## PREPARATION OF BIODIESEL FROM WASTE COOKING OIL AND REFINES BLEACHED DEODORIZED OIL USING SINGLE STEP BATCH TRANSESTERIFICATION PROCESS WITH THE AID OF KOH AS THE CATALYST

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

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#### DECLARATION

"I declare that this thesis entitled "PREPARATION OF BIODIESEL FROM WASTE COOKING OIL AND REFINES BLEACHED DEODORIZED OIL USING SINGLE STEP BATCH TRANSESTERIFICATION PROCESS WITH THE AID OF KOH AS THE CATALYST" is the result of my own research and findings except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any degree.

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Date	: 30 <sup>th</sup> April 2009

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The last dedication of this book is dedicated to each of Biodiesel group member. Thank you for the most challenging one year of education life we've been together. For sticking together until the very end.

#### Wassalam

#### ABSTRACT

Biodiesel is a cleaner burning diesel replacement fuel processed from natural, renewable derived from biological sources such as waste cooking oil and refined bleached deodorized palm oil. The type of process that needs to be done to produce biodiesel is called transesterification. The transesterification of waste cooking oil and refined bleached deodorized palm oil with short-chain alcohols, in the presence of basecatalyst potassium hydroxide (KOH) and methanol as solvent, by means of single step batch transesterification process in order to obtain biodiesel fuel was studied. The reaction has been done in water bath. The process variables that been investigated are catalyst concentration and reaction time. The variables that are fixed throughout the whole experiment were molar ratio of methanol to raw oil with 6: 1, reaction temperature at 40°C and mixing degree of mechanical stirrer at 1300 rpm. This paper also studied the combustion characteristic which is the carbon monoxide emission between WCO and RBD to be compared with conventional diesel, and determined the optimal transesterification reaction conditions that produce the maximum methyl ester content or purity and biodiesel yield. The best result for highest yield and highest purity is at 60 minutes reaction time and using 1.5% catalyst concentration

#### ABSTRAK

Biodiesel adalah sumber minyak yang lebih bersih yang boleh menggantikan diesel dan boleh didapati dari sumber biologi yang semulajadi seperti minyak masak terpakai dan minyak masak kelapa sawit. Proses yang diperlukan untuk menghasilkan biodiesel dipanggil transesterifikasi. Proses transesterifikasi dijalankan untuk minyak masak terpakai dan juga minyak masak kelapa sawit dengan campuran pemangkin alkali iaitu Kalium Hidroksida (KOH) dan methanol sebagai pelarut. Tindakbalas ini di lakukan di dalam besen air. Proses ini dinamakan proses transesterifikasi langkah pertama untuk mendapatkan biodiesel. Faktor-faktor yang mempengaruhi transesterifikasi trigliserida adalah seperti kepekatan pemangkin dan tindakbalas masa akan dikaji. Factor-faktor yang telah ditetapkan sepanjang eksperimen adalah nisbah molar methanol kepada minyak iaitu 6:1, tindakbalas suhu pada 40°C dan juga darjah kacauan sebanyak 1300 rpm oleh pengacau mekanikal. Kertas kajian ini juga mengkaji ciri-ciri pembakaran iaitu pembebasan karbon monoksida antara minyak masak terpakai dan minyak sawit mentah dengan diesel. Selain itu, kondisi tindakbalas transesterifikasi yang optima yang menghasilkan kandungan kepekatan metal ester dan kadar hasilan biodiesel yang optima juga akan dikaji. Keputusan terbaik diperoleh pada masa tindakbalas 60 minit dan kepekatan pemangkin pada 1.5%.

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## LIST OF ABBREVIATIONS

°C	Degree celcius
FFA	Free fatty acid
h	Hour
min	minutes
g	gram
kg	kilogram
L	Liter
ml	mililiter
ppm	parts per million
КОН	Potassium Hydroxide
WCO	Waste Cooking Oil
WVO	Waste Vegetable Oil
RBD	Refined Bleached Deodorized Oil
FAME	Fatty acid methyl ester
NOx	Nitrogen Oxide
$CO_2$	Carbon Dioxide
HC	Hydrocarbon

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#### **CHAPTER 1**

#### **INTRODUCTION**

#### **1.1 Introduction**

The world consumption of fuels is undoubtedly unstable causing world economic crisis; the worst compared to other economic recession that took place at different era. This factor has urged all nations especially the government and the academics to find another alternatives to replace the usage of petroleum. Therefore there is a rising demand to globally provide renewable energy by means of a sustainable and ethical approach. Sustainable development is a concept that has become significant and increases the awareness of its necessity.

There are many alternatives nowadays. There is three generation of biofuel. First-generation biofuels are biofuels made from sugar, starch, vegetable oil, or animal fats using conventional technology. These feedstocks could instead enter the animal or human food chain, and as the global population has risen their use in producing biofuels has been criticised for diverting food away from the human food chain, leading to food shortages and price rises. Second generation biofuel production processes are in development. These allow biofuel to be derived from any source of biomass, not just from food crops such as corn and soy beans but also from waste cooking oil. Algae fuel, also called oilgae or third generation biofuel, is a biofuel from algae.

#### **1.2 Background of Study**

Biodiesel is a fuel made from natural, renewable sources, such as new and used vegetable oils and animal fats, for use in a diesel engine. Biodiesel has physical properties very similar to petroleum-derived diesel fuel, but its emission properties are superior. Using biodiesel in a conventional diesel engine substantially reduces emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter. Diesel blends containing up to 20% biodiesel called B20 can be used in nearly all diesel-powered equipment, and higher-level blends and pure biodiesel, B100 can be used in many engines with little or no modification. Lower-level blends are compatible with most storage and distribution equipment, but special handling is required for higher-level blends.

One of the most used renewable energy is biodiesel which is the most common biofuel in Europe. It is produced from oils or fats using transesterification and is a liquid similar in composition to mineral diesel. Its chemical name is fatty acid methyl ester (FAME). In our study, oils are mixed with potassium hydroxide KOH as catalyst and methanol and the chemical reaction produces biodiesel (FAME) and glycerol. 1 part glycerol is produced for every 10 parts biodiesel.

Biodiesel can be used in any diesel engine when mixed with mineral diesel. In some countries manufacturers cover their diesel engines under warranty for 100% biodiesel use. Many people have run their vehicles on biodiesel without problems. However, the majority of vehicle manufacturers limit their recommendations to 15% biodiesel blended with mineral diesel. In many European countries, a 5% biodiesel blend , B5 is widely used and is available at thousands of gas stations. Biodiesel can be made from waste and virgin vegetable and animal oil and fats (lipids). Virgin vegetable oils can be used in modified diesel engines. In fact the diesel engine was originally designed to run on vegetable oil rather than fossil fuel. There are also studies and efforts to commercialize biodiesel from algae.

#### **1.3 Problem Statement**

Petroleum price is undoubtedly agreed to be very unstable. At some point the price roars to maximum price at \$145 per barrel. Then it decrease till \$40 per barrel. This sort of trend has affected the world economic growth. Each human being in this mother earth can feel the effect of economic crisis that is mainly caused by unstable price of petroleum. Thus, by using biodiesel as alternative, the problem could be tackle.

Malaysia is famously known as one of the nett producer of palm oil. It has the potential to lead the way in biofuel production looking at its vast production of palm oil. By using Refined-Bleached-Deodorized (RBD) palm oil, Malaysian would have a consistent supply and provision to replace the usage of diesel petroleum. Besides palm oil is also one of the most highly efficient feedstock for biodiesel compared to other vegetable oils. (Ang, Catharina Y. W., KeShun Liu, et al, 1999)

Another raw material that will be use in the research is waste cooking oil. It seems as a practical way for waste cooking oil (WCO) to be converted as biodiesel as it will give a comparable and cheap price than subsidized diesel. Furthermore, the usage of waste cooking oil will promote into a cleaner environment because the water and land will be less polluted by waste cooking oil. But the main problem of using waste cooking oil is the existence of free fatty acid as the by product in transesterification process.

Thus the aim of this project is to produce biodiesel as diesel substitute at a feasible way. The research of which types of feedstock is the best have to be conduct. The result of the study will provide a clear picture as to which feedstock will be sustainable in alleviating the energy crisis.

Single step transesterification process will be used in synthesizing raw material to methyl ester. Single step transesterification process provides less time in reaction, lower temperature and pressure, and hence will result in less cost of production. The high content of free fatty acid in waste cooking oil need to be synthesize by using homogenous catalyst, Potassium Hydroxide (KOH). Even though the use of homogenous catalyst resulted in higher formation of soap, homogenous catalyst provides shorter reaction time compare to heterogeneous. In the transesterification process, methanol will be use as alcohol solvent because of its price is cheaper among other alcohol solvent.

#### **1.4 Objective**

Aim of this project is to determine the best condition in producing biodiesel with high purity of methyl ester and environmental friendly biodiesel, from Refined Bleached Deodorized palm oil and Waste Cooking Oil by using single step batch transesterification process.

#### **1.5 Scope of Research**

In order to achieve the objective, three scopes have been identified to be studied in this experiment. They are:

- To study the effect of catalyst concentration and reaction time from both Refined-Bleached-Deodorized (RBD) palm oil and waste cooking oil (WCO) by using single step transesterification process.
- ii. To analyze methyl ester concentration or purity by using Gas Chromatography.
- iii. To compare the combustion characteristic of biodiesel produced from both Refined-Bleached-Deodorized (RBD) palm oil and waste cooking oil (WCO) with standard diesel by usong gas analyzer.

In the research that will be conducted, we will fix the temperature at 40°C. While the catalyst concentration used is between 0.5, 0.75, 1.0 and 1.5wt% and the time that be conducted is from 30, 40, 50 and 60 minutes.

#### **CHAPTER 2**

#### LITERATURE REVIEW

#### 2.1 Biodiesel

Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which conform to American Society for Testing and Materials, ASTM D6751 specifications for use in diesel engines. It is a clean burning alternative fuel, produced from domestic, renewable resources. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics. Biodiesel is made through a chemical process called transesterification whereby the glycerin is separated from the fat or vegetable oil. The process leaves behind two products: methyl esters or biodiesel and glycerin.

Biodiesel is much cleaner than fossil-fuel diesel. It can be used in any diesel engine with no need for modifications. In fact diesel engines run better and last longer with biodiesel. And it can easily be made from common waste product, used cooking oil. Biodiesel is better for the environment because it is made from renewable resources and has lower emissions compared to petroleum diesel (UNH Biodiesel Group). It is less toxic than table salt and biodegrades as fast as sugar.

#### 2.1.1 Biodiesel emission and engine relation

A major benefit of biodiesel is lower emissions. The use of biodiesel reduces emission of carbon monoxide and other hydrocarbons by 20 to 40%. Biodiesel burns up to 75% cleaner than conventional petroleum diesel fuel. Biodiesel reduces unburned hydrocarbons (-93%), carbon monoxide (-50%) and particulate matter (-30%) in exhaust fumes, as well as cancer-causing PAH (-80%) and nitrited PAH compounds (-90%). (US Environmental Protection Agency).

Sulphur dioxide emissions are eliminated as biodiesel contains no sulphur. Biodiesel is plant-based and using it adds no extra  $CO_2$  to the atmosphere. The ozoneforming (smog) potential of biodiesel emissions is nearly 50% less than petro-diesel emissions. Nitrogen oxide (NOx) emissions may increase or decrease but can be reduced to well below petrol-diesel fuel levels. Biodiesel exhaust is not offensive and does not cause eye irritation. Biodiesel is environmentally friendly, it is renewable, "more biodegradable than sugar and less toxic than table salt" (US National Biodiesel Board, based on US Environmental Protection Agency studies).

Biodiesel is a much better lubricant than petro-diesel and extends engine life. Even a small amount of biodiesel means cleaner emissions and better engine lubrication. 1% biodiesel added to petro-diesel will increase lubricity by 65% (UNH Biodiesel Group). Biodiesel can be mixed with petrol-diesel in any proportion, with no need for a mixing additive. Biodiesel has a higher cetane number than petroleum diesel because of its oxygen content. The higher the cetane number the more efficient the fuel, the engine starts more easily, runs better and burns cleaner. With slight variations depending on the vehicle, performance and fuel economy with biodiesel is the same as with petrol-diesel.

#### **2.1.2 Biodiesel Properties**

Table 2.1 shows a comparison of chemical properties and fatty acid composition (%) of WCO and RBD palm oil. Both results are varies. Fatty acid is a carboxylic acid often with a long unbranched aliphatic tail (chain). These long-chain fatty acids generally have an even number of carbon atoms; unbranched chains predominate over branched chains. They may be saturated (e.g. palmitic (hexadecanoic) acid and stearic (octadecanoic) acid) or unsaturated, with one double bond (e.g. oleic (cis-octodec-9-enoic) acid) or two or more double bonds, in which case they are called polyunsaturated fatty acids (e.g. linoleic acid and linolenic acid). As for specific gravity, WCO has higher specific gravity because it has much residue such as water as water has mixed inside the WCO as a result of condensation of cooking process. So, the density of WCO is higher compared to RBD palm oil.

Property	WCO	RBD Palm oil
Palmitic acid C16:0	16	44.3
Stearic acid C18:0	5.21	4.6
Oleic acid C18:1	34.28	38.7
Linoleic acid C18:2	40.76	10.51
Specific gravity	0.92	0.88

 Table 2.1: Comparison of chemical properties and fatty acid composition (%) of WCO and RBD palm oil

Table 2.2 shows major properties comparing between premium diesel and B100. The density for biodiesel is among 0.86 g/mL for RBD to 0.92 g/mL for WCO. Flash point is the temperature at which the vapour above a volatile liquid forms a combustible mixture with air. At the flash point the application of a naked flame gives a momentary flash rather than sustained combustion, for which the temperature is too low. So from

the table shown, biodiesel has higher flash point and it makes as an advantage because it would not easily vaporized to air compared to premium diesel. This will save the cost of fuel for transport especially if the temperature ambient is high. As for cetane number, a higher cetane number indicates greater fuel efficiency (Ya-fen Lin, Yo-ping Greg Wu and Chang-Tang Chang, 2006). In this case, B100 scores higher cetane number and it shows that the performance rating of a diesel fuel, corresponding to the percentage of cetane in a cetane-methylnaphthalene mixture with the same ignition performance.

	Premium diesel	B100	Test method
Density at 20 °C (g/mL)	0.826	0.86	ASTM D 1298
Kinematic viscosity at 40 °C (cSt)	2.73	4.49	ASTM D 445
Cetane index	46.2	48.05	EN ISO 4264
Flash point (°C)	89	122	ASTM D 93
Water and sediment (vol.%)	<1	0.22	ASTM D 2709
Gross Heating Value (cal/g)	11411.4	9850.6	ASTM D 240

**Table 2.2:** Major properties of premium diesel and biodiesel used in this study

From Table 2.3, some significant differences were found between Reference (REF) and biodiesel fuel. These differences are within the daily differences typically found in samples taken from urban collectors, and, in any case, they did not lead to any significant difference in ultimate composition and to very small differences in the unsaturation level (iodine number). The reference fuel (REF) is a typical low sulphur diesel fuel similar to those available in Spanish petrol stations in winter. It was supplied by Repsol YPF, and fulfils the current European norm EN-590. (Magín Lapuerta, José M. Herreros, Lisbeth L. Lyons, Reyes García-Contreras and Yolanda Briceño, 2008)

Properties	REF	WCO
Density at 15 °C (kg/m <sup>3</sup> )	834	887
Kinematic viscosity at 40 °C (cSt)	2.72	5.16
Gross heating value (MJ/kg)	45.54	39.26
Lower heating value (MJ/kg) <sup>a</sup>	42.49	36.59
Acid number (mg KOH/g)	0.10	0.55
% C (wt.)	86.13	76.95 <sup><u>b</u></sup>
% H (wt.)	13.87	12.14 <sup>b</sup>
% O (wt.)	0	10.91 <sup><u>b</u></sup>
Sulphur content (ppm wt.)	34	$0^{\underline{b}}$
Water content (ppm wt.)	57	466
IBP (°C)	172	320
T10 (°C)	211	325
T50 (°C)	270	333
T90 (°C)	340	356
Molecular weight	211.7 <sup><u>c</u></sup>	293.2 <sup>b</sup>
Stoichiometric fuel/air ratio	1/14.67	1/12.55
CFPP (°C)	-18	-6
Iodine number <sup>b</sup>	-	97.46
Renewable fraction	0	90.11 <sup>d</sup>

 Table 2.3: Specifications of biodiesel fuels

<sup>a</sup> Calculated from composition and gross heating value.

<sup>b</sup> Calculated from speciation.

<sup>c</sup> Calculated by Aspen-Advisor software.

<sup>d</sup> Calculated from waste cooking oil composition.

From Table 2.4, it shows that biodiesel sample meet EN14214 standards for density, kinematic viscosity, copper corrosion, acid value, cetane number, free glycerol and total glycerol. There was slight difference in density and viscosity compared to diesel but completely acceptable. The higher flash-point of biodiesel sample is beneficial in safety aspect, and the low sulfur content is the reason for the extremely low SOx emission associated with its use as fuel. The cetane number is higher than diesel resulting in a smoother running of the engine with less noise. Biodiesel sample is an oxygenated fuel naturally with oxygen content about 10% which contributes to the favorable emission, but leads to a little bit low caloric value compared with petro-diesel. Biodiesel nearly meets all the properties of normal diesel fuel, according to diesel and EN14214 standards, which indicates that Biodiesel derived from WCO has adequate values compared to diesel fuel. (Xiangmei Meng, Guanyi Chen and Yonghong Wang, 2008)

Parameter	Samples	Diesel fuel	EN14214
Density (15 °C, kg/m <sup>3</sup> )	890	NA	860–900
	171	<u> </u>	101
Flash point (°C)	1/1	> 65	> 101
Kinematic viscosity (40 $^{\circ}$ C, mm <sup>2</sup> /s)	4.23	3.0-8.0	3.5-5.0
Sulfur content (wt.%)	0.007	< 0.05	< 0.01
10% Conradson carbon residue	0.2	0.3	0.3

 Table 2.4: The properties of biodiesel sample compared to diesel fuel and EN14214

 biodiesel standard

Copper strip corrosion (3 h, 50 °C)	1a	class1	class1
Water content (mg/Kg)	150	NA	< 500
Cold filter plugging point (°C)	1	≤4	NA
Free glycerol (%)	0.008	NA	0.02
Total glycerol (%)	0.21	NA	0.25
Acid value (mg KOH/g)	0.48	< 0.1	≤ 0.5
Cetane number	54.5	> 49	≥ 51
Caloric value (MJ/kg)	32.9	41.8	NA

#### 2.1.3 Green House Gases and Global Warming Impacts and Benefits

Human-caused global warming is one of the greatest and most urgent challenges facing humanity and life on earth today. The main culprit is the enormous amount of the potent greenhouse gas carbon dioxide (CO<sub>2</sub>) released into the atmosphere by the burning of fossil fuels (petroleum, coal, natural gas). Burning fossil fuels releases more than 6 billion tons of CO<sub>2</sub> per year, twice as much as the biosphere can absorb. The excess CO<sub>2</sub> is clogging the atmosphere, with the result that less solar heat is reflected away, more heat reaches the earth's surface, and global temperatures rise.

Using vegetable oils or animal fats as fuel for motor vehicles is in effect running them on solar energy. All biofuels depend on the conversion of sunlight to energy (carbohydrates) that takes place in the green leaves of plants. Plants use water and  $CO_2$ from the atmosphere as the raw materials for making carbohydrates. Burning plant (or animal) products in an engine releases the  $CO_2$  back into the atmosphere, to be taken up again by other plants. The  $CO_2$  is recycled.

Natural mechanisms work to hold the amount of  $CO_2$  in the atmosphere at a stable level, maintaining a balance between the  $CO_2$  removed from the atmosphere to be

"fixed" into growing organic matter and the  $CO_2$  released back into the atmosphere when the organic matter burns or dies and decays. The net amount of  $CO_2$  in the atmosphere stays the same. Activitities that don't disrupt this balance are described as carbon-neutral.

In fact, there's no actual reduction in the amount of  $CO_2$  produced when biodiesel is burned instead of petrol-diesel. The same amount of  $CO_2$  will come out of the exhaust pipe with either fuel. But the  $CO_2$  released by burning biodiesel is part of the current natural cycle; it does not raise the level of  $CO_2$  in the atmosphere and does not act as a greenhouse gas. Biodiesel is carbon-neutral and does not increase global warming.

Petrol-diesel is not carbon-neutral. Burning petrol-diesel unleashes  $CO_2$  that has been trapped beneath the earth for millions of years, upsetting the natural balance and raising the level of  $CO_2$  in the atmosphere, causing global temperatures to rise. Fossilfuel  $CO_2$  is an active greenhouse gas. In practice however, not all biodiesel is carbonneutral. It depends how it's produced. "Life-cycle" studies of the whole production process from sowing the seed to filling the fuel tank can show a different picture.

Industrialised agricultural production of oil crops like soy or rapeseed depends heavily on fossil-fuel inputs which must be included in the equation, and biodiesel made from these crops is not carbon-neutral. But petrol-diesel is a lot worse. Organic farms don't use fossil-fuel-based chemical fertilizers and their fossil-fuel inputs are much lower, shrinking to zero when they produce their own fuel and energy on-farm, as a growing number of organic farmers are doing.

Biodiesel made from waste vegetable oil (WVO) should also qualify. Most WVO ends up in the sewers and landfills where it does no good and doesn't offset any fossil-fuel use. Converting it to biodiesel is a much better option, a social service. Reduce, reuse, and recycle. The US produces an estimated 4.5 billion gallons a year of used cooking oil, and most of it goes to waste. By comparison, US commercial production of biodiesel in 2006 was only 250 million gallons, most of it made from new soy oil, very little from used oil.

According to a model developed by the USA's Argonne National Laboratory (ANL), neat (100%) biodiesel from soybeans can cut global warming pollution by more than half relative to conventional petroleum based diesel. The emissions benefits are higher for canola oil. In the future, non-conventional sources like algae may have the potential to provide dramatic (90%) reductions in global warming pollution. However, significant technological hurdles remain before algae and other advanced feedstocks can be processed into biodiesel for commercial purposes.

It is important to note that the ANL model of global warming impacts does not take into account changes in land use. When soybeans are used for fuel, they are taken out of the market for food. This increases prices and stimulates demand that farmers around the world respond to by bringing more land into cultivation. With soybean production increasing in the Amazon, it is possible that the lifecycle global warming pollution of soybean biodiesel is even higher than petroleum diesel, once indirect land use changes are considered.

When biodiesel is made from recycled food oil or other waste products these land use considerations do not apply. Also advanced technologies including biomass gasification may allow the use of other waste streams to be converted to synthetic diesel fuels, expanding the pool of potentially low carbon diesel. In addition to land use, there is also some controversy over the emissions impact of fertilizer use and other land use practices, such as tillage practices. As a result, the estimated emissions from biodiesel can be expected to change as our understanding of the lifecycle improves.

Large scale production of biodiesel would require more virgin plant oils or other waste stream sources to meet larger demands. However, such large-volume biodiesel use could raise concerns about genetically modified crops, pesticide use, and land-use impacts common to ethanol and all other plant-based fuels. Crops for biodiesel must be grown in a manner that supports wildlife habitat, minimizes soil erosion, avoids competition for food crops, and does not rely on the use of harsh chemicals and fertilizers.



Figure 2.1: Tailpipe Emissions of Biodiesel relative to Conventional Diesel (Source US EPA)

Although biodiesel's lifecycle emissions impact depends on the source and fuel blend, biodiesel can offer distinct environmental advantages over petroleum diesel fuel. As shown in Figure 2.1, the use of biodiesel blends in an existing diesel vehicle can reduce the emissions of the tailpipe pollutants associated with conventional diesel including particulate matter and hydrocarbons (HC). However, using biodiesel may result in greater emissions of smog-forming nitrogen oxides than using conventional diesel.

On a lifecycle basis the estimates of global warming pollution for biodiesel vary greatly depending on how land use is accounted for. Particularly, the effects of displaced crop production can have significant impacts, especially if it is moved to previously virgin forest land.

#### 2.2 Raw Material

#### 2.2.1 Vegetable Oil

Vegetable fats and oils are substances derived from plants and are composed of triglycerides. Nominally, oils are liquid at room temperature, and fats are solid; a dense brittle fat is called a wax. Although many different parts of plants may yield oil, in commercial practice, oil is extracted primarily from the seeds of oilseed plants. 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) or pure plant oil (PPO) to distinguish it from biodiesel.

Vegetable oils are used to make biodiesel, which can be used like conventional diesel. It has similar fuel properties to diesel fuel, except for higher viscosity and lower oxidative stability. Some vegetable oil blends are used in unmodified vehicles but straight vegetable oil needs specially prepared vehicles which have a method of heating the oil to reduce its viscosity. The vegetable oil economy is growing and the availability of biodiesel around the world is increasing. The only problem is that, if there are too many production of biodiesel from vegetable oils, the world food supply will be unbalanced due to excess production of biodiesel. This whole phenomenon is agreed and is being debated by the World Food Foundation of the United Nation (UN).

The second source of raw material is algae;

#### 2.2.2 Algae

Compared with second generation biofuels, algae are high-yield high-cost feedstocks to produce biofuels. Since the whole organism converts sunlight into oil, algae can produce more oil in an area the size of a two-car garage than an entire football field of soybeans. With the record oil price increases since 2003, competing demands between foods and other biofuel sources and the world food crisis, there is much interest in algaculture (farming algae) for making biofuels.

The production of biofuels to replace oil and natural gas is in active development, focusing on the use of cheap organic matter in the efficient production of liquid and gas biofuels which yield high net energy gain. One advantage of many biofuels over most other fuel types is that they are biodegradable, and so relatively harmless to the environment if spilled.

The difficulties in efficient biodiesel production from algae lie in finding an algal strain with a high lipid content and fast growth rate that is not too difficult to harvest, and a cost-effective cultivation system using the type of photobioreactor that is best suited to that strain. Another obstacle preventing widespread mass production of algae for biofuel production has been the equipment and structures needed to begin growing algae in large quantities. Open-pond systems for the most part have been given up for the cultivation of algae with high-oil content.

Currently most research into efficient algal-oil production is being done in the private sector, but predictions from small scale production experiments bear out that using algae to produce biodiesel may be the only viable method by which to produce enough automotive fuel to replace current world diesel usage.

The third source of raw material is by recycling waste cooking oil;

#### 2.2.3 Waste Cooking Oil (WCO)

In this study, we are using waste cooking oil because of the feasibility of getting the raw material and the low cost feedstock for biodiesel production. We collect the waste cooking oil from canteen, restaurants and hotels. This collected wasted cooking oil has variety of qualities and posses properties different from neat vegetable oil (D.Y.C Leung and Y. Guo, 2006). Waste cooking oil contains higher free fatty acid than neat vegetable oil. The high temperature that involved during cooking processes and water from the foods accelerate the hydrolysis of triglycerides and increase the free fatty acid content in the oil. By using WCO, we are reducing the environment pollution. Waste cooking oil need to be treat before dispose to the environment to prevent pollution. Due to the high cost of disposal, many individuals dispose waste cooking oil directly to the environment especially in rural area. Thus by recycling waste cooking oil will help to prevent pollution in the environment (D.Y.C Leung and Y. Guo, 2006). The result between WCO and neat palm oil are shown in Table 2.5 as follow.

		Neat
Property	WCO	Palm Oil
Acid value (mg KOH/g)	2.1	< 0.5
Kinematic viscosity at 40 °C (cSt)	35.3	30.2
Myristic (C14:0)	0.9	1
Palmitic (C16:0)	20.4	42.8
Stearic (C18:0)	4.8	4.5
Oleic (C18:1)	52.9	40.5
Linoleic (C18:2)	13.5	10.1
Linolenic (C18:3)	0.8	0.2
Others	6.7	0.9

Table 2.5 : Physical and chemical properties of used frying oil and neat canola oil

#### **2.3 Process**

#### 2.3.1 Transesterification

Biodiesel is composed of long-chain fatty acids with an alcohol attached, often derived from vegetable oils. It is produced through the reaction of a the raw material with methyl alcohol or ethyl alcohol in the presence of a catalyst. Commonly used catalysts are potassium hydroxide (KOH) or sodium hydroxide (NaOH). The chemical process is called transesterification which produces biodiesel and glycerin.



Figure 2.2: Basic Transesterification Technology

Chemically, biodiesel is called a methyl ester if the alcohol used is methanol. If ethanol is used, it is called an ethyl ester. They are similar and currently, methyl ester is cheaper due to the lower cost for methanol. Biodiesel can be used in the pure form, or blended in any amount with diesel fuel for use in compression ignition engines. Figure 2.2 shows basic transesterification technology.



Figure 2.3: Transesterification of vegetable oils

The transesterification process of converting vegetable oils to biodiesel is shown in Figure 2.3. The "R" groups are the fatty acids, which are usually 12 to 22 carbons in length. The large vegetable oil molecule is reduced to about 1/3 its original size, lowering the viscosity making it similar to diesel fuel. The resulting fuel operates similar to diesel fuel in an engine. The reaction produces three molecules of an ester fuel from one molecule of vegetable oil.

#### 2.3.2 Pyrolysis

Pyrolysis of biomass is the direct thermal decomposition of the organic matrix in the absence of oxygen, or is partially combusted in a limited oxygen supply, to produce a gas mixture (containing mainly carbon oxides, some methane and higher gaseous hydrocarbons in minor quantities), a carbon rich solid residue (char and coke) and liquid oil (bio-oil) (Demirbas, 2003 and Yaman, 2004).

Low temperature (450–550 °C), high heating rate and short gas residence time of biomass pyrolysis could result in maximum yield of liquid product (bio-oil) (Zhang et al., 2005). The pyrolysis liquids are complex mixtures of oxygenated aliphatic and aromatic compounds (Meier and Faix, 1998). High temperature (500–850 °C), low heating rate and long gas residence time of biomass pyrolysis are required to maximize the yield of fuel gas (Chen et al., 2003). The pyrolysis gas contains CO<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, minor amounts of higher gaseous organics and water vapour (Klass, 1998).

#### 2.3.3 Two Step Catalyzed Process



Figure 2.4: Synthesis of biodiesel by two-step catalyzed process

The mechanism of this new two-step catalyzed process for the preparation of biodiesel was shown in Figure 2.4. At the first step, ferric sulfate was introduced to catalyze the esterification reaction in which the FFA in the WCO reacted with methanol. The ferric sulfate that had very low solubility in the oil was separated from the liquid after the methanol recovery, and could be recovered by ashing process. At the second step, potassium hydroxide was added to catalyze the transesterification reaction in which triglyceride reacted with methanol. Without wastewater, reusable catalyst and low cost of reaction tank, this two-step catalyzed process exhibits potential application in the biodiesel industry.

#### 2.4 Catalyst

Catalysts are chemical compounds capable of directing and accelerating thermodynamically feasible reactions while remaining unaltered at the end of the reactions. Catalysts influence chemical reactions by increasing the rate of approach to equilibrium, from either direction, while not altering the equilibrium position. Catalysts may function by decreasing the expenditure of chemical potential required to form the activated complex at the transition state, lowering the activation energy compared to that required in the absence of catalyst, thus increasing the reaction rate. Catalysts enable the formation of an entirely different activated complex from that involved in the uncatalyzed reaction, thus altering the selectivity of reaction.

The development of the catalysts and catalytic processes are essential with the capability and flexibility to adjust and optimize performance in response to the changes in feedstock and market demands. The development of catalysts that facilitate highly selective conversion of substrate to desired products is one of the challenges encountered in the process (Miller and Jackson, 2004). The thermally stable, effective and cost effective catalysts with high selectivity towards desired products are required (Westermann et al., 2007).

#### 2.4.1 Alkali and Acid Catalyst

The choice of catalyst, alcohol/vegetable oil molar ratio, temperature, water content and free fatty acid (FFA) content influence the transesterification process (Demirbas, 2003). Conventionally, transesterification reactions rate are improved by alkali- or acid-catalyst. The alkali-catalysts include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. The acid catalysts include sulfuric acid, sulfonic acids and hydrochloric acid (Ma and Hanna, 1999). The FFA and water contents have significant effects on the transesterification of glycerides with alcohols using alkaline and acid catalysts (Demirbas, 2003). If a glyceride has a higher free fatty acid content and more water, acid-catalyzed transesterification is suitable (Ma and Hanna, 1999). The alkali-catalysts, however, are most commonly used in industrial processes due to the faster reaction rates at the moderate reaction conditions. These catalysts include sodium hydroxide, potassium hydroxide and sodium methoxide (Schuchardt et al., 1998, Al-Zuhair, 2007 and Vicente et al., 2007). So far, there is no acid-catalyzed process reported in the commercial biodiesel plants (Al-Zuhair, 2007).

Alkaline metal alkoxides gave high yields of more than 98% within short reaction times (30 min) at low molar concentration (0.5 mol%) (Schuchardt et al., 1998).

Demirbas (2008) reported that 100 g of vegetable oil is transesterified in methanol (200 mL) containing fresh sodium (0.8 g) for the purpose of sodium methoxidecatalyzed transesterification. The reaction was quite fast between a vegetable oil and sodium methoxide in methanol. The triglycerides were completely transesterified in 2– 5 min at room temperature (293–298 K) through sodium methoxide-catalyzed transesterification compared to 60–360 min in acid- and alkali-catalyzed processes at higher temperature of 303–338 K.

However, there are limitations associated with both alkali- and acid-catalyzed transesterification. The alkali-catalyzed process is sensitive to both water and FFA content due to occurrence of saponification reaction under alkaline conditions. On the other hand, the reaction rate of the acid-catalyzed process is relatively slower (Al-Zuhair 2007). The transesterification reaction is generally completed in several hours. The removal of homogenous catalysts is sometime difficult and brings extra cost to the final product (Wang and Yang, 2007). The high consumption of energy and costly separation of the homogeneous catalyst from the reaction mixture have drawn to the need of development of heterogeneous catalyst for transesterification which are easily separated from the reaction mixture and recyclable.

During the last decade, solid acid catalysts have been used in many industrial processes (Clark, 2002). Solid acids contain a variety of acid sites with different strength of Bronsted or Lewis acidity, compared to the homogenous acid catalysts (Chai et al., 2007). The vegetable oil contain FFA content that would react with the base catalyst forming soap which would deactivate the base catalyst and result in inefficient target reaction. Park et al. (2008), hence reported the transesterification of vegetable oil using heterogeneous acid catalysts sulfated zirconia ( $SO_4^{2^-}/ZrO_2$ ) and tungstated zirconia ( $WO_3/ZrO_2$ ). These catalysts efficiently converted the FFA to FAME prior to the biodiesel production. The pellet-type  $WO_3/ZrO_2$  was used for the reaction with longer time and it was found that 65% conversion could be maintained for up to 140 h (Park et al., 2008).

Chai et al. (2007) reported the production of high-quality biodiesel fuel from vegetable oil using the solid heteropolyacid  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  as a catalyst. The solid acid catalyst was efficient at the expense of producing high yield (99%) of biodiesel using only low catalyst concentration  $(1.85 \times 10^{-3}:1 \text{ weight ratio of catalyst-to-oil})$ , low methanol-to-oil ratio (5.3:1) in a relatively short reaction time (45 min) at low temperature (338 K). The process was environmentally benign and economical since the activity of the  $Cs_{2.5}PW$  was not considerably affected by the free fatty acid and moisture content in the vegetable oil, and the catalyst could be easily separated from the product mixture and reused number of times (Chai et al., 2007).

#### 2.4.2 Heterogeneous Catalyst

In recent years, there are considerable studies on the utilization of heterogeneous catalysts for transesterification of vegetable oils. A great variety of catalysts such as zeolites, hydrotalcites, oxides,  $\gamma$ -alumina were studied in catalytic transesterification of vegetable oils. Table 2.6 shows the different heterogenous catalysts reported for transesterification of vegetable oils in the literature. Most of these catalysts are alkali or alkaline oxides supported over large surface area supports. Generally, solid basic catalysts are more active than solid acid catalysts, similar to their homogeneous counterparts (Arzamendi et al., 2007 and Arzamendi et al., 2008). Both solid acid and basic catalysts have advantages and disadvantages in the transesterification reaction. CaO, used as a solid basic catalyst, possess many advantages such as long catalyst lifetimes, higher activity and requirement of only mild reaction conditions. The reaction rate, however, was slow in producing biodiesel (Liu et al., 2008). Solid acid catalysts, such as Nafion<sup>®</sup> NR50, sulphated zirconia and tungstated zirconia efficiently catalyzed biodiesel-forming transesterification due to the presence of sufficient acid site strength. Among the solid catalysts, Nafion<sup>®</sup> gave higher selectivity towards the production of methyl ester and glycerol due to its significant acid strength (Lopez et al., 2007). However, Nafion<sup>®</sup> has disadvantages of high cost and lower activity compared to liquid acids (Chai et al., 2007).
Heterogeneous catalyst is reported to be used in the fatty acid methyl esther (FAME) plant of Diester Industrie (Paris) at Sete, France. The Esterfip-H process produces FAME by esterification of plant oils such as that from rapeseed, soybean or sunflower. The heterogeneous catalyst is a spinel mixed oxide of two (non-noble) metals, which eliminates several neutralization and washing steps needed for processes using homogeneous catalysts. The purity of methyl esters exceed 99%, which yield close to 100%. In addition, the heterogeneous process produces glycerol as byproduct with purity of better than 98% compared to about 80% from homogeneous process. The overall production economic improves through the utilization of the byproduct (Chementator, 2004).

Table 2.6: Different heterogeneous catalysts used for transesterification of vegetable

01	Catalant		Der		Conv	Defenences	Domonica
	Catalyst	Temp (°C)	Time (h)	Methanol/ oil ratio	(%)	Kelerences	Kemarks
Soybean oil	La/zeolite beta	160	4	14.5	48.9	Shu et al. (2007)	Using higher energy and methanol ratio but less conversion. Not compatible
Sunflower	NaOH/γ- alumina	150	24	6	82	(Arzamendi et al., 2007) and (Arzamendi et al., 2008)	Solid basic catalysts are more active than solid acid catalysts
Refined cottonseed oil	Mg–Al–CO <sub>3</sub> (hydrotalcite)	200	10	6	85	Barakos et al. (2008)	Higher conversion Higher cost of energy
Soybean oil	ETS-10	120	24	6	94.6	Suppes et al. (2004)	Compatible since conversion is higher.

oils

							Long catalyst
							lifetimes, higher
							activity and
							requirement of
							only mild
Sunflower	CaO/					Albuquerque	reaction
oil	SBA-14	160	5	12	95	et al. (2008)	conditions

# 2.4.3 Homogeneous Catalyst

Homogeneous catalysis is when the catalyst is soluble in the reaction medium. An example of homogeneous catalysis is the trans-esterification of oil by NaOH and CH<sub>3</sub>OH. Most homogeneous catalysis processes take place in the liquid medium.

#### 2.5 Process control variables

In this experiment, there are a few process control variables which can affect the result of the experiments. Those parameters are:

- i) Effect of molar ratio of alcohol to oil
- ii) Effect of reaction temperature
- iii) Effect of reaction time
- iv) Effect of catalyst concentration

# 2.5.1 Effect of molar ratio of alcohol to oil

The molar ratio of methanol to oil is one of the most important variables that affect conversion efficiency as well as production cost of biodiesel. Xiangmei Meng, Guanyi Chen and Yonghong Wang found that the addition of methanol/oil molar ratio less than 1.5 resulted in the creation of a unique and foamy layer. Molar ratio up to 2.5 produced two layers, although the lower layer was gelatinous and the upper layer was opaque, because of the presence of unreacted triglycerides. Thus, indicating that methanol was insufficient to perform a complete reaction. With the methanol/oil molar ratio increasing, WCO conversion efficiency will be correspondingly increased. The maximum conversion efficiency (88.9%) was achieved at 1:6 methanol/oil molar ratio. With further increase in molar ratio the conversion efficiency more or less remained the same. The WCO conversion efficiency (88.4%) at 1:6 methanol/oil molar ratio was similar to the results obtained by 1:6 methanol/oil molar ratio. Considering that excessive methanol needs to remove from higher methanol/oil molar ratio, so 1:6 methanol/oil molar maybe is more suitable in practical process.

This higher molar ratio than the stoichiometric value resulted in a greater ester conversion and could ensure complete reaction. Moreover, it was observed that for high molar ratio a longer time was required for the subsequent separation stage since separation of the ester layer from the water layer becomes more difficult with the addition of a large amount of methanol. This is due to the fact that methanol, with one polar hydroxyl group, can work as an emulsifier that enhances emulsion. Therefore, increasing the molar ratio of methanol/oil beyond 1:6 did not increase the product yield as well as the ester content, but complicated the ester recovery process and raised the cost for methanol recovery.

#### 2.5.2 Effect of reaction temperature

Transesterification can occur at different temperatures depending on the oil used. Xiangmei Meng, Guanyi Chen and Yonghong Wang had done the experiment and stated that the maximum WCO conversion efficiency was obtained at 50 °C temperature, and other researcher achieved better results at temperatures above 50 °C and up to 70 °C while using refined linseed oil and brassica carinata oil, respectively. Results revealed that the WCO conversion efficiency decreased when other reaction temperatures were used. When the reaction temperature closes or exceeds the boiling point of methanol, the methanols will vaporize and form a large number of bubbles then inhibit the reaction. Although a reflux condenser was used in the experiment to avoid methanol losses, the WCO conversion efficiency significantly decreased at temperatures more than 60 °C. As well as economic reasons considered, 50 °C was selected during transesterification.

# 2.5.3 Effect of Reaction Time

Xiangmei Meng, Guanyi Chen and Yonghong Wang claims that to achieve perfect contact between the reagents and the oil during reaction, they must be stirred well at constant rate and well mixed together. The WCO conversion efficiency rapidly increased with the reaction time ranges between 30 min and 60 min, after that, the conversion efficiency kept rising very slowly and then practically constant above 86% at 90 min. So the reaction approved to be in equilibrium and the rate was quite slow.

#### 2.5.4 Effect of Catalyst Concentration

The amount of catalyst used in the process is another variable to take into account, because it not only determines the reaction rate, but cause hydrolysis and saponification. Both reactions interfere with the separation of the glycerol rich phase and with the methyl esters purification. Xiangmei Meng, Guanyi Chen and Yonghong Wang used sodium hydroxide in their experiment. The effect of sodium hydroxide amount on WCO conversion efficiency is presented in Figure 3. From the ranges 0.5–1.0 wt.%, the WCO conversion efficiency increased proportionally with increasing sodium hydroxide amount. The maximum WCO conversion efficiency (85.0%) was observed at 1.0 wt.% sodium hydroxide. Addition of excess amount catalyst, gave rise to the formation of an emulsion, which increased the viscosity and led to the formation of gels. Thus sodium hydroxide amount beyond 1.0 wt.% was not necessary. (Xiangmei Meng, Guanyi Chen and Yonghong Wang, 2008)

# **CHAPTER 3**

# METHODOLOGY

# **3.1 General Process**

The process starts with waste cooking oil collection, experimental procedure and sample analysis. The proposed procedure is by doing transesterification process at a different parameter. The parameters that we are going to observe are optimum reaction time and temperature. Below are the procedures of doing the experiment:

- i) Raw material : Waste cooking oil collection
- ii) Equipment selection
- iii) Experimental procedure
  - a. Transesterification process
  - b. Settling
  - c. Washing and methanol recovery
- iv) Sample analysis



Figure 3.1: Experimental Methodology

## **3.2 Materials**

#### 3.2.1 Raw Material

For the proposed research, we are using waste cooking oil and RBD as the main raw materials to be converted into biodiesel. Raw material are been provided by Faculty of Chemical Engineering & Natural Resource (FKKSA). The collection of waste cooking oil is from restaurants, café, hotels and food stalls.

# **3.2.2 Chemical Material**

The chemicals that are going to be use in the experiment are methanol and Potassium Hydroxide, KOH. KOH is the alkali based catalyst whereas methanol is as solvent. All of the chemical materials are being provided by FKKSA.

## 3.3 Equipment

The experiment is going to be run on laboratory scale. The equipments that we are going to use are:

- i. Filter Press: to filter solid compound and impurities in waste cooking oil.
- ii. Hot Plate: to vaporized the excess water in the waste cooking oil and RBD.
- iii. Shaking Water Bath: use during transesterification process.
- iv. Rotary Evaporator: to recover methanol after transesterification process.
- v. Gas Chromatography: to analyze methyl ester content.
- vi. Gas Analyzer: to test gas characteristic.

#### **3.4 Experimental Procedure**

#### 3.4.1 Filtration

The waste cooking oil that had been collected will undergo filtration process under vacuum to remove any different solid impurities. The waste cooking oil is going to be preheated around 80°C to 90°C to remove water. The oil was left to cool before it can proceeds to the next steps. For RBD, no filtration and preheating are needed.

# **3.4.2 Transesterification Process**

The transesterification process is going to be run in shaking water bath connected to mechanical stirrer (1300 rpm). The raw material is about 1 liter. A solution consists of methanol solvent and KOH catalyst can be mix into a beaker and stir until it mixes well. The catalyst concentration is varied from 0.5, 0.75, 1.0 and 1.5wt%. The mix solution of methanol and KOH catalyst is poured on 1 liter beaker of raw material. Reaction mixture is blend under fixed temperature at 40°C and certain desired time (30, 40, 50, 60 min). The reaction will take place once the solvent and catalyst is added to the waste cooking oil. The blending process will be done in shaking water bath. After that, the beaker will be leave for about 12 hours to let the settling process to take place. In this transesterification process, the molar ratio of oil to methanol is 6:1.

# 3.4.3 Settling

The settling process is going to take time for about 12 hours. The observations from the settling process are two layers are going to form. The upper layer is the biodiesel and the bottom layer is the glycerine. The biodiesel will be transfer to rotary evaporator.

# 3.4.4 Methanol Recovery and Washing Unit

The methanol recovery is being done in rotary evaporator. Its function is to recover the excess methanol that is still left in the biodiesel. Then the crude biodiesel is wash with water at 80°C by slowly pouring hot water into the solution to remove any

remaining methanol, catalyst and glycerine. Then the water is drain and these washing steps were repeated for two times or until the drain water is clear. After washing, the biodiesel is filtrate using filter paper to remove any remaining solid. Finally the biodiesel is going to be heat up to  $100^{\circ}$ C with hot plate to dry up remaining residual water in biodiesel. The biodiesel is now ready for analysis.

#### **3.5 Analysis**

There are three parameters that are going to be analyzed which are biodiesel concentration in GC, optimum catalyst concentration and optimum reaction time. Vary sample will give different results and the highest biodiesel yield will be selected as the optimum condition. Finally, the sample which is produced based on the optimum condition will be tested to ensure that it meets the standard requirement of ASTM D6751 for biodiesel B100.

# 3.5.1 Yield

Product yield is defined as the weight percentage of the final product (purified biodiesel) relative to the weight of waste coking oil at the start. The biodiesel yield (% wt) relative to the amount of waste cooking oil use will be calculated.

$$\frac{\text{Product yield(\%)} = \frac{\text{Final mass} - \text{Initial mass}}{\text{Initial mass}} \quad x \text{ 100\%} \quad (\text{Eq 3.1})$$

# **3.5.2 Gas-Chromatography Analysis**

The biodiesel sample is taken to analyze the purity by Gas Chromatography (Agilent 6890), equipped with an HP Innowax capillary column ( $30 \text{ m} \times 0.25 \text{ mm}$ ) and a flame ionization detector (FID). Nitrogen was used as the carrier gas at a constant flow rate of 20 ml/min. The column oven temperature was programmed from 50 to 130 °C (at the rate of 20 °C/min) and held at 130 °C for 5 min, then raised to 260 °C at 2.5 °C/min and maintained at this temperature for 10 min.

This is the formula to determine methyl ester percentage in the biodiesel. The higher the percentage, the more efficient it is.

$$C = \underbrace{\sum A - A_{EL}}_{A_{EL}} x \underbrace{C_{EL} X V_{EL}}_{M} x 100\%$$
(Eq 3.2)

Where;

 $\sum A = \text{total peak area for Methyl Ester in } C_{14} \text{ to } C_{24:1}$   $A_{EL}=$  peak area corresponding to methyl ester stock solution  $V_{EL}=$  volume in ml of methyl ester solution being used M = mass, mg of the sample

# **3.5.3** Combustion Test

The biodiesel from optimum condition will be test. Combustion test is being done by using Gas Analyzer NU-WAY and P.A Hilton brand. The gas analyzed will be note down and be compare with diesel combustion test.



Figure 3.2: Gas Analyzer

#### **CHAPTER 4**

#### RESULT

#### **4.1 Introduction**

The experiment was conducted by using 1 liter of waste cooking oil (WCO) and refined-bleached-deodorized oil (RBD) each as raw material. The technique use in this experiment is single step batch transesterification with the aid of potassium hydroxide (KOH) as the catalyst.

The optimum time for the process to take time is set at 40 minutes. The optimum and best parameters that need to be determined are categorized into three phases. The first phase is to find the optimum or best catalyst concentration (0.5, 0.75, 1, and 1.5%). The second phase is to find the optimum or best time (30, 40, 50, 60 minutes). These conditions were determined by using methyl ester concentration or purity calculated from gas chromatography test. Yield test is also determined to analyze the yield of biodiesel. The last phase was to do combustion test to compare the emission gases from conventional diesel.

# 4.2.1 EFFECT OF CATALYST (KOH) CONCENTRATION

## 4.2.1.1 Effect of Catalyst (KOH) Concentration on Methyl Ester Content or Purity

The concentration of the catalyst was the first parameter studied. The effect of KOH concentration on the transesterification of RBD palm oil and WCO was investigated with its concentration varying from 0.5, 0.75, 1.0, 1.5 to 1.5wt%. The operation conditions during the whole reaction process were fixed at: reaction temperature of 40°C, reaction time at 40 minutes and molar ratio of methanol to oil at 6:1 while the mixing degree is set at 1300 rpm for mechanical stirring process.

Figure 4.1 shows that the changes in methyl ester content or purity with catalyst concentration followed an asymptotic curve for all the oil samples. As the KOH concentration increased, the conversion of triglycerides to methyl ester also increased. Insufficient amount of KOH concentration resulted an incomplete conversion of triglycerides into methyl ester. The ester content reached the best value when the KOH concentration reached at 1.5wt%. We cannot conclude that the reading at 1.5wt% is at the optimal because a series of experiment should be add up just to make sure that the level remained relatively constant with a further increase in catalyst concentration.

For both RBD palm oil and WCO, a KOH concentration of 1.5wt% was adequate to complete the transesterification process. Further increase in catalyst concentration might or might not enhance further conversion nor raises the ester content or purity. That is why the result is best addressed to be best parameter and not as optimum parameter.

Catalyst		
concentration(%)	Methyl Ester	Purity (%)
	RBD	WCO
0.5	67.3	37.26
0.75	76.73	70.26
1	72.99	81.025
1.5	78.34	84.714

 Table 4.1: Effect of Catalyst Concentration on Purity



Figure 4.1: Effect of Catalyst Concentration on Purity

#### 4.2.1.2 Effect of Catalyst (KOH) Concentration on Biodiesel Yield

Based on Figure 4.2, the product yield under the cases of excess KOH concentration was examined. It can be seen that when the KOH concentration was increased from 0.5, 0.75, 1.0, 1.5 to 1.5wt%, the yield of the biodiesel dropped from 84% to 67% for RBD, a reduction of 17wt%. As for WCO, the reduction is only from 74wt% to 73wt% and the trend of the result is quite stagnant. However the trend is still decreasing even though the amount is not as significant as RBD palm oil. During preparation of the catalyst, KOH will be added and dissolved in the anhydrous methanol forming potassium methoxide together with a small amount of water according to the following equilibrium equation:

$$CH_3OH + KOH \rightarrow CH_3OK + H_2O$$
 (eq 4.1)

The water in the reaction system predominantly reacts with oils (triglycerides) and the  $K^+$  to form potassium soaps. This is the saponification reaction of triglycerides leading to the loss of triglycerides and hence reductions in final product yield. On the other hand, the pure CH<sub>3</sub>OK catalyst only dissociates into CH<sub>3</sub>O<sup>-</sup> and K<sup>+</sup> without forming any water as side product in the reaction that will cause a drop in product yield (D.Y.C Leung, Y. Guo, 2006).

Yield is decreasing because of saponification process occurred. Large amount of soaps were observed during the experiment as excess KOH was added, which was responsible for the yield reduction. This is because more addition of KOH caused more triglycerides participating in the saponification reaction with KOH producing more soap, thereby reducing the biodiesel yield.

Catalyst		
concentration(%)	Yield	(%)
	RBD	WCO
0.5	84.5	74.67
0.75	81.4	73
1	77.16	74.3
1.5	67.73	73.67

 Table 4.2 : Effect of Catalyst (KOH) Concentration on Yield



Figure 4.2: Effect of Catalyst (KOH) Concentration on Yield

Maximum methyl ester content or purity was obtained at 1.5wt% of KOH concentration, with reasonably high yield. These were identified to be the best values for transesterifying RBD palm oil and WCO. Further excess KOH catalyst addition will led to a marked reduction in the product yield and also added extra cost to the process for removing excess catalyst and soaps. As a whole, the catalyst concentration had a large effect on the purity and yield of biodiesel obtained, and should be controlled accurately and carefully.

For WCO, best KOH concentration was 1.5wt%, which produced a maximum ester content or purity of 84.714% and yield at 73.67%. This highest purity amount was 6% larger than that found in the transesterification of RBD palm oil at 78.34% and yield at 67.73%. It means that WCO proved to be better raw material compared to RBD palm oil because it has superceded RBD palm oil for purity and yield aspects.

#### **4.2.2 EFFECT OF REACTION TIME**

#### 4.2.2.1: Effect of Reaction Time on Methyl Ester Content or Purity

For Phase 2, the reaction time of the transesterification reaction conducted was fixed at 40 minutes and at temperature 40°C. The mixing degree is set at 1300 rpm for the mechanical stirring process and molar ratio of methanol to oil is 6:1 with the best concentration at 1.5wt% for both RBD palm oil and WCO, respectively.

Figure 4.3 shows a plot of methyl ester content or purity vs. reaction time for both RBD palm oil and WCO. The results showed that the reaction trend was increasing fast as the time is increasing from 30 minutes to 60 minutes. So, from the figure, we can assume that the best reaction time was at 60 minutes. This happen because as more time were provided, than more transesterification process will took place. A perfect contact between the reagents and the oil will be achieved. When the time increase more than 60 minutes, the result may slow down and enters a constant rate till the reaction equilibrium was reached eventually. (D.Y.C Leung, Y. Guo, 2006)

Time (min)	Methyl Ester	Purity (%)
	RBD	WCO
30	52.98	52
40	56.1	54.58
50	57.18	56
60	59	58.8

 Table 4.3: Effect of Reaction Time on Purity



Figure 4.3: Effect of Reaction Time on Purity

# 4.2.2.2: Effect of Reaction Time on Biodiesel Yield

As can be observed, the methyl ester content or purity increased with reaction time and reached a maximum at 60 minutes. Based on this, the product yield observed from Figure 4.4 was examined. The results indicated that an extension of the reaction time will led to the reduction in the product yield. This is because longer reaction time enhanced the hydrolysis of esters (reverse reaction of transesterification), resulted in a loss of esters as well as causing more fatty acids to form soap. More visible soaps were observed experimentally with gradually extending reaction time. Accordingly, it can be concluded that the reaction time was also a controlling factor of product yield and extending the reaction time had a negative effect on the product yield.

Time (min)	Yield	(%)
	RBD	WCO
30	76.9	72.67
40	76	71
50	75	70
60	74	69

Table 4.4 : Effect of Reaction Time on Yield



Figure 4.4 : Effect of Reaction Time on Yield

#### 4.2.3 Summarization from Phase 1 and Phase 2

From Phase 1, the best catalyst concentration had been determined which turned out that 1.5wt% KOH concentration is the best result for both RBD palm oil and WCO. The yield and purity was determined at 1.5wt%. As the KOH concentration increased, the methyl ester content or purity is also increased whereas the yield is decreased. This happened because as the catalyst concentration increased, the catalyst will help saponification to occur thus lowering the final mass and yield. Whereas for purity, more reaction will be favored to the product side and therefore at higher KOH concentration, the result will be higher for methyl ester purity. Phase 2 is resumed based from the purity reading calculated from Gas Chromatography Test.

For Phase 2, the best reaction time is determined and the best reaction time is at 60 minutes for both RBD palm oil and WCO. The last reading for biodiesel yield and methyl ester content or purity is; RBD palm oil yield is 74% and purity is 59%, WCO yield is 69% and purity is 58.8% equal to 59%.

From the results showed in Table 4.5, we can conclude that at the same purity of RBD palm oil and WCO (59%), the yield for RBD palm oil is higher than WCO with 74% to 69%. Therefore, RBD palm oil is the best raw material for biodiesel in terms of quantity. Thus, industrialists may have options to choose RBD palm oil as their raw material in biodiesel production.

Sample	Catalyst	Conc	Reaction	Time	Biodiesel	Yield	Methyl	Ester
	(%)		(min)		(%)		Purity (%	)
RBD Palm oil	1.5		60		74		59	
WCO	1.5		60		69		58.8	

 Table 4.5: Summary of Best Parameters

#### 4.2.4 Combustion Test Studies from Gas Analyzer

For Phase 3, combustion test had been done by measured the emit gas using gas analyzer. Reductions in carbon monoxide (CO) have been determined in the gas sensor inside gas analyzer. The combustion characteristic that can be determined from the result is the carbon monoxide result. From Figure 4.5, standard diesel has highest CO concentration emitted compared to RBD palm oil and WCO. From this result, it has been proven that biodiesel has lesser CO concentration emission thus shows that biodiesel is a clean alternative to replace conventional biodiesel.

In many researchs, concentrations of CO that emit from combustion from biodiesel are supposedly reduced up to 50%. For example, Labeckas and Slavinskas found that the carbon monoxide emissions and visible smoke emerging from the biodiesel over all load and speed ranges are lower by up to 51.6%. However, for RBD CO emission, only 25% of CO concentration emissions were reduced. WCO successfully reduced the CO concentration emissions up to 40%. These results were assumed to be success and meet the objective even though the reading did not meet the 50% reduction.

Van Gerpen reported that biodiesel combustion had a higher burning rate than normal diesel fuel due to the presence of oxygen in biodiesel, hence increasing the efficiency of combustion, thereby reducing the formation of CO emissions. Biodiesel also has less compressibility and higher cetane number. These two behaviors are also effective on the CO reduction. The higher cetane number, which means shorter ignition delay, causes longer combustion duration and increases complete combustion reaction regions. (Mustafa Canakci, Ahmet Necati Ozsezen et al, 2008). A combustion test had been done and the results stated as follow:

	Standard Diesel	RBD	WCO
O2 (%)	9.3	9.3	9.3
Ratio	0.0042	0.0032	0.0025
CO (ppm)	376	282	222
CO2 (%)	8.7	8.7	8.7
XAir (%)	81	81	81
Eff N (%)	58.1	58.3	58.3
Dry Loss (%)	41.7	41.6	41.6
μCO Loss (%)	0.2	0.1	0.1

 Table 4.6: Combustion Characteristics



Figure 4.5: Carbon Monoxide Characteristics

#### **CHAPTER 5**

# **CONCLUSION & RECOMMENDATIONS**

# **5.1** Conclusion

The WCO and RBD palm oil can be converted into biodiesel directly by single step batch based catalyze transesterification process and can be used as a fuel in diesel engines. Biodiesel of good quality can be produced from WCO and RBD palm oil in the following reaction conditions: methanol/oil 6:1 molar ratio, with 1.5 wt.% potassium hydroxide, temperature at 40 °C and reaction time 60 min. Combustion test showed that biodiesel fuels reduced significantly CO emissions by 25% for RBD, and 40% for WCO. This is due to the oxygen contents of the fuels.

At the same amount of methyl ester content or purity, RBD palm oil will give higher yield. This means at the same quality, it has much more quantity compared to WCO. However the CO emission for RBD palm oil is slightly higher than WCO. Therefore it is up to manufacturer's whether to choose RBD palm oil or WCO to produce biodiesel. RBD palm oil can still be used because of its abundance sources since Malaysia is one of the net producers of palm oil. With more appropriate quality upgrading treatment, CO emission for RBD can be reduced.

Potassium Hydroxide acted as homogeneous alkali catalyst shows good activity to catalyze the methanolysis of FFA in the oil. This catalyst is environmental friendly, easy to be separated from the system, more efficient, and does not demand for high cost equipment for anti-corrosion. It is important to determine the optimum condition of the reaction because it will provide the high yield and conversion of the biodiesel. Malaysia has so many kinds of waste oils and palm oil for biodiesel production. Therefore the government should make full use of these resources and ensure national diesel security as a long lasting supplement.

#### **5.2 Recommendations**

For future studies, student can use two step batch transesterification process to reduce the free fatty acid content inside WCO. Therefore at the end of the result, much higher yield can be get. To get best results, student can continue the experiment by adding up the parameter to get the optimum result as to make sure the result will be much reliable and accountable.

The other recommendations are to store the WCO at room temperature condition to prevent the oil from solidifies. Student should use the same equipment in every experiment to minimize the error and to get accurate result. Besides, student must ensure that all vial and equipment used during gas chromatography analysis should be completely dry so that the GC reading would not been intrude. The last recommendation is to store the biodiesel sample at air proof place to prevent other element from contaminating the sample.

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# A. CALCULATION FOR WCO

WCO = 1 Liter

Density = 0.92 kg/LDensity =  $\frac{\text{mass}}{1\text{L}}$ Mass WCO = 0.92 kg

Mass KOH= 0.5, 0.75, 1.0, 1.5 wt%

Wt% KOH	Calculation
0.5	$\frac{0.5}{100} \times 0.92 \text{ kg} = 0.0046 \text{ kg} = 4.6 \text{ g}$
0.75	$\frac{0.75}{100} \times 0.92 \text{ kg} = 0.0069 \text{ kg} = 6.9 \text{ g}$
1.0	$\frac{1.0}{100} \times 0.92 \text{ kg} = 0.0023 \text{ kg} = 9.2 \text{ g}$
1.5	$\frac{1.5}{100} \times 0.92 \text{ kg} = 0.00138 \text{ kg} = \mathbf{13.8 g}$

 $0.92 \text{ kg} = \frac{856 \text{ g/mol}}{\text{X}}$  methanol

X = 0.9304 mol methanol

Scale down =  $\frac{192.24 \text{ g/mol}}{0.9304 \text{ mol}}$  methanol

= 206.613 g methanol

Volume = 
$$\frac{206.31 \text{ g}}{0.791 \text{ g/cm}^3}$$
  
= 261.2 cm<sup>3</sup> = **261.2 ml methanol**

# **B. CALCULATION FOR RBD**

# RBD = 1 Liter

Density = 0.88 kg/LDensity =  $\frac{\text{mass}}{1\text{L}}$ Mass RBD = 0.88 kg

# Mass KOH= 0.5, 0.75, 1.0, 1.5 wt%

Wt% KOH	Calculation
0.5	$\frac{0.5}{100} \times 0.88 \text{ kg} = 0.0046 \text{ kg} = 4.4 \text{ g}$
0.75	$\frac{0.75}{100} \times 0.88 \text{ kg} = 0.0069 \text{ kg} = 6.6 \text{ g}$
1.0	$\frac{1.0}{100} \times 0.88 \text{ kg} = 0.0023 \text{ kg} = 8.8 \text{ g}$
1.5	$\frac{1.5}{100} \times 0.88 \text{ kg} = 0.00138 \text{ kg} = \mathbf{13.2 g}$

 $0.88 \text{ kg} = \frac{847.3 \text{ g/mol}}{X} \text{ methanol}$ 

X = 1.0386 mol methanol

Scale down =  $\frac{192.24 \text{ g/mol}}{1.0386 \text{ mol}}$  methanol = 185.097 g methanol

Volume = 185.097 g0.791 g/cm<sup>3</sup> = 234 cm<sup>3</sup> = **234 ml methanol** 

# C. Yield Calculation

Assumption: RBD mass = 880 g WCO mass = 900 g Beaker mass = 486 g

# PHASE 1: Effect of catalyst KOH concentration

# RBD's Yield

KOH concentration	Mass RBD	Calculation	Yield (%)
(wt%)	Biodiesel (g)		
0.5	1230.54	<u>1230.54–486</u> x 100 880	84.50
0.75	1202.62	<u>1202.62–486</u> x 100 880	81.40
1.0	1165.30	<u>1165.30–486</u> x 100 880	77.16
1.5	1082.56	<u>1082.56–486</u> x 100 880	67.73

# WCO's Yield

KOH concentration	Mass WCO	Calculation	Yield (%)
(wt%)	Biodiesel (g)		
0.5	1158.10	<u>1158.10–486</u> x 100 900	74.67
0.75	1144.58	<u>1144.58–486</u> x 100 900	73
1.0	1155.22	<u>1155.22–486</u> x 100 900	74.3
1.5	1149.58	<u>1149.58–486</u> x 100 900	73.67

# PHASE 2: Effect of Reaction Time

Reaction Time	Mass RBD	Calculation	Yield (%)
(minutes)	Biodiesel (g)		
30	1163.25	<u>1163.25–486</u> x 100 880	76.9
40	1155.85	<u>1155.85–486</u> x 100 880	76.0
50	1150.66	<u>1150.66–486</u> x 100 880	75.0
60	1140.71	<u>1140.71–486</u> x 100 880	74.0

# RBD's Yield

# WCO's Yield

Reaction Time	Mass WCO	Calculation	Yield (%)
(minutes)	Biodiesel (g)		
30	1140.88	<u>1140.88–486</u> x 100 900	72.67
40	1126.78	<u>1126.78–486</u> x 100 900	71
50	1117.25	<u>1117.25–486</u> x 100 900	70
60	1108.92	<u>1108.92–486</u> x 100 900	69

D

# GAS ANALYZER ANALYSIS

*** TELEGAN *** TEMPEST 100 V3.3	*** TELEGAN *** TEMPEST 100 V3.3
DATE 06-03-09 TIME 15:54:27	DATE 06-03-09 TIME 15:55:54
HEAVY OIL	HEAVY OIL
AMBIENT C 30 STACK C 703 NETT C 673	AMBIENT C 30 STACK C 702 NETT C 672
02 % 9.3 RATIO 0.0042 CO PPM 376 CO2 % 8.7 XAIR % 81 EFF % (N) 58.1 DRY LOSS % 0.0 uCO LOSS % 0.2 Prs. inWG -0.06 NO PPM 0 NOX PPM 0 H2S PPM 0 REF. %02 3.0	02 % 9.3 RATIO 0.0032 CO PPM 282 CO2 % 8.7 XAIR % 81 EFF % (N) 58.3 DRY LOSS % 41.6 WET LOSS % 0.0 UCO LOSS % 0.1 Prs. inWG -0.05 NO PPM 0 H2S PPM 0 REF. %02 3.0
*** TELEGAN *** TEMPEST 100 V3.3	
DATE 06-03-09 TIME 16:03:56	
HEAVY OIL	
AMBIENT C 30 STACK C 702 NETT C 671	
02 % 9.3 RATIO 0.0025 CO PPM 222 CO2 % 8.7 XAIR % 81 VEFF % (N) 58.3 DRY LOSS % 41.6 WET LOSS % 0.0 uCO LOSS % 0.1 Prs. inWG -0.06	

WCO READING

DIESEL READING

PPM ..... PPM ..... 0

H2S PPM ..... 0 REF. 402 ... 3.0

NO

NO×

0

**RBD READING** 

GAS CHROMATOGRAPHY ANALYSIS

E

57



eak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[pA*s]	[pA]	8
3	7.424	BB	0.0997	284.59708	47.60416	0.02063
4	8.339	BV	0.1011	1.10220e4	1808.68591	0.79909
-5	8.748	vv	0.0977	1.68132e4	2868.54712	1.21895
6	9.031	VB	0.1136	1.72838e4	2412.35132	1.25307
7	9.508	BB	0.0957	70.11716	12.45866	0.00508
8	9.870	BV	0.0989	60.54845	10.25754	0.00439
9	10.051	VB	0.0962	105.37751	18.55705	0.00764
10	11.115	BV	0.1113	14.47203	2.07681	0.00105
11	11.429	VB	0.1078	29.53933	4.42874	0.00214
12	14.312	BB	0.1078	21.29862	3.19429	0.00154
otal	s :			1.37932e6	2.31008e5	
				46790		

Instrument 1 10/01/2009 13:59:59 FIZA-PSM 2009 100109

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.
Data File C:\CHEM32\1\DATA\BIODIESEL PSM 2009 SEQ\SIG1000005.D Sample Name: 1.5% WCO Pujah Acq. Operator : FIZA120109 Acq. Instrument : Instrument 1 Injection Date : 12/01/2009 12:00:08 Seq. Line : 5 Location : Vial 5 Inj : 1 Inj Volume : 1 µl Acq. Method : C:\CHEM32\1\METHODS\BIODIESEL.M Last changed : 10/01/2009 13:21:49 by FIZA-PSM 2009 100109 Analysis Method : C:\CHEM32\1\METHODS\BIODIESEL.M anged : 13/01/2009 11:31:22 by FIZA120109 (modified after loading) FID1A, (BIODIESEL PSM 2009 SEQ\SIG1000005.D) Last changed 9.036 0.464 pA 3000 2500 8.333 2000 1500 1000 500 10.895 7.430 14.314 19.173 6.467 0 Ó 2.5 5 7.5 10 12.5 17.5 20 15 min -----External Standard Report Sorted By : Signal Multiplier : 1.0000 Dilution 1.0000 Use Multiplier & Dilution Factor with ISTDs . Area Percent Report -----Sorted By Signal : : Multiplier 1.0000 Dilution 1.0000 : Use Multiplier & Dilution Factor with ISTDs Signal 1: FID1 A, 
 Peak RetTime Type Width
 Area
 Height
 Area

 # [min]
 [min]
 [pA\*s]
 [pA]
 %

 0.464
 BBAS
 0.0961
 1.60001e6
 2.77382e5
 96.63370

 6.467
 BB
 0.0992
 158.91362
 26.79533
 0.00960

 7.430
 BB
 0.1065
 526.83081
 82.48402
 0.03182

 8.333
 BB
 0.1067
 1.25351e4
 1906.18066
 0.75707

 8.757
 BV
 0.0996
 2.01153e4
 3365.55371
 1.21488
1 2 3 4 5 Instrument 1 13/01/2009 11:33:18 FIZA120109 Page 1 of 2

60

Data Sam	a File aple N	C:\CHEN ame: 1.5	432\1\ 5% WCC	DATA\BIO Pujah	DDIESEL PSM	2009 SEQ\SI	G1000005.D
2	Peak #	RetTime [min]	Туре	Width [min]	Area [pA*s]	Height [pA]	Area %
	6	9.036	VB	0.1172	2.14286e4	2866.96924	1.29420
	7	9.499	BV	0.0943	85.22381	15.00410	0.00515
	8	9.658	VV	0.1081	223.35249	33.35521	0.01349
	9	9.866	VV	0.1097	161.23820	25.18106	0.00974
	10	10.050	VB	0.0969	93.47636	16.29550	0.00565
	11	10.895	BV	0.1403	283.27988	29.95972	0.01711
	12	11.429	VB	0.1127	74.80302	10.54971	0.00452
	13	14.314	BB	0.1077	20.05935	3.01234	0.00121
	14	19.173	BB	0.1245	31.07239	3.83744	0.00188
	Totals :				1.65574e6	2.85767e5	
					55730		

\*\*\* End of Report \*\*\*

Instrument 1 13/01/2009 11:33:18 FIZA120109

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