising of bio-ethanol and bio-diesel, biogas and biomass are derived from a variety of agricultural crops such as sugar cane, rapeseed coconut, Jojoba, Jatropha, palm oil, soybean and sunflower. As most of the crops used for biofuels are grown predominantly in developing countries, they hold the great potential for boosting these producing countries' trade, investment and development. Malaysia in practicing sustainable forest and crop management is unlikely to sacrifice its pristine forests to increase the area for producing palm oil for biofuel.

1.1 Background of study

Biodiesel is a clean-burning alternative fuel, produced from renewable resources such as vegetable oils and animal fats that are usually produced by a transesterification, reaction of vegetable or waste oil respectively with a low molecular weight alcohol and short chain alcohol, such as methanol and ethanol. During this process, the triglyceride molecule from vegetable oil is removed in the form of glycerin.

Palm oil, often said to be God's gift to Malaysia and Malaysia's gift to the rest of the world, certainly has the advantage over other vegetable oils in the production of biodiesel. The Malaysian government is refocusing the use of palm oil to the production of biodiesel due to the huge demand from European countries that has encouraged the building of biodiesel plants. Strong demand for biodiesel from Europe as well as Colombia, India, South Korea and Turkey has fueled the industry's growth as more countries seek to reduce their reliance on fossil fuels. Malaysia has already begun preparations to change from diesel to bio-fuels by 2008, including drafting legislation that will make the switch mandatory. From 2007, all diesel sold in Malaysia must contain 5% palm oil. Being the world's largest producer of crude palm oil, Malaysia intends to take advantage of the rush to find cleaner fuels.

World production of palm oil in 2003 and 2004 rose by 3% to 28.13 million metric tons from 27.21 million in 2002 and 2003. Palm oil is the world's second largest vegetable oil crop, running only slightly below soybean oil production of 31.98 million metric tons in 2003/4. The large production year in 2003 and 2004 for palm oil outpaced demand and that led to an 11% increase in stocks to 2.31 million metric tons from 2.09 million in 2002/3, although that is still a relatively tight stocks level compared to the 1999 to 2002 period. The world's largest producer of palm oil by far is Malaysia with 48% of world production and Indonesia is the second largest producer with 36% of world production. Together they account for 84% of world production. Malaysian production in 2002 and 2003 rose by 6% to 12.520 million metric tons from 11.856 million in 2001/2. Indonesian production in 2002/3 rose by 8% to 9.480 million

metric tons from 8.790 million in 2001/2. Figure 1 shows that the total consumption of palm oil in 2004

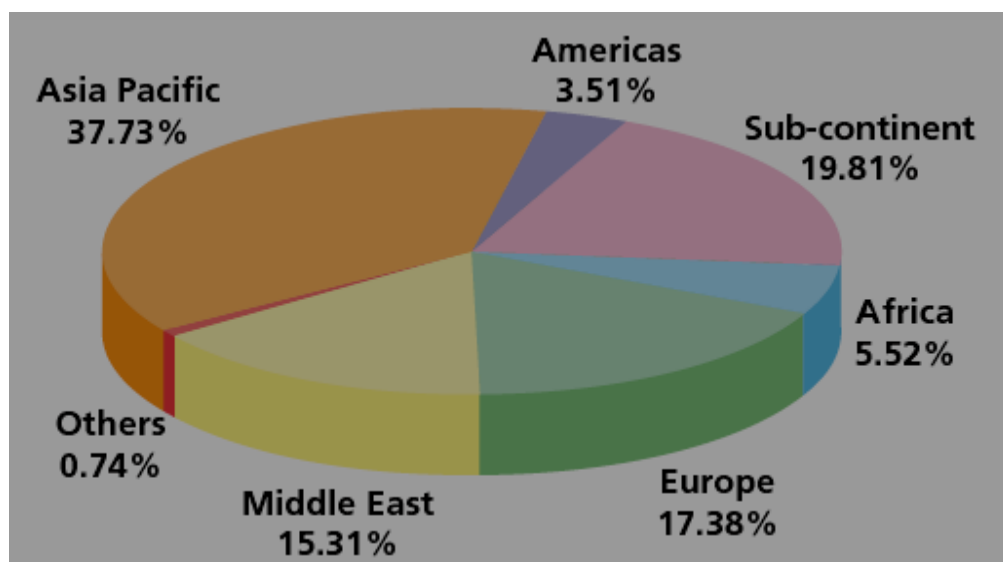


Figure 1: Total consumption of palm oil in 2004 (source: MPOB)

1.2 Objectives

To study the effects of catalyst concentration, reaction time and temperature on the two steps catalyze transesterification process in producing biodiesel

1.3 Scope of study

- To study the effect of reaction temperature and catalyst concentration on methyl ester (biodiesel) yield.
- To study the effect of reaction temperature and catalyst concentration on free fatty acid content.

- c) To study the effect of reaction temperature and catalyst concentration on acid value.

1.4 Problem statement

Recently, increasing in crude oil prices and environment concerns about pollution from the car gases because the needs for alternative fuels that is more environmental friendly. Vehicles engines can contribute to the main pollutants when injected fuel does not find the necessary air for the complete combustion. These main primary pollutants such as carbon oxides, nitrogen oxides, alcohols, aldehydes, ketones, sulfur compounds and hydrocarbons can react with each other or with the sunlight to produce secondary pollutants like ozone that can be harmful to the environment.

Among different possible resources, diesel fuels from biological sources have shown great potential as substitutes for petroleum-based diesel fuels. Biodiesel that is produced from vegetable oils can be used as an alternative diesel fuels because its properties are similar to the conventional diesel. Other biological sources such as vegetable oil, soybean oil and animal fats, waste cooking oil also can be the raw material for biodiesel production. Waste cooking oil can cause environment pollution if not suitable treatment available when it is discharged. But, recently, it was found that waste cooking oil can be good commercial choice to produce biodiesel. Waste cooking oil gives interesting properties because it can be converted to biodiesel and waste cooking oil is available with low prices compared to fresh vegetable oil.

In our research, we have chosen two-step catalyzed transesterification process to improve the yield of biodiesel by the waste cooking oil. Biodiesel produced by transesterification reactions can be catalyzed with acid, alkali or enzyme. But, the former two types have received more attention due to their short reaction time and have lower cost. When free fatty acid content was lower than 0.5%, the sulfuric acid was

drained and solid alkali was introduced into the system to complete the transesterification.

But, long reaction time, no recovery of catalyst and high cost of reaction equipment were disadvantages of this process. In addition to biodiesel, transesterification also yields glycerol as a valuable by-product for the pharmaceutical and cosmetics industry.

CHAPTER 2

LITERATURE REVIEW

2.0 General Overview

The high energy demand in the industrialized world as well as in the domestic sector and pollution problems caused due to the widespread use of fossil fuels make it increasingly necessary to develop the renewable energy sources to overcome these problems and preserving the global environment. Also, the need to search the alternative diesel fuels arises mainly from the concern about long term supplies of conventional hydrogen-based diesel fuels. Among the different possible sources, biodiesel that is manufactured from biological sources such as vegetable seed oil, soybean oil and some recovered animal fats present a promising alternative to substitute diesel fuels. It is becoming important position as an environmentally friendly substitute of diesel fuel in the markets of developed countries as well as developing one. Biodiesel or fatty acid alkyl esters chemically simple and defined as a “additive to diesel fuel that is derived from the oils and fats of plants and animals “or mono-alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat (ASTM). “Bio” represents its renewability and biodegradability in contrast to traditional petroleum-based diesel fuel. “Diesel” refers its

use as fuel for diesel engines. In this context, it can be used in diesel engines and heating systems [Mittlebach *et al.*, 1983; Staat and Vallet, 1994]

Biodiesel has many advantages compared to diesel fuel. The most important are the reduction of greenhouse effect and emissions from gas combustion. Biodiesel, which has low emissions profiles, is considered to be more sustainable and ‘environmentally-friendly’ than conventional diesels because the bio-component of these fuels is a biodegradable, nontoxic and clean renewable fuel with properties similar to conventional diesel. Historically, the use of neat biodiesels, particularly unrefined vegetable oils, and ‘bio-rich’ biodiesel (\geq B40) blends has been associated with reduced vehicle or engine performance, such as impeded fuel flows, blocked fuel filters and fouled injectors and piston chambers [Bagby, 1987; Knothe *et al.*, 1992; Graboski and McCormick, 1998 and references therein; Srivastava and Prasad, 2000]. In addition, biodiesel does not require engine modification and has lower carbon monoxide releases to the atmosphere and hydrocarbon emissions than petroleum-based diesel fuels when burned. Biodiesel can become an excellent alternative fuel for diesel engine if it is free from aromatic compounds and sulfur.

However, the cost of biodiesel is high due to the high cost of raw material (about 70-75% of the total cost) and high production cost involved, though this fuel has been developed about three decades [Hanna, 1999, Allen *et al.* 1999, Leung, 2001]. So, biodiesel is not commonly used in daily life. The viscosity of vegetable oils is 10-20 times higher than of petroleum fuel, therefore using directly vegetable oils as a fuel can cause engine problems like injector fouling and has some drawbacks such as deposits at the injection system with consequent plugs or low atomization, hardening of seals, and low lubricating properties. One limitation to the use of biodiesel is its tendency to crystallize at low temperatures below 0°C. Methyl and ethyl esters of vegetable oils will crystallize and separate from diesel at temperatures often experienced in winter time operation. Such crystals can plug fuel lines and filters, causing problems in fuel pumping and engine operation. Another method to improve the cold flow properties of

vegetable oil esters is to remove high-melting saturated esters by inducing crystallization with cooling, a process known as winterization

2.1 Renewable resources as the raw material for biodiesel

Among the different possible resources, diesel fuels derived from triglycerides have shown potential as substitutes for petroleum-based diesel fuels [Fukuda, Kondo, Nuda., 2001]. The use of animal fats and vegetable oils, such as palm, soya bean, sunflower, peanut olive oils, waste cooking oil, as alternative fuels for diesel engines have been studied and the rapid decline in crude oil reserves. But, the high cost of the fresh vegetable oil, waste cooking oil gives interesting properties because it can be converted to biodiesel and available with relatively cheap price [Nisworo, 2005; Zhang et al., 2003].

2.1.1 Animal fats

Currently, biodiesel is produced from a number of products, including soy bean oil, cotton seed oil, and yellow grease, among other things. Turning animal fat into biodiesel is not new. Animal fat begins to turn cloudy at a higher temperature than soybean biodiesel which also means that it could thicken up when it gets to a temperature lower than about 40 degrees Fahrenheit. Biodiesel production costs about a dollar more per gallon than conventional diesel.

2.1.2 Vegetable Oil

Vegetable oils occupy a prominent position in the development of alternative fuels although, there have been many problems associated with using it directly in diesel engine (especially in direct injection engine). These include carbon deposits oil ring sticking and lubricating problems. Biodiesel produced from vegetable oils can be used as an alternative diesel fuels because its characteristics are almost the same to those of petroleum-based diesel fuels. For example, they have a similar viscosity with petroleum-based diesel fuel, their volumetric heating values are little lower, but they have high cetane and flash points [Fukuda, Kondo, Nuda., 2001]. The basic constituent of vegetable oils is triglyceride. Figure 2 shows a typical triglyceride molecule. Vegetable oils comprise 90 to 98% triglycerides and small amounts of mono- and diglycerides.

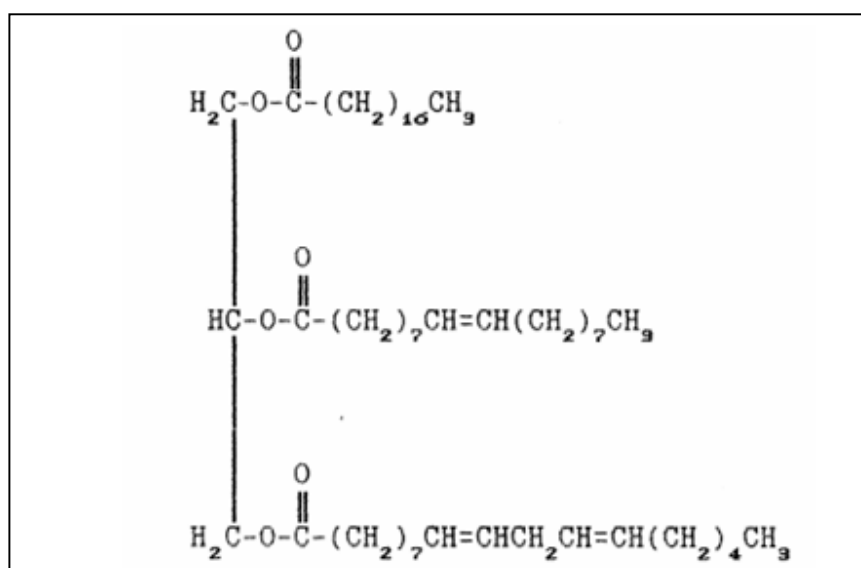


Figure 2.1: Structure of typical triglyceride molecules

Triglycerides are esters of three fatty acids and one glycerol. These contain substantial amounts of oxygen in its structure. Fatty acids vary in their carbon chain length and in the number of double bonds. The structures of common fatty acids are

given in Table 1 [5]. Tables 2.2 summarize the fatty acid composition of some vegetable oils [Goeing, Schwab, Pyrde *et. al.*, 1982; Kapur, Bhasin, Mathur., 1982]. The fatty acids which are commonly found in vegetable oils are stearic, palmitic, oleic, linoleic and linolenic. Vegetable oils contain free fatty acids (generally 1 to 5%), phospholipids, phosphatides, carotenes, tocopherols, sulphur compounds and traces of water [Markley; 1960].

Table 2.1 Chemical structure of common fatty acids

Fatty acid	Systematic name	Structure	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docoasanoic	22:0	$C_{22}H_{44}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$
Oleic	<i>cis</i> -9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	<i>cis</i> -9, <i>cis</i> -12-octadecenoic	18:2	$C_{18}H_{32}O_2$
Linolenic	<i>cis</i> -9- <i>cis</i> -12, <i>cis</i> -15-octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Erucic	<i>cis</i> -13-Docosanoic	22:1	$C_{22}H_{42}O_2$

Table 2.2 Chemical composition of vegetable oils

Vegetable oil	Fatty acid composition %									
	14:0	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	0	12	2	Tr	0	0	25	0	6	Tr
Cottonseed	0	28	1	0	0	0	13	0	58	0
Crambe	0	2	1	2	0	1	19	59	9	7
Linseed	0	5	2	0	1	0	20	0	18	55
Peanut	0	11	2	1	0	1	48	0	32	1
Rapeseed	0	3	1	0	0	0	64	0	22	8
Sunflower	0	9	2	0	0	0	12	0	78	0
H ₂ O ₂ sunflower	Tr	5	2	Tr	0	0	79	0	13	0
Sesane	0	13	4	0	0	0	53	0	30	0
Soya bean	0	12	3	0	0	0	23	0	55	6
Sunflower	0	6	3	0	0	0	17	0	74	0

The modified engines that have been built by Elsbett in Germany and Malaysia and Diesel Morten und Geratebau GmbH (DMS) in Germany and in USA show a good performance when fuelled with vegetable oils of different composition and grades [Krawczyk;1996].

2.1.3 Virgin Oil

Pure plant oil (PPO) (or Straight Vegetable Oil (SVO)), also, can become a raw material in producing biodiesel. In contrast to waste vegetable oil, is not a byproduct of other industries, and thus its prospects for use as fuels are not limited by the capacities of other industries. Production of vegetable oils for use as fuels is theoretically limited only by the agricultural capacity. For engines designed to burn diesel fuel, the viscosity of vegetable oil must be lowered to allow for proper atomization of fuel; otherwise

incomplete combustion and carbon build up will ultimately damage the engine. Many enthusiasts refer to vegetable oil used as fuel as waste vegetable oil (WVO) if it is oil that was discarded from a restaurant or straight vegetable oil (SVO) to distinguish it from biodiesel.

2.2 Solvent

Actually, there are many types of alcohols such as methanol and ethanol that can be used in the transesterification. Short-chain alcohols such as methanol, ethanol, and butanol are the most commonly used as a solvent. Therefore, selection of the alcohol is depends on cost and performance consideration. Ethanol can be produced from agricultural renewable resources, thereby attaining total independence from petroleum-based alcohols. For example, if methanol is used, the resulting biodiesel is fatty acid methyl ester (FAME), which has proper viscosity, boiling point and high cetane number [Gryglewitz;1999]. But, methanol is the most common alcohol because of it has lower price compared to other alcohols. Handling methanol might be considered an exception to that generality. However, ethanol, as extraction solvent, is preferable to methanol for the transesterification of vegetables oils because of its much higher dissolving power for oils. Therefore, producing ethyl esters rather than methyl esters is of considerable interest, because, in addition to the entirely agricultural nature of the ethanol, the extra carbon atom brought by the ethanol molecule slightly increases the heat content and the cetane number. Finally, another important advantage in the use of ethanol is that the ethyl esters have cloud and pour points that are lower than the methyl esters. This fact improves the cold start.

2.3 Process

The plant oils usually contain free fatty acids, phospholipids, sterols, water, odourants and other impurities. Because of these, the oil cannot be used as fuel directly. Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of the hydrocarbon-based diesel fuels. The problems with substituting triglycerides for diesel fuels are mostly associated with their high viscosities, low volatilities and polyunsaturated character. These can be changed in at least four ways, such as pyrolysis, microemulsification, dilution and also transesterification. Figure 2 shows the process flow schematic for biodiesel production.

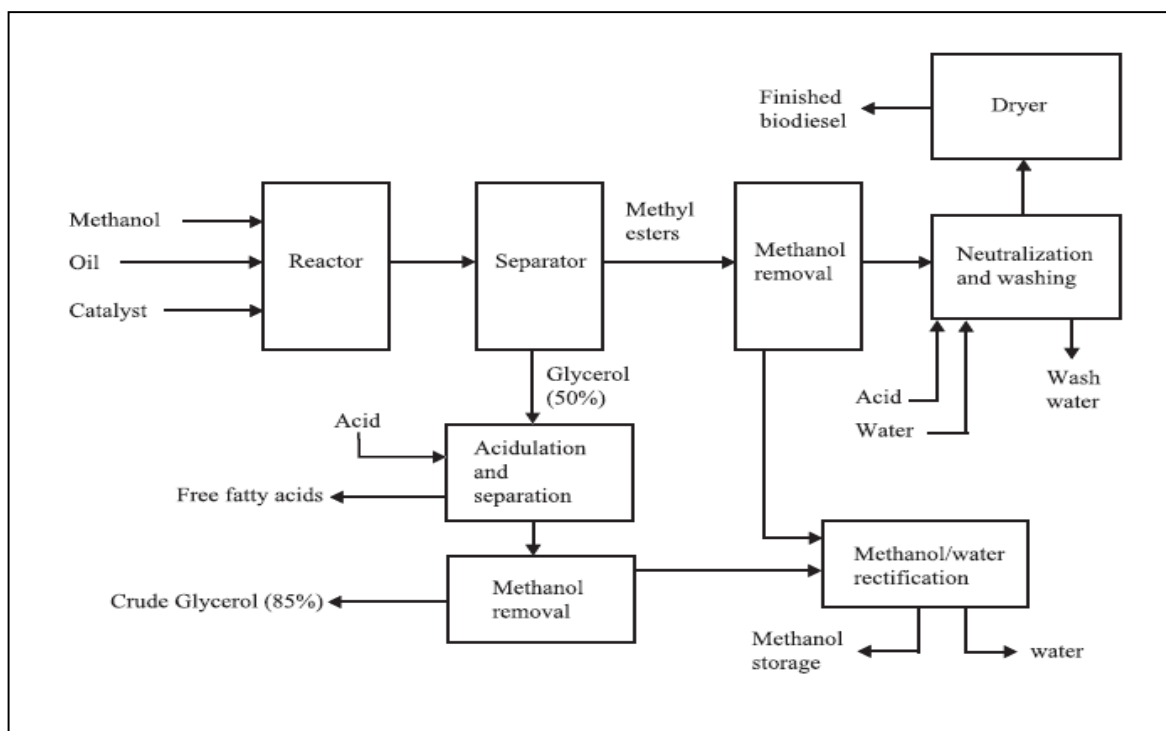


Figure 2.2: Process flow schematic for biodiesel production

2.4 Pyrolysis

Pyrolysis or thermal cracking is the conversion of one substance into another by means of heat or by heat in presence of a catalyst. The paralyzed material can be vegetable oils, animal fats, natural fatty acids or methyl esters of fatty acids. Pyrolysis refers to a chemical change caused by the application of thermal energy in the presence of air or nitrogen sparge. Many investigators have studied the pyrolysis of triglycerides to obtain products suitable for diesel engines. These studies include the effect of temperature on the type of products obtained, the use of catalysts, largely metallic salts, to obtain paraffin's and olefins similar to those present in hydrocarbon-based diesel fuels, the characterization of the thermal decomposition products. Thermal decomposition of triglycerides produces the compounds of classes including alkanes, alkenes, alkadienes, aromatics and carboxylic acids. Different types of vegetable oils produce large differences in the composition of the thermally decomposed oil. Figure 3 outlines a schematic that accounts for the formation of alkanes, alkenes, alkadienes, aromatics and carboxylic acids from pyrolysis of triglycerides. Mechanisms for the thermal decomposition of triglycerides are likely to be complex because of many structures and multiplicity of possible reactions of mixed triglycerides.

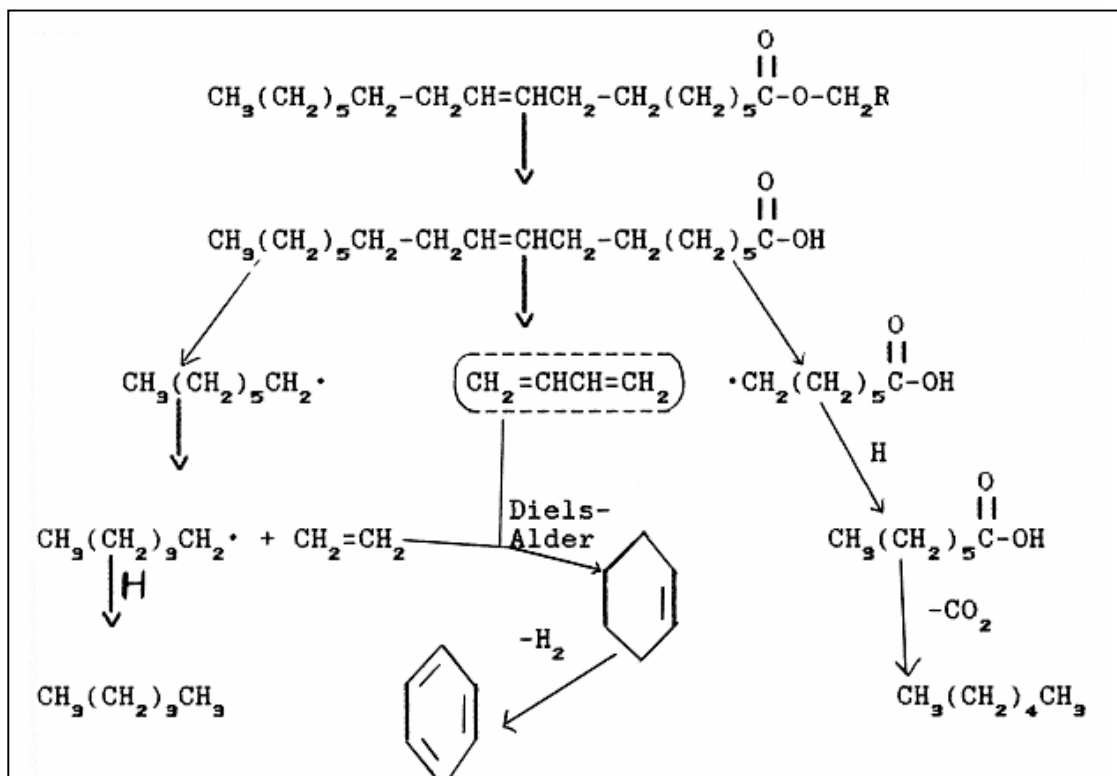


Figure 2.3: Thermal decomposition mechanisms

2.5. Microemulsification

To overcome the problem of the high viscosity of vegetable oils, microemulsions with solvents such as methanol, ethanol and 1-butanol have been investigated. A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimension generally in the 1-150nm range, formed spontaneously from two normally immiscible liquid that can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. Microemulsions are clear or translucent thermodynamically stable dispersions of oil, water, surfactant, and often a small lamphiphilic molecule, called cosurfactant. [Bagby; 1987, Schwab]

2.6 Transesterification

Among these, the transesterification is the key and foremost important step to produce the cleaner and environmentally safe fuel which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol. Methanol is the most commonly used alcohol because of its low cost [Hobson; 1984, Marckley; 1960]. Free and bonded glycerols, mainly depending on the technical process of transesterification, are the main parameters for defining the quality of biodiesel.

During the transesterification process, free glycerol can easily be removed by washing steps, whereas a low content of glycerides can only be achieved by the use of specific catalysts and reaction conditions or by further distillation of the product. A higher content of free glycerol may cause problems during storage or in the fuel system, due to separation of glycerol, or can lead to injector fouling or the formation of higher aldehyde emissions. A higher content of glycerides, especially triglycerides, may cause formation of deposits at the injection nozzles, at the piston and at the valves (Mittelbach et al., 1983; Moser et al., 1991). As the limits of free glycerol and glycerides are very low, there is a need for precise and reliable analytical methods for the determination of free and bonded glycerol, as well as the individual glycerides. One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglycerides. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right.

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water [Hobson; 1984]. This process has been widely used to reduce the high viscosity of triglycerides. In the transesterification of different types of oils, triglycerides react with an alcohol, generally methanol or ethanol to produce esters and glycerin. The fatty acid alkyl esters (known as biodiesel) are attractive as alternative diesel fuels. To make it

possible, catalyst is added to the reaction. Transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants. However, the presence of a catalyst (a strong acid or base) accelerates the conversion.

2.6.1 Reaction

The biodiesel that is considered as a possible substitute or extender of conventional diesel fuel is commonly composed of fatty acid methyl esters that are prepared from the triglycerides in vegetable oils by transesterification with methanol. Transesterification of triglycerides produce fatty acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the forward reaction is pseudo-first order and the reverse reaction is found to be second order. It was also observed that transesterification is described in Figure 4. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglycerides molecule, which results in the formation of tetrahedral intermediate. The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step. In the last step rearrangement of the tetrahedral intermediate gives rise to an ester and diglyceride [SEA news; 1996]. In the transesterification [SEA news; 1996]. Of different types of oils, triglycerides react with an alcohol, generally methanol or ethanol, to produce esters and glycerin. To make it possible, a catalyst is added to the reaction.

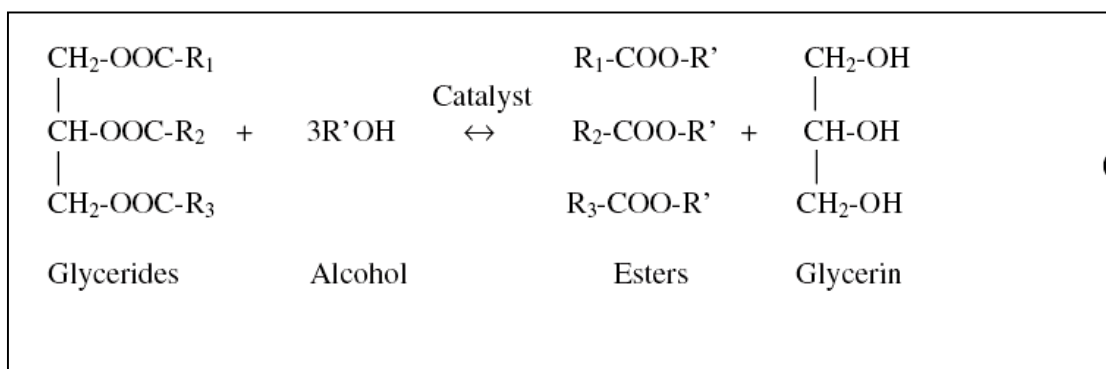
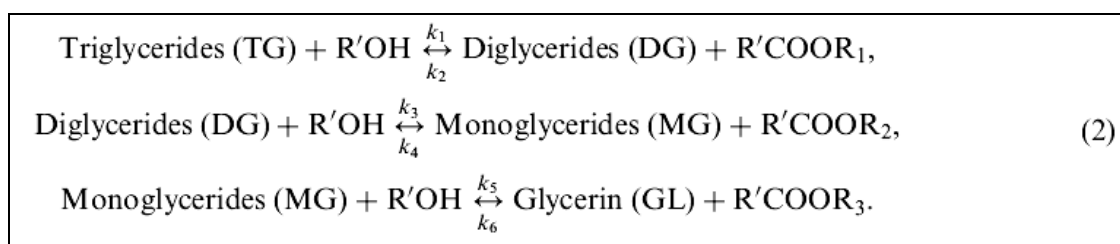


Figure 2.4: Reaction of transesterification

The overall process is normally a sequence of three consecutive steps, which are reversible reactions. In the first step, from triglycerides diglyceride is obtained, from diglyceride monoglyceride is produced and in the last step, from monoglycerides glycerin is obtained. In all these reactions esters are produced. The stoichiometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product:

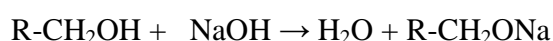


Transesterification reaction can be alkali-catalyzed, acid-catalyzed (Bunyakiat et al., 2006). An excess of methanol is used to shift the reaction to the right side in order to achieve high yield of methyl esters or biodiesel.

2.6.2 Catalyst

2.6.2.1 Alkali catalyst

For a basic catalyst, either sodium hydroxide (NaOH) or potassium hydroxide (KOH) should be used with methanol or ethanol as well as any kind of oils, refined, crude or frying. In this process, it is better to produce the Alcoxy before the reaction to obtain a better global efficiency. The alcoxyl reaction is,



The amount of catalyst that should be added to the reactor varies from 0.5% to 1% w/w [Barnwall, Sharma; 2005, Srivastava; 2004], but some authors prefer advice any values between 0.005% and 0.35% w/w [Hanna; 1990] should be used. Truck *et.al* has investigated the negative influence of base catalyzed transesterification of triglycerides containing substantial amount of free fatty acids. Free fatty acids react with the basic catalyst added for the reaction and give rise to soap, as a result, one part of the catalyst is neutralized and is therefore no longer available for transesterification.

These high FFA content oils/fats are processed with an immiscible basic glycerol phase by means of monovalent alcohols. The triglycerides are subjected to transesterification, using base as a catalyst, to form fatty acid alkyl ester, characterized after its separation, the basic glycerol phase during transesterification the triglycerides is used for processing the oils/fats for removal of free fatty acids. Most studies of the basic-catalyzed transesterification of vegetable oils involve the calculations of the triglyceride conversion rate, the changes in product composition during reaction or some of the quality parameters of biodiesel. [Feuge and Gros, 1949; Fredman *et. al.*, 1984, 1986; Schwab *et.al.* 1987]. Alkali process can achieve high purity and yield of biodiesel product in a short time (30-60 min) [Freedman, Butterfield; 1986, Darnoko; 2000, Mittlebach; 1990].

2.6.2.2 Acid catalyst

This way of production is the second conventional way of making the biodiesel. The suggestion is to use the triglycerides with alcohol and instead of a base to use an acid. The most commonly used is sulfuric acid [Freedman, Pryde; 1984, Freedman, Butterfield; 1990, Harrington; 1985] and some authors prefer sulfonic acid [Stern; 1990]. This type of catalyst gives very high yield in esters but the reaction is very slow, requiring almost more than one day to finish. Freedman and Pryde [Freedman,Butterfield;1990] get the desirable product with 1 mol% of sulfuric acid with a molar ratio of 30:1 at 65°C and they get 99% of conversion in 50h, while the butanolysis will need 117°C and the ethanolysis 78°C but the times should be 3 and 18h, respectively. An acidic catalyst such as sulfuric acid slowly catalyzes the transesterification of triglycerides. Alkaline metal hydroxides, such as KOH and NaOH are preferred as the basic catalysts. Most industries use pre-treatment step to reduce the free fatty acid and water content of the feed stream. Usually, free fatty acid is reduced via an esterification reaction with methanol in the presence of sulfuric acid. The pre-treatment step not only causes the production process to be less efficient (Kusdiana and Saka, 2004) but also increase the capital cost. Also, the combined process with acid catalyzed pre-treatment was developed to improve the yield of biodiesel by the waste cooking oil. The pretreated step of this process was to esterify the free fatty acid with methanol by acid catalysis. When the free fatty acid content was lower than 0.5%, the sulfuric acid was drained and the solid alkali was introduced into the system to complete the transesterification [Harrington;1985,Perez;2003]. However, there has several disadvantages of this process such as long reaction time, no recovery of catalyst and high cost of reaction equipment [Nelson;1996]. To overcome the disadvantages of acid catalyzed process or pretreatment, the homogeneous Lewis acid catalyst (carboxylic salts) was used [Shimada; 2003].

2.6.2.3 Enzyme

Lipases are enzymes used to catalyze some reaction such as hydrolysis of glycerol, alcoholysis, but it has been discovered that they can be used as catalyst for transesterification and esterification reactions too. Biocompatibility, biodegradability and environmental acceptability of the biotechnical procedure are the desired properties in agricultural and medical applications. The extra cellular and the intracellular lipases are also able to catalyze the transesterification of triglycerides effectively. It took 34 hour to convert 97.3% of tryglycerides of the refined vegetable oil to fatty acid methyl ester in a two-step batch enzymatic process. While the waste cooking oil was used as reactant, the conversion of the oil was only 90.4% by a three-catalyzed process with 48 hours.

Table 2.4 Advantages and disadvantages of using lipases.

ADVANTAGES	DISADVANTAGES
1. Possibility of regeneration and reuse of the immobilized residue, because it can be left in the reactor if you keep the reactive low	1.Can lose some initial activity due to volume of the oil molecule
2. Use of enzymes in reactors allows use of high concentration of them that makes for a longer activation of the lipases	2.Number of support enzyme is not uniform
3. A bigger thermal stability of the enzyme due to the native state	3.Biocatalyst is more expensive that the natural enzyme

4. Immobilization of lipase could protect it from the solvent that could be used in the reaction and that will prevent all the enzymes particles getting together.	
5. Separation and product will be easier using this catalyst [15]	

CHAPTER 3

METHODOLOGY

3.1 Overall methodology

The overall method involved two major steps; preparation of biodiesel analysis on biodiesel. In preparing biodiesel, waste cooking oil has to undergo pre-treatment process before mixing with methanol in the presence of acid and alkali catalyst. Mixture will separate into two layers, the upper layer was methyl ester and lower layer was glycerol. Then, water was washed by water to remove soap. Biodiesel was analyzed to determine the quality and the purity of biodiesel.

3.2 Material

Sample of biodiesel which is waste cooking oil was collected from rehabilitation centre at gambang and UMP café. After the filtration of sample, sample was taken to analyze the purity by GC.

3.2 Experimental work

The sample of waste cooking oil (WCO) was mixed with methanol and acid sulfuric (H_2SO_4) with molar ratio are 10:1. WCO that has mixed with catalyst was recovered in water bath with temperature is 95°C and the reaction time was 4 hours. Crude biodiesel will undergo gravity settling process about 17 hours. The mixture was left to settle to separate into two layers. The upper oil layer was the FAME (biodiesel) and unreacted triglyceride that was subjected to the second step transesterification and the down layer was water with H_2SO_4 . The collected oil layer was transferred to a 250ml round bottom neck flask. The mixture was reacted at with 5 levels of reaction temperature (40, 50, 60, 70, 80°C), five levels of catalyst concentration (NaOH), 0.2, 0.4, 0.6, 0.8, 1.0 % with mole ratio is 6:1. The excess of methanol will settle in gravity settling about 17 hours. Then, the mixture was left to settle to separate into two layers. The upper layer was the methyl ester with the lighter colour and the down layer was the glycerol. The crude biodiesel was washed by 10% of water to remove soap which was produced by reaction of the alkali and free fatty acid.

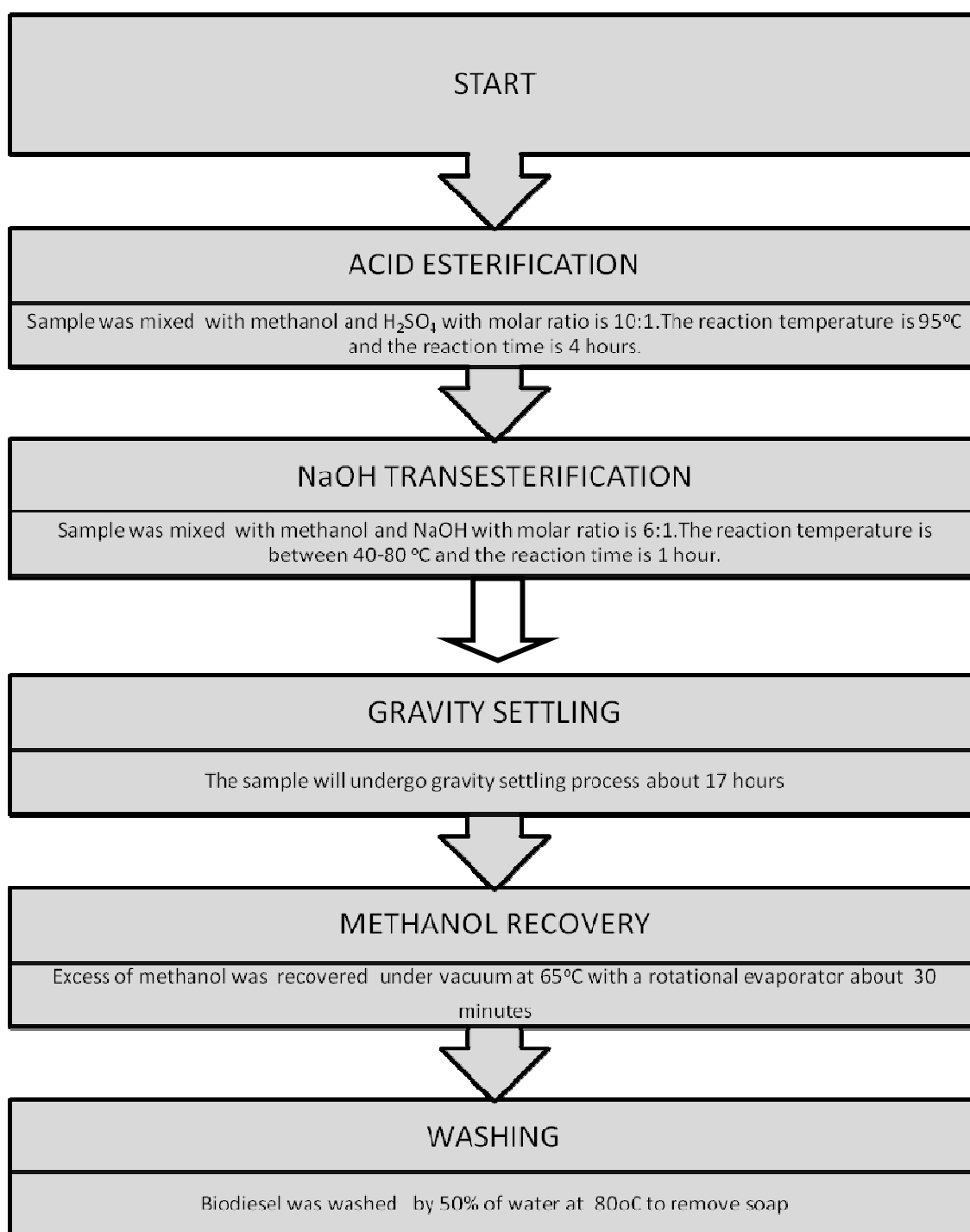


Figure 3.1: Flow Diagram of experimental work

3.2 Analysis on biodiesel

a) Yield

The yield of biodiesel can be calculated by taking the volume of raw material and volume of methyl ester after washing.

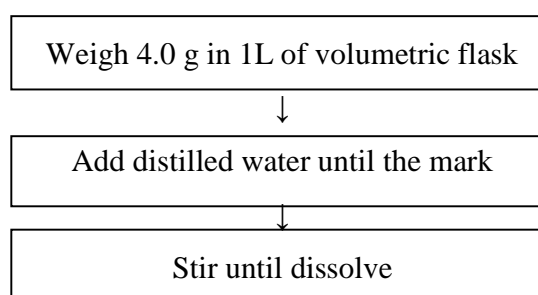
$$\text{BD yield} = \frac{\text{Volume of FAME (biodiesel)}}{\text{Volume of raw material}} \times 100\%$$

b) Free fatty acid

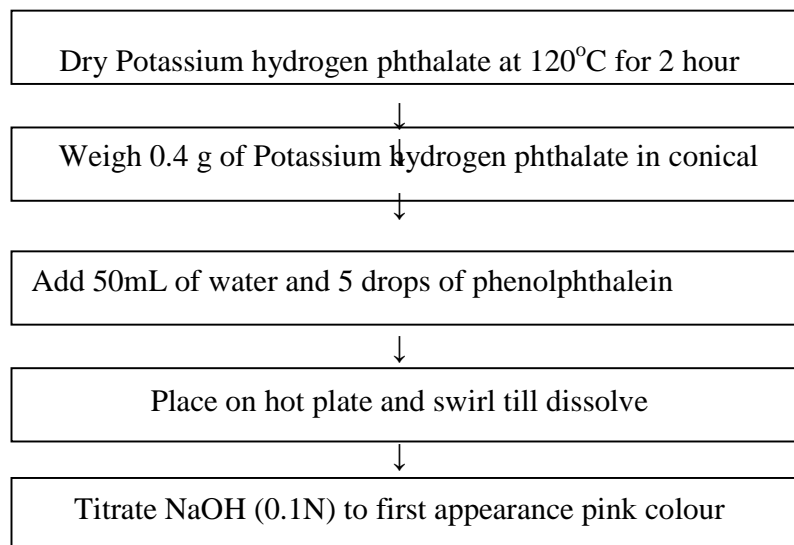
Specifically, it is used titrimetric method for the determination of acidity in palm oil and palm oil products. The acidity is usually expressed as free fatty acid content or alternatively acid value. The sample has to ensure that is taken is stored away from strong light, kept cool and contained in completely filled glass containers. To calculate free fatty acid,

Free fatty acid and acid value analysis

i) Preparation of NaOH



ii) Standardize NaOH (0.1N)



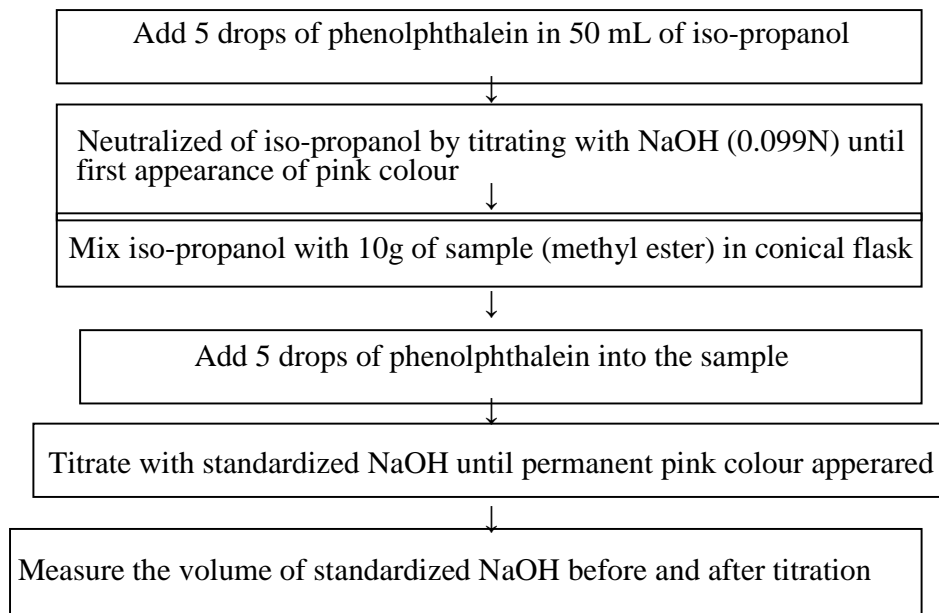
Calculation:

$$\text{Molarity of alkali} = \frac{M \times 1000}{V \times 204.2}$$

M = mass, in grams of phthalate taken

V = volume in mL of NaOH

iii) Titration of biodiesel



Calculation:

$$\text{FFA} = \frac{25.6 \times 0.099\text{N} \times (\text{A}-\text{B})}{\text{wt of sample}}$$

$$\text{Acid value} = \frac{56.1 \times 0.099\text{N} \times (\text{A}-\text{B})}{\text{wt of sample}}$$

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Results

Raw material = 2.046 mg NaOH/g of FFA,
= 4.480 mg NaOH/g of AV

After acid esterification = 1.314 mg NaOH/g of FFA,
= 2.890 mg NaOH/g of AV

Total reduction= 35.77%

a) For first phase:

Fix parameter : Catalyst concentration (1 %wt), reaction time (1 hour)

Manipulate parameter: Reaction temperature (40-80°C)

Sample	Temperature (°C)	Yield (%)	Free Fatty acid (mg NaOH/g)	Acid Value (mg NaOH/g)
1	40	72	0.127	0.277
2	50	80	0.127	0.277
3	60	60	0.101	0.222
4	70	60	0.100	0.221
5	80	62	0.076	0.166

b) For second phase

Fix parameter : Reaction temperature (80°C), reaction time (1 hour)

Manipulate parameter: Catalyst concentration (0.2-1.0 % wt)

Sample	Catalyst concentration (%wt)	Yield (%)	Free Fatty acid (mg NaOH/g)	Acid Value (mg NaOH/g)
1	0.2	52	0.176	0.388
2	0.4	47	0.151	0.333
3	0.6	52	0.126	0.277
4	0.8	46	0.101	0.222
5	1.0	62	0.076	0.166

4.2 Discussions

First phase:

i) Yield

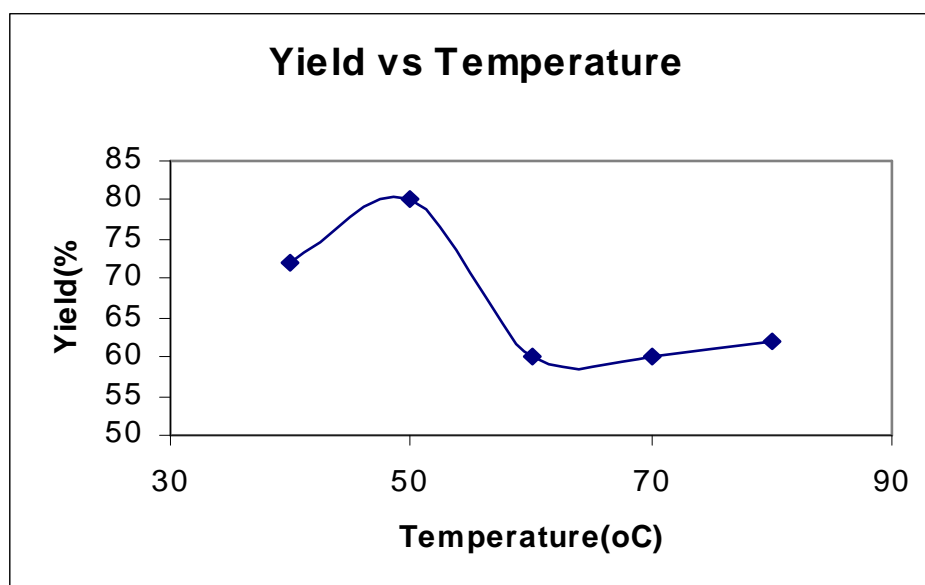


Figure 4.1: Graph temperature (°C) vs yield (%)

Figure 4.1 shows that the highest yield achieved when the reaction temperature was 50°C and the lowest temperature achieved at 80°C. When increasing the temperature, it will give the negative impact on ester yield due to acceleration of saponification. But, increasing the temperature can complete the conversion in shorter time and the higher purity can be achieved at higher temperature.

ii) Free fatty acid

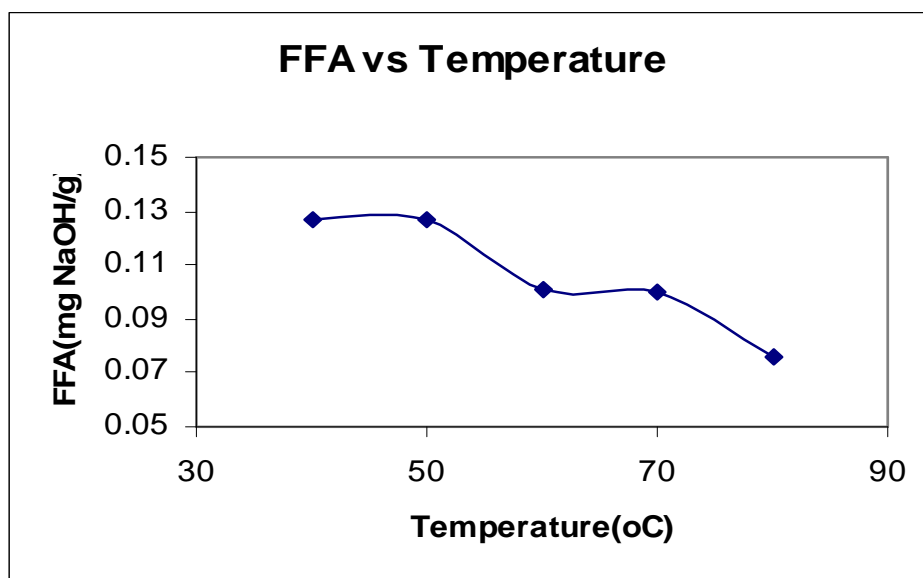


Figure 4.2: Graph temperature (°C) vs FFA content (NaOH mg/g)

Figure 4.2 shows the response on free fatty acid to temperature. The highest free fatty acid content achieved when the reaction temperature was 80°C, which about 0.076 NaOH mg/g. And, the lowest free fatty acid content achieved when the reaction temperature was approximately 40°C, which about 0.127 NaOH mg/g. When the temperature increases, free fatty acid content in waste cooking oil decreases and vice versa because increasing the temperature can increase the reaction rate of transesterification and freer fatty acid can be removed. So, shorter reaction time was needed for completion due to highest reaction rate at 80°C.

iii) Acid Value

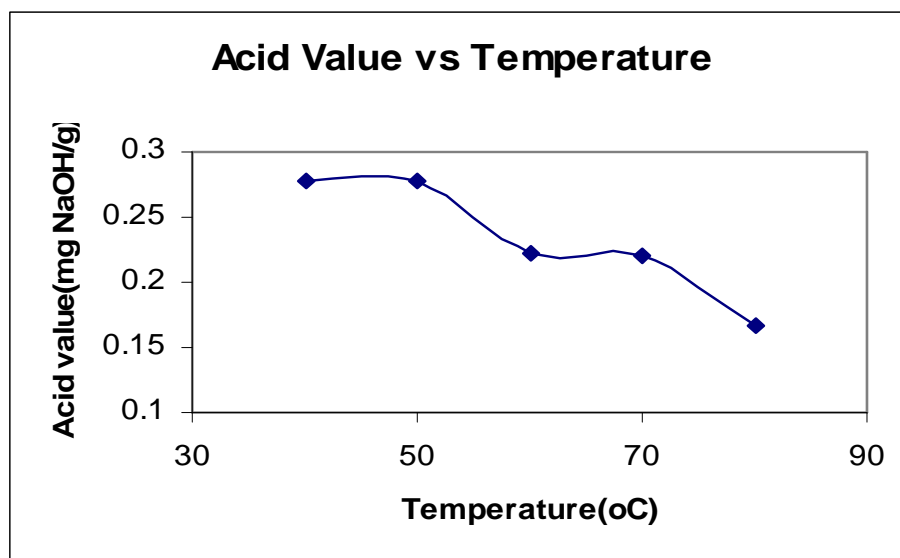


Figure 4.3: Graph temperature (°C) vs acid value (NaOH mg/g)

Figure 4.3 shows that the highest acid value content achieved when the reaction temperature was 80°C, which about 0.166 NaOH mg/g. And, the lowest acid value content achieved when the reaction temperature was 40°C, which about 0.277 NaOH mg/g. So, when the temperature increases, the acid value content in waste cooking oil was reduced and vice versa because increasing the temperature can increase the reaction rate of transesterification and more acid can be removed. But, insufficient amount of catalyst can cause soap formation. Adding more sodium hydroxide can compensate higher acidity.

Second phase:

i) Yield

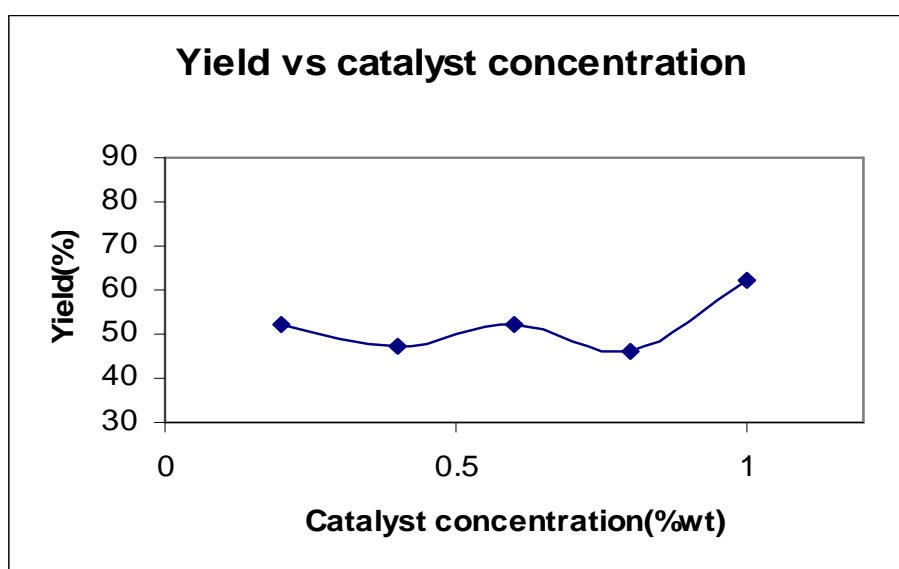


Figure 4.4: Graph catalyst concentration (%wt) vs yield (%)

Figure 4.4 shows that the highest yield achieved when the catalyst concentration was 1wt% and the lowest yield achieved when the catalyst concentration was 0.2 wt%. When increasing the catalyst concentration, the yield increases because it can accelerate the transesterification process. But, insufficient amount of catalyst can lead to saponification and more soap would be produced.

ii) Free fatty acid

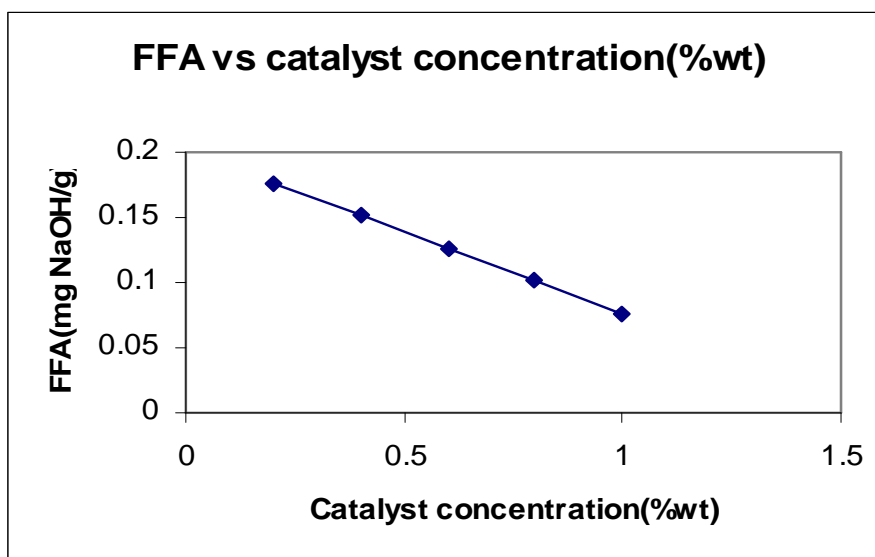


Figure 4.5: Graph catalyst concentration (%wt) vs FFA content (NaOH mg/g)

Figure 4.5 shows that the highest free fatty acid content achieved when the catalyst concentration was 1wt%, which approximately 0.076 NaOH mg/g. And, the lowest free fatty acid content achieved when the catalyst concentration was 0.2 wt%, which about 0.387 NaOH mg/g. When NaOH concentration increases, the conversion of tryglycerides also will increased and freer fatty acid can be removed. However, insufficient amount of NaOH resulted in incomplete conversion of tryglycerides into the esters as indicated from its lower ester content. This might happen because, addition of excess alkaline catalyst such as NaOH, caused more tryglycerides participating reaction with NaOH producing more soap, thereby reducing the ester yield

iii) Acid value

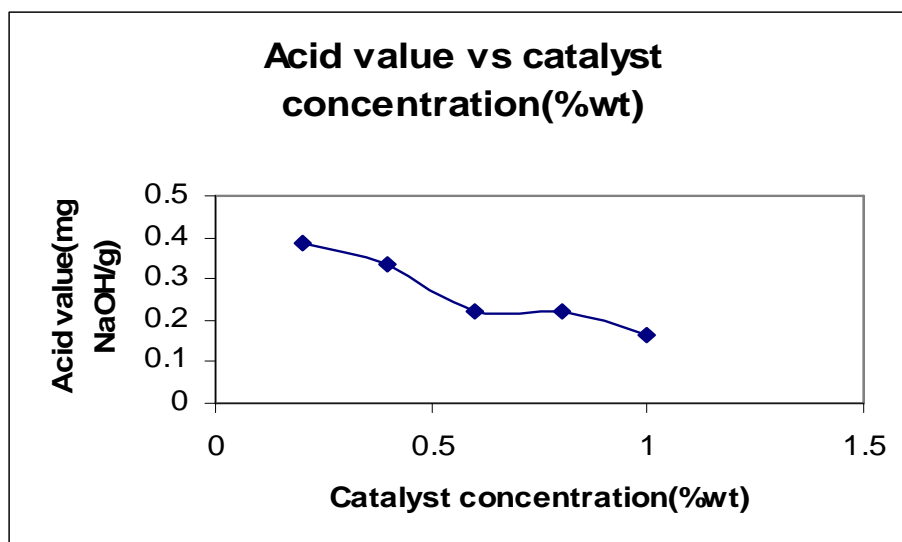


Figure 4.6: Graph catalyst concentration (% wt) vs acid value (NaOH mg/g)

Figure 4.6 shows that the highest acid value content achieved when the reaction temperature was 80°C, which about 0.166 NaOH mg/g. And, the lowest acid value content achieved when the reaction temperature was 40°C, which about 0.277 NaOH mg/g. When the temperature increases, acid value content in waste cooking oil can be reduce and vice versa because adding more catalyst can reduce acid value content in waste cooking oil.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Biodiesel that is produced from vegetable oils can be used as an alternative diesel fuels because its properties are similar to the conventional diesel. In our research, we have chosen two-step catalyzed transesterification process to improve the yield of biodiesel by the waste cooking oil. Biodiesel produced by transesterification reactions can be catalyzed with acid, alkali or enzyme. But, the former two types have received more attention due to their short reaction time and have lower cost

From the research and experiment that has been conducted, the study on the two step batch catalyzed indicated that the reaction temperature and catalyst concentration were the main factors affecting the reaction. When increasing the temperature, the yield is decreased because of acceleration on saponification but the purity is higher if compared to low temperature that the highest yield achieved when the reaction temperature was 50°C and the lowest temperature achieved at 80°C Besides that, free fatty acid and acid value can be removed better when increasing the temperature because when increasing the temperature, the reaction rate of transesterification is

The highest free fatty acid content achieved when the reaction temperature was 80°C, which about 0.076 NaOH mg/g. And, the lowest free fatty acid content achieved when the reaction temperature was approximately 40°C, which about 0.127 NaOH mg/g. that the highest acid value content achieved when the reaction temperature was 80°C, which about 0.166 NaOH mg/g. And, the lowest acid value content achieved when the reaction temperature was 40°C, which about 0.277 NaOH increased and freer fatty acid and acid value can be removed. So, shorter reaction time is needed for completion due to highest reaction rate at 80°C.

Other than that, analysis also has proved the effects of catalyst concentration to the ester yield, FFA and acid value content. The highest yield achieved when the catalyst concentration was 1wt% and the lowest yield achieved when the catalyst concentration was 0.2 wt%. When increasing the catalyst concentration, the yield is increased because it can accelerate the transesterification process. But, insufficient amount of NaOH resulted in incomplete conversion of tryglycerides into the esters as indicated from its lower ester content can lead to saponification and more soap would be produced.

Moreover, the highest free fatty acid content achieved when the catalyst concentration was 1wt%, which approximately 0.076 NaOH mg/g. And, the lowest free fatty acid content achieved when the catalyst concentration was 0.2 wt%, which about 0.387 NaOH mg/g. And, the highest acid value content achieved when the reaction temperature was 80°C, which about 0.166 NaOH mg/g. And, the lowest acid value content achieved when the reaction temperature was 40°C, which about 0.277 NaOH. When NaOH concentration increases, the conversion of tryglycerides also will increased and freer fatty acid and acid value can be removed

5.2 Recommendation

5.2.1 Analysis by gas chromatography

Using gas chromatography to analyze biodiesel can ensure the data that we get is more accurate. For biodiesel, GC can determine the amount of glycerol, mono and diglycerols and methyl esters in biodiesel sample.

5.2.2 Using mechanical stirrer in shaking water bath

Efficiency in shaking water bath can be improved by using mechanical stirrer to mix completely the mixture.

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Calculation:

$$\text{BD yield} = \frac{\text{Volume of FAME (biodiesel)}}{\text{Volume of raw material}}$$

Sample 1 (40°C):

$$\begin{aligned}\text{BD yield} &= \frac{180 \text{ ml}}{250 \text{ ml}} \times 100\% \\ &= 72\%\end{aligned}$$

Sample 2 (50°C):

$$\begin{aligned}\text{BD yield} &= \frac{200 \text{ ml}}{250 \text{ ml}} \times 100\% \\ &= 80\%\end{aligned}$$

Sample 3 (60°C):

$$\begin{aligned}\text{BD yield} &= \frac{150 \text{ ml}}{250 \text{ ml}} \times 100\% \\ &= 60\%\end{aligned}$$

Sample 4 (70°C):

$$\begin{aligned}\text{BD yield} &= \frac{150 \text{ ml}}{250 \text{ ml}} \times 100\% \\ &= 60\%\end{aligned}$$

ii) Free Fatty Acid

$$\text{FFA} = \frac{(25.6) (N) (A-B)}{W_t}$$

Sample 1 (40°C):

$$\begin{aligned} \text{FFA} &= \frac{(25.6) (0.099) (30.0-29.5)}{10.009} \\ &= \underline{\underline{0.1267 \text{ mg NaOH/g}}} \end{aligned}$$

Sample 2 (50°C):

$$\begin{aligned} \text{FFA} &= \frac{(25.6) (0.099) (30.0-29.5)}{10.009} \\ &= \underline{\underline{0.1267 \text{ mg NaOH/g}}} \end{aligned}$$

Sample 3 (60°C):

$$\begin{aligned} \text{FFA} &= \frac{(25.6) (0.099) (30.0-29.5)}{10.009} \\ &= \underline{\underline{0.101 \text{ mg NaOH/g}}} \end{aligned}$$

Sample 4 (70°C):

$$\begin{aligned} \text{FFA} &= \frac{(25.6) (0.099) (30.0-29.6)}{10.009} \\ &= \underline{\underline{0.100 \text{ mg NaOH/g}}} \end{aligned}$$

Sample 5 (80°C):

$$\begin{aligned} \text{FFA} &= \frac{(25.6) (0.099) (30.0-29.7)}{10.009} \\ &= \underline{\underline{0.076 \text{ mg NaOH/g}}} \end{aligned}$$

iii) Acid Value

$$\text{Acid Value} = \frac{(25.6) (N) (A-B)}{W_t}$$

Sample 1 (40°C):

$$\text{Acid Value} = \frac{(25.6) (0.099) (30.0-29.)}{10.009}$$

$$= 0.277 \text{mg } \underline{\text{NaOH/g}}$$

Sample 2 (50°C):

$$\text{Acid Value} = \frac{(25.6) (0.099) (30.0-29.)}{10.009}$$

$$= 0.277 \text{mg } \underline{\text{NaOH/g}}$$

Sample 3 (60°C):

$$\text{Acid Value} = \frac{(25.6) (0.099) (30.0-29.6)}{10.009}$$

$$= 0.222 \underline{\text{mg NaOH/g}}$$

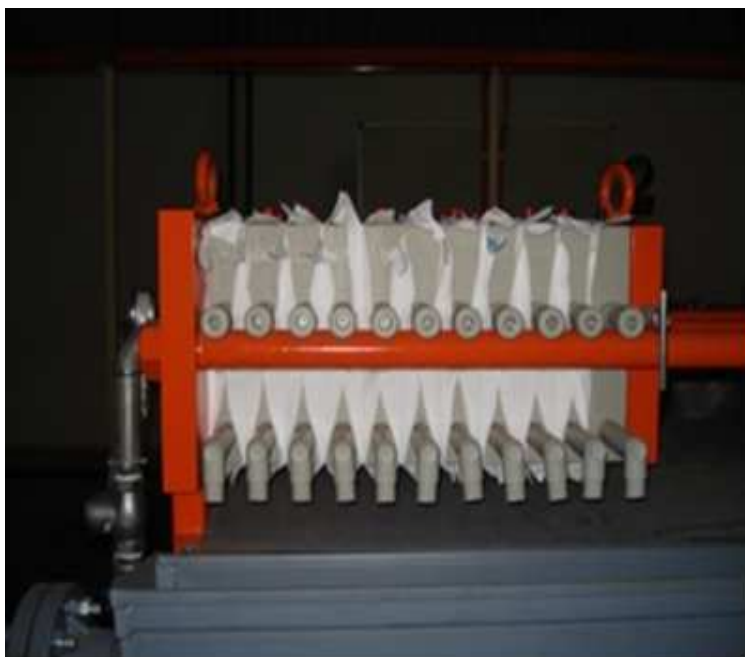
Sample 4 (70°C):

$$\text{Acid Value} = \frac{(25.6) (0.099) (30.0-29.6)}{10.009}$$

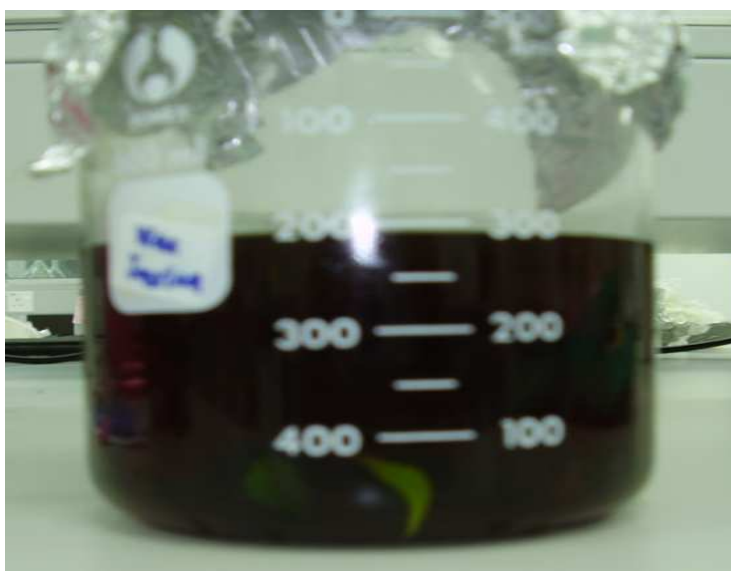
$$= 0.222 \text{mg } \underline{\text{NaOH/g}}$$

Sample 5 (80°C):

$$\text{Acid Value} = \frac{(25.6) (0.099) (30.0-29.)}{10.009}$$
$$= 0.166 \text{ mg NaOH/g}$$



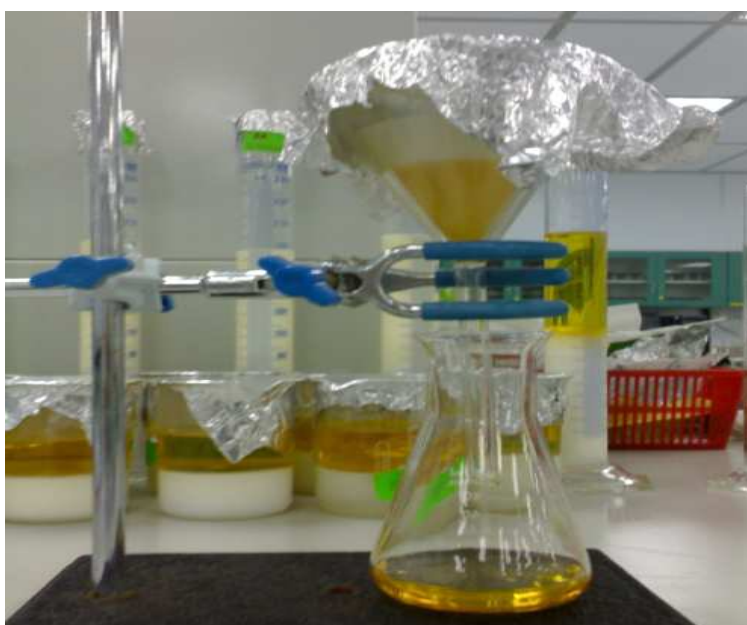
Filter press to remove any contaminants in waste cooking oil.



Sample of methyl ester after first step process



Sample of methyl ester after second step process



Separation of methyl ester



Methanol recovery at 65°C with a rotational evaporator about 30 minutes.



Biodiesel was washed by 50% of water at 80°C to remove soap



Product collection

