A COMPARISON BETWEEN THE PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL AND REFINED-BLEACHED-DEODORIZED PALM OIL USING ULTRASONIC TRANSESTERIFICATION WITH POTASSIUM HYDROXIDE AS A CATALYST

CHARLENE ANGELA A/P J. N. SUNDRARAJ

UNIVERSITI MALAYSIA PAHANG

BORANG PENGESAHAN STATUS TESIS

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Alamat Teta	p: 43 Jalan Koop C	uepacs 3A	Puan Hamidah Bt. Abdullah	
	Taman Cuepacs, 43	3200	Nama Penyelia	
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CHARLENE ANGELA A/P J.N. SUNDRARAJ

Thesis submitted to the Faculty of Chemical and Natural Resources Engineering in Partial Fulfillment of the Requirement for the Degree of Bachelor Engineering in Chemical Engineering

> Faculty of Chemical & Natural Resources Engineering Universiti Malaysia Pahang

> > **APRIL**, 2009

I declare that this thesis entitled "A Comparison between the Production of Biodiesel from Waste Cooking Oil and Refined-Bleached-Deodorized Palm Oil using Ultrasonic Transesterification with Potassium Hydroxide as a Catalyst" 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 submitted in candidature of any degree.

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I dedicate this thesis to my family, without whom none of this would have been worth the challenge...

Supportive parents; John Nepomus Sundraraj Balachandran and Mary Lucia Morais

Not-so-little brothers; Adrian Thomas John Balachandran and Steven Emanuel John Balachandran

This is for the four of you.

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ABSTRACT

The recent issue of peak oil and environmental concerns has prompted deeper research into the area of alternative fuels, particularly biofuel. Two types of feedstock for biodiesel production was researched in this project, namely waste cooking oil (WCO) and Refined-Bleached-Deodorized (RBD) palm oil. The performance of the alkaline catalyst potassium hydroxide was investigated towards the methyl ester purity of the product produced using ultrasonic transesterification. The methanol oil molar ratio used in this research was 6:1. The best conditions for biodiesel production were determined in terms of reaction time and catalyst concentration. The range of catalyst concentration and reaction time studied were 0.75 to 1.75 weight percent and 20 to 50 minutes respectively. Catalyst concentration and reaction time played a significant role in the purity of the product produced. The results show that the best catalyst concentration to produce methyl ester of high purity is at 1.75 weight percent, while the best reaction time necessary is 50 minutes. The resulting conditions were then used to synthesize the final product that was then subjected to a combustion test to determine the quantity of carbon monoxide and carbon dioxide emitted. WCO biodiesel was found to have 19.1% lower carbon monoxide emissions than RBD palm oil biodiesel. In terms of the amount of carbon dioxide released, WCO biodiesel had emissions higher than that of RBD palm oil biodiesel by 2.3%. In conclusion, WCO biodiesel was found to be more environmentally friendly compared to RBD palm oil biodiesel upon combustion.

ABSTRAK

Disebabkan oleh isu sumber bahan api fosil yang semakin kurang, kajian saintifik terhadap bahan api alternatif sedang giat dijalankan. Projek penyelidikan ini adalah berkaitan dengan bahan mentah yang digunakan untuk menghasilkan biodiesel, iaitu minyak masak yang terguna (WCO) dan minyak kelapa sawit yang ditapis, diluntur, dan dinyahbau (minyak kelapa sawit RBD). Keberkesanan pengunaan mangkin kalium hidroksida terhadap darjah pertukaran bahan mentah kepada produk (ketulenan produk) dikaji menggunakan transesterifikasi ultrasonik. Nisbah molar metanol terhadap minyak yang digunakan dalam kajian ini ialah 6:1. Keadaan tindakbalas kimia yang terbaik untuk menghasilkan biodiesel yang bermutu tinggi ditentukan melalui kajian terhadap keadaan suhu dan masatindalbalas transesterifikasi. Julat kelarutan mangkin kalium hidroksia yang dikaji adalah dari 0.75 hingga 1.75 wt % manakala julat tempoh masa tindakbalas adalah dari 20 hingga 50 minit. Kelarutan mangkin dan tempoh masa tindakbalas didapati memainkan peranan yang penting dalam memastikan ketulenan produk yang dihasilkan. Keputusan penyelidikan menunjukkan bahawa kelarutan mangkin yang terbaik adalah 1.75 wt % dan 50 minit adalah tempoh masa tindakbalas yang terbaik. Keadaan kelarutan mangkin dan tempoh masa tindakbalas yang terbaik ini digunakan untuk menghasilkan produk terakhir yang kemudian menjalani ujian pembakaran untuk supaya kuantiti karbon diosida dan karbon monoksida yang dibebaskan oleh sampel apabila dibakar dapat diketahui. Biodiesel WCO didapati membebaskan karbon monoksida dengan jumlah 19.1 % kurang daripada biodiesel minyak kelapa sawit RBD. Biodiesel WCO didapati membebaskan 2.3% lebih banyak karbon monoksida daripada biodiesel minyak kelapa sawit RBD. Kesimpulannya, biodiesel WCO menghasilkan pencemaran alam sekitar yang kurang berbanding dengan biodiesel minyak kelapa sawit RBD.

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LIST OF ABBREVIATIONS

ASTM	American Society of Testing and Materials
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
PAH	Polycyclic Aromatic Hydrocarbon
PPO	Pure Plant Oil
RBD	Refined-Bleached-Deodorized
SVO	Straight Vegetable Oil
WCO	Waste Cooking Oil
WVO	Waste Vegetable Oil

LIST OF SYMBOLS

%	Percentage
ρ	Density
ΣA	Total peak area of methyl ester in C_{14} to $C_{24:1}$
A_{E1}	Peak area corresponding to methyl ester
C_{E1}	Concentration of methyl ester stock solution
V_{E1}	Volume of methyl ester solution being used
Μ	Mass of sample
m _{KOH}	Mass of catalyst
С	Methyl ester purity
X	Ratio

CHAPTER 1

INTRODUCTION

1.1 Background

The energy source, fossil fuel, upon which we have come to rely on so heavily, is in higher demand than ever before that more energy is needed to fulfill this demand. Fossil fuel alone seems to be insufficient to cater to the needs of the global community. In light of this, it is in the world's best interest to devote a substantial amount of resources towards alternative forms of energy. Biofuel, as biodiesel in this context, is at the forefront of these alternatives due to its ability to fuel conventional diesel engines with minimum or no modifications, as well as form blends with fossil diesel.

Biodiesel is defined as fatty acid methyl esters prepared from any kind of feedstock including vegetable oils, animal fats, single cell oils, and waste material. Fatty acid ethyl esters can also be defined as and used to produce biodiesel. However, due to the relatively high price of ethanol compared to methanol, the use of ethyl esters has not been established to a level on par with methyl esters. The preparation of fatty acid methyl esters can be achieved by a process called transesterification, which is the exchange of alcohol or acid moiety of an ester. Alcoholysis is the transesterification of an ester with an alcohol, whereby methanolysis is the term used in the case of methanol.

All feedstocks that contain fatty acids or glycerol can be used for biodiesel production including waste cooking oil. In European countries, rapeseed oil is used

due to its widespread availability. Soybean oil is used in the Unites States of America, while palm oil is used widely in tropical regions such as Malaysia. The use of methyl esters as fuel requires a low proportion of saturated fatty acids in order to make the fuel function at low temperatures. In colder climates, rapeseed oil and olive oil have proven to be one of the best options. The usage of palm oil is ideal in Malaysia due its abundant availability as well as its suitability in warm climates. Palm oil can also be used as blends with other types of oil. The type of feedstock chosen is also influenced by national and international specifications of biodiesel that need to be fulfilled.

Among the many benefits of biodiesel is that there is no net output of carbon in the form of carbon dioxide (CO2). This is due to the fact that the same amount of carbon dioxide is absorbed during the growth period of oil crops as is emitted by fuel combustion. One ton of fossil fuel combusted releases 3 tons of carbon dioxide into the atmosphere while biodiesel only releases the that which it has taken in while the plants it is made from were growing. Therefore, there is no negative impact on the carbon cycle.

Biodiesel has many favourable emissions characteristics in comparison to conventional fossil diesel. It is known to have 100% reduction of net carbon dioxide, 100% reduction of sulphur dioxide, 40-60% reduction of soot emissions and 10-50% reduction of carbon monoxide. Biodiesel also exhibits a reduction of all polycyclic aromatic hydrocarbons (PAHs) and specifically the reduction of carcinogenic PAHs such as phenanthren by 97%, benxofloroanthen by 56%, benz-a-pyrene by 71%, aldehydes and aromatic compounds by 13% asl well as 5-10% reduction of nitrous oxide depending on the age and tuning of the vehicle concerned.

Biodiesel is completely non-toxic and rapidly biodegradable. Biodiesel is biodegradable and non-toxic. B-100, which represents 100% biodiesel, is as biodegradable as sugar and less toxic than conventional table salt. The rate of biodegradation of biodiesel is up-to four times higher than that of fossil diesel fuel. It has up to 98% biodegradation in three weeks. It also stores without letting up in completely full, cool, dark containers Therefore, spillages of biodiesel present a significantly lower risk compared to fossil diesel. Since biodiesel has a flash point higher than that of fossil diesel, it poses less of a threat in the event of a crash.

1.2 Problem Statement

The current energy crisis has beckoned upon us to look towards an energy alternative that is feasible and sustainable in the long run. Being a direct solution to the current shortage of liquid fuel, biodiesel is one of the most popular alternatives of all time. Even so, we need to look towards feedstock that will be suitable for Malaysia, as well as sustainable and economical in the long run. This research seeks to solve this uncertainty in feedstock sustainable selection, by comparing two of the most researched types of biodiesel feedstock on Malaysian shores, namely Refined-Bleached-Deodorized (RBD) palm oil and waste cooking oil.

Waste cooking oil is a cheap feedstock for biodiesel production, making its procurement a very economical affair. If it is proven that waste cooking oil is an efficient and suitable feedstock for biodiesel production, a systematic collection system should be introduced to the members of the public so that they may collect and sell their waste cooking oil for biodiesel production. With this, there would be a steady supply of waste cooking oil, which is far cheaper than using virgin oil. Although the usage of waste cooking oil as a feedstock would require additional steps in biodiesel production, such as prefiltration and preheating as well as a relatively high catalyst concentration, that may incur additional costs of processing, it is argued that the additional costs can be offset by the cheap price of feedstock. It would also be an avenue for members of the public to take responsibility and to play an active role in combating the energy crisis.

Refined-Bleached-Deodorized (RBD) palm oil as a popular feedstock in biodiesel research in Malaysia since it is abundant in palm oil and the usage of it is suitable for the warm climates. Although the cost of RBD palm oil is significantly higher than that of WCO, the amount of catalyst used would be significantly lesser. In addition to this, the procedure for production would also be simpler as RBD palm oil would not need to be filtered before transesterification and neither would it need preheating. The cost of machinery, processing as well as the energy needed to run an RBD stocked biodiesel plant would be significantly lower than that of WCO. Using RBD palm oil would benefit Malaysians in terms of relatively low maintenance costs due to lesser machinery and simpler processing. The result would be a feasible fuel alternative at an affordable price for Malaysians.

Ultrasonic transesterification in biodiesel production can reduce processing time to 25% of the time needed otherwise. Industrially, along with producing 99% yield, it is highly more efficient that conventional agitation that can take up to 12 hours, reducing this time frame to less than 60 minutes. The amount of catalyst required can also be reduced by up to 50% due to the increased chemical activity in the cavitations formed due to ulltrasonication. In addition to this, it also extensively reduces the amount of excess alcohol required for processing while increasing the purity of the glycerin formed. This type of processing, coupled with a comparative research of the two said feedstock, would provide a feasible, sustainable, and efficient choice of feedstock for biodiesel production.

1.3 Objectives

The objective of this research is to determine the best conditions of catalyst concentration and reaction time in producing biodiesel that is environmentally friendly with high purity of methyl ester from Refined-Bleached-Deodorized (RBD) palm oil and waste cooking oil (WCO), using ultrasonic transesterification with potassium hydroxide as the catalyst.

1.4 Scope of Research

To analyze and compare the methyl ester concentration of biodiesel produced from both Refined-Bleached-Deodorized (RBD) palm oil and waste cooking oil using Gas Chromatography.

To study and compare the emission levels of carbon monoxide and carbon dioxide upon the combustion of fossil diesel as well as biodiesel produced from both RBD palm oil and WCO.

The temperature is fixed at 40 degrees Celsius through the whole experiment (B.Rice et.al., 1997). First, reaction time is set at 40 minutes while the catalyst concentration is varied at 0.20, 0.5, 0.75, 1.0, and 1.5 wt %. Then the catalyst concentration is fixed at the optimum level obtained while the reaction time is varied at 20,30,40,50, and 60 minutes.

1.5 Rationale and Significance

The rationale of this proposed research project is to provide empirical evidence to compare the purity of products of biodiesel production from WCO and RBD palm oil. The results of this research would signify the identification of a feedstock for biodiesel production that is feasible, sustainable and efficient for Malaysia. The identification of this feedstock will be a basis for the production of biodiesel on an industrial scale to counter the current global shortage of fuel.

The numerous advantages of using Ultrasonic transesterification would bring about volumes of significance in the biodiesel production industry. This is due to the fact that aside from giving relatively high yield, it would monumentally reduce the length of processing time needed for production, and this would go well to supply the ever increasing rate of demand for alternative liquid fuel. With Ultrasonic transesterification, the biodiesel production industry in Malaysia would be able to cater to the needs of Malaysians at a faster rate, thereby eliminating the need for any dependence on foreign alternative fuel that may arise in the future. Malaysia would be able to deal with its own fuel crisis, at an optimal rate using its abundant feedstock resources and ultrasonic transesterification.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Rudolf Diesel (1858-1913) developed the first engine to run on peanut oil. He demonstrated this invention at the World Exhibition in Paris in 1900. A vegetable oil powered engine however, was not fully realized in his lifetime. He firmly believed that since the diesel engine can be fed with vegetable oils, it would help considerably in the development of agriculture of the countries which use it. Although the use of vegetable oils for engine fuels seemed insignificant during his day, such oils have come to be as important as the petroleum and coal tar products used at that time.

The rapid development of the petroleum industry produced a cheap byproduct called diesel fuel that eventually became the source of power to a modified diesel engine. As a result, vegetable oil was forgotten as a renewable source of power. Diesel engines today are designed to run on fuel that is less viscous than vegetable oil. However, times of fuel shortages saw cars and trucks were successfully run on biodiesel made from preheated peanut oil and animal fat. The upper rate for inclusion of rapeseed oil with diesel fuel is about 25% but crude vegetable oil as a diesel fuel extender induces poorer cold-starting performance compared with diesel fuel or biodiesel made with fatty esters (McDonnel *et al.*, 1999).

Present day diesel engines have need of a clean-burning, stable fuel that can operate under a variety of conditions. Biodiesel as fatty esters was developed as an alternative to petroleum diesel due to the fuel shortages of the mid 1970s and further interest spewed forth in the 1990s due the large pollution reduction benefits coming from the use of biodiesel.

The use of biodiesel is affected by legislation and regulations in all countries (Knothe *et al.*, 2002). In the Philippines, the Government directed all of its departments to incorporate one percent by volume coconut biodiesel in diesel fuel for use in government vehicles. The EU Council of Ministers adopted pan-EU rules for the detaxation of biodiesel and biofuels. In the United States, by 1995, 10 percent of all federal vehicles were to be using alternative fuels to set an example for the private automotive and fuel industries.

Biofuel is at the forefront of the array of alternative energy sources that are being researched and developed today. Having physical and chemical properties that are compatible with its fossil counterpart has placed biodiesel as one of the most suitable alternatives to complement today, and perhaps even replace fossil diesel tomorrow. Its ability to fuel conventional diesel engines with minimum or no modifications, and to form blends with fossil diesel make it the most practical, and feasible alternative energy source to invest in.

There are many ways how biodiesel serves to benefit the environment more than fossil diesel. One major aspect of life cycle assessments is the potential of global warming, expressed as carbon dioxide, CO2 equivalents. CO2 is produced during the whole production process of fuels, biological based and fossil based alike. Due to the positive energy balance of biodiesel and the fact that biodiesel mainly consists of renewable material one could expect a large saving of greenhouse gases compared to fossil fuel. Now, while this remains true in the case of CO2, certain parties argue that if other greenhouse gases like N2O and CH4 are considered, which have higher global warming potential, the advantages of biodiesel are slightly diminished. Even so, the relative savings of greenhouse gases for the use of biodiesel over fossil diesel is 2.7kg of saved CO2 equivalents for every kg of substituted fossil diesel fuel. Pure biodiesel is also completely free of sulfur and, this inadvertently reduces sulfur dioxide exhaust from diesel engines to virtually zero. Biodiesel production and utilization when compared to petroleum diesel, produces 78.5% less CO2 emissions. Carbon dioxide is consumed by the annual production of crops and then released when vegetable oil based biodiesel is combusted. Research conducted in the United States of America has shown that biodiesel emissions have decreased levels of all target polycyclic aromatic hydrocarbons (PAH) and nitrited PAH compounds, as compared to fossil diesel exhaust. Aside from being nontoxic and biodegradable, biodiesel helps in preserving and protecting natural resources. For every one unit of energy needed to produce biodiesel, 3.24 units of energy are gained.

2.2 Raw Materials

The feedstock for biodiesel include virgin oil, waste vegetable oil and animal fat. The type of feedstock that is the most suitable varies from country to country and is dependent on an array of factors. These factors encompass the availability of the said feedstock, price, its suitability with the local climate and the adherence of the final product towards national and international specifications.

Virgin oil feedstock comprises oils such as rapeseed, soybean, field pennycress and Jatropha. Rapeseed and soybean are the two types of oils that are most commonly used. In fact, soybean oil accounts for ninety percent of all fuel stocks in the United States of America. Virgin oils can also be obtained from. Other types of virgin oils include mustard, flax, sunflower, palm oil, and hemp.

Waste vegetable oil (WVO) is oil that has been discarded after use. It is also known as straight vegetable oil (SVO) or pure plant oil (PPO). The most common type used in the UK is rapeseed oil, that is widely known as canola oil, in the United States and Canada. It has a freezing point of -10°C. Sunflower oil, on the other hand, freezes at -17°C and is currently being investigated on its suitability as a means of improving cold weather starting. Oils with lower gelling points tend to be less

saturated, causing them to polymerize more easily in the presence of atmospheric oxygen.

Animal fats include tallow, lard, yellow grease, chicken fat, and the byproducts of the production of Omega-3 fatty acids from fish oil. Omega-3 fatty acids are a family of unsaturated fatty acids that have in common a carbon–carbon double bond in the third bond from the methyl end of the fatty acid.

Algae is another type of feedstock which can be produced using waste materials such as sewage. This can be done without displacing land that is currently allocated for food production.

2.2.1 Waste Cooking Oil (WCO)

The use of waste cooking oil (WCO), animal fat and tall oil instead of refined vegetable oil will help in improving the economical feasibility of biodiesel. The amount of WCO generated in each country varies depending on the use of vegetable oil. In the European Union, the potential amount of WCO is estimated at approximately 0.7 to 1.0 Mt per year while the United States and Canada produce, on average, 9 and 8 pounds of yellow grease respectively, per person. The inexpensive and large quantity of WCO from households and restaurants are currently collected and used as either animal feed or disposed causing environmental pollution. Thus, WCO offers significant potential as an alternative low –cost biodiesel feedstock which could decrease dependency on fossil fuel.

The production of biodiesel from WCO is challenging due to the presence of undesirable components such as free fatty acids (FFAs) and water. Serious limitations of formation of undesirable side reactions such as saponification result in the usage of homogeneous alkali catalyst for transesterification of such feedstock. The problem of product separation substantially lowers ester yield. Acid catalysts have the potential to replace alkali catalysts since they do not show significant susceptibility to FFAs and can catalyze esterification and transesterification simultaneously. Even so, a slow reaction rate, requirement of high temperature, high molar ratio of oil and alcohol, separation of the catalyst, serious environmental and corrosion related problems make their use nonpractical for biodiesel production. (K.Jacobson *et al.*, 2008).

2.2.2 Refined-Bleached-Deodorized (RBD) Palm Oil

Palm oil can be used to create biodiesel for internal combustion engines. It has been discovered that biodiesel made from palm oil grown on sustainable nonforest land as well as from established plantations can effectively reduce greenhouse gas emissions.

Crude palm oil, palm olein, palm stearin, RBD palm oil, fractionated palm olein and pal mid-fraction are the types of forms in which palm oil is made available today. Most of the palm oil that is exported by Malaysia is RBD palm oil and RBD palm olein. However, the range of products available can be chosen to suit a variety of manufacturing needs, in forms that are ready-to-use and require no further processing. Palm oil comprises mainly triglyceries, mono and diglycerides. It also contains unsaponifiable matter, that includes varying quantities of free fatty acids, moisture, dirt and minor components of non oil fatty matter.

Tryglycerides are the chemical compounds of one molecule of glycerol bound to three molecules of Fatty Acid as shown in Equation 2.1.



Equation (2.1)

There are certain quarters that claim that several disadvantages exist with palm oil being channeled towards biodiesel. These parties, such as the non governmental organization, Greenpeace, claim that first generation biodiesel extracted from new palm oil plantations may contribute to global warming. This would happen in cases whereby forests that are cleared for palm plantations do not use the wood for bioenergy, but have it burned instead. It may take decades before the biodiesel produced from palm oil reduces as much carbon dioxide as much as the trees used to.

2.3 Processes

There are several types of processes from which biodiesel can be produced. These processes include blending, pyrolysis, microemulsion, and lastly, transesterification. Although the process in this research is transesterification of oil using potassium hydroxide as a catalyst, literature on the other available processes have been reviewed as well.

2.3.1 Direct use and Blending

The direct use of vegetable oils including the use of blends of different vegetable oils are not satisfactory and impractical for both direct and indirect diesel engines (Fangrui *et al.*, 1998). The vegetable oils require chemical modifications prior to usage by the diesel engines. Although its usage is feasible in certain diesel engines, it is known to bring about engine problems in turbo charged direct injection engines such as those used by trucks. As more extensive research is required to produce biodiesel as a feasible alternative fuel in all diesel engines, biodiesel is currently used in the form of blends with fossil diesel.

In order to be used commercially, biodiesel blends with fossil diesel must meet certain accredited standards, the most prominent of which is ASTM International. B20 which is 20% biodiesel blended with 80% Ultra Low Sulfur Diesel, that meets ASTM specifications can be used in diesel engines with minimum or no modifications. Major automakers and engine manufacturers in the United States accept the use of at least B5, while 50 percent of U.S. manufacturers already accept the use of B20 blends or higher in some of their equipment. Now that the final ASTM specifications for B6-B20 blends have been approved and published, several more companies are anticipated to raise their approvals to B20. Companies such as Chrysler LLC, stated that the need for an accredited as well as standardized, specification was the single greatest hurdle preventing its full-scale acceptance of B20 use in its diesel vehicles.

2.3.2 Pyrolysis

Pyrolysis is also known as thermal cracking, and is defined as the thermal decomposition of materials in the absence of oxygen when significantly less oxygen than required is present for complete combustion. It is the thermochemical process that converts organic materials into usable fuels with high fuel-to-feed ratios. Pyrolysis converts biomass into a useful fuel. Rapid heating and rapid quenching produce intermediate pyrolysis liquid products that condense before further reactions breakdown higher-molecular weight species into gaseous products.

Straight vegetable oil can be used as fuel in adapted diesel engines. However, since vegetable oil is 10-20 times more viscous than diesel fuel, cause problems in such engines over time (Jansson *et al* 1998). For biodiesel production that has a viscosity closer to that of diesel, the oil can be modified through the controlled pyrolysis of bio-oil, that decreases its molecular weight.

	Soybean oil		Cracked soybean oil		Diesel fuel	
	А	В	А	В	А	b
Cetane number	38.0	37.9	43.0	43.0	51.0	40.0
Higher heating	39.3	39.6	40.6	40.3	45.6	45.5
value, MJ/kg						
Pour point, C	-12.2	-12.2	4.4	7.2	-6.7 max	-6.7 max
Viscosity, cSt at	32.6	32.6	7.74	10.2	2.82	1.9-4.1
37.8 °C						

Table 2.1 : Fuel properties of thermally cracked soybean oil

Source: Niehaus et al. (1986) and Schwab et al. (1988).

2.3.3 Microemulsion

Microemulsion diesel fuel technology utilizes oxygenates to assist in compatibilizing a biomass derived or hydrocarbon petroleum phase and water phase. Oxygenate selection is therefore, a crucial stage in the miroemulsion process.

Microemulsions are clear, stable, two-phase nanodispersions which readily form upon mixing water with an oil phase. Water-in-oil microemulsions are made up of a continuous non-polar hydrocarbon phase and a discontinuous aqueous phase. Microemulsion diesel fuel technology utilizes a microemulsifier to compatibilize biodiesel fuel and a water phase. The microemulsifier contains a surfactant and a compatibilizing agent also known as an oxygenate. The resulting microemulsion fuel is clean-burning, gives no power loss or increase in fuel consumption, and is thermal and shear stable in the fuel handling system of conventional diesel engines.

2.3.4 Transesterification Process

2.3.4.1 Pretreatment

Pretreatment is carried out to remove impurities such as water, dirt, and fried food residue as well as free fatty acids (FFAs) is in the collected WCO. It is essential that water is removed because it causes the formation of fatty acid salts from the hydrolysis of triglycerides. This occurs instead of transesterification to produce biodiesel. The removal of water is generally carried out by heating the oil to a temperature of 120 degrees Celsius at which point the water will vaporize out of the oil. A drying agent may be used to remove the water in the form of water of crystallization, such as magnesium sulphate. A disadvantage is that the viscosity of the oil may complicate the thorough mixing of the drying agent. The dirt and fried food residue can be removed through prefiltration using a filter press.WCO tends to contain large amounts of FFAs. The WCO must thus be titrated with a standard solution of base in order to determine the quantity base required to neutralize the acid (Gerpen *et al.*, 2005).

2.3.4.2 Transesterification Reaction

Transesterification, is also known as Alcoholysis. It is the displacement of alcohol from an ester by another alcohol in a similar manner in that of hydrolysis, except than alcohol is used instead of water. Each reaction step is reversible. This process is used widely in reducing the viscosity of vegetable oils. Methanol and ethanol are most frequently used, especially methanol because of its low cost and its physical and chemical advantages. If methanol is used in this process it is called methanolysis. Thus, fatty acid methyl esters or FAMEs, known as biodiesel fuel are formed. The FAME's obtained by transesterification are similar to conventional diesel fuel in its main characteristics and can be used as an alternative fuel or used in blends with fossil diesel for diesel engines. (Song *et al.*,2007).



Transesterification is an equilibrium reaction and transformation occurs by mixing the reactants. The presence of a catalyst which is nomally a strong acid or base, accelerates considerably the adjustment of the equilibrium. A high yield of the ester can be achieved by using excess alcohol. The transesterification process is not restricted to a laboratory scale. This reaction is used by relevant industries to produce different types of compounds (Otera *et al.*, 1993). For example, the production of PET (polyethylene terephthalate), involves a step where dimethylterephthalate is transesterified with ethylene glycol in the presence of zinc acetate as catalyst is a process carried out in related industries (Weissermel *et al.*, 1993). A large number of acrylic acid derivatives is also produced by the transesterification of methyl acrylate with different alcohols, in the presence of acid catalysts (Rehberg *et al.*, 1944; Rehberg *et al.*, 1955; Haken *et al.*, 1963). Equation 2.3 shows the general equation for a transesterification reaction while Equation 2.4 shows the transesterification reaction of dimethylterephthalate with ethylene glycol.



The transesterification of vegetable oils comprises a triglyceride that reacts with an alcohol in the presence of a strong acid or base. This produces a mixture of fatty acids alkyl esters and glycerol (Wright *et al.*, 1944; Freedman *et al.*, 1986). The

overall process is a sequence of three consecutive and reversible reactions. The intermediates formed are di and monoglycerides (Freedman *et al.*, 1986). Stoichiometrically, the reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. Excess alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed.

Other factors, primarily the type of catalyst whether alkaline or acid, alcohol/vegetable oil molar ratio, temperature, purity of the reactants which is mainly water content, and free fatty acid content have an influence on the course of the transesterification. These aspects influence the process based on the type of catalyst used.

2. 3.4.3 Catalysts used in Transesterification

The transesterification reaction to produce biodiesel can be catalyzed by alkalis, acids or enzymes. For an alkali-catalyzed transesterification, the glycerides and alcohol must be significantly anhydrous because water makes the reaction partially change to saponification, which produces soap. The yield of esters is lowered by the soap formation and tends to make the separation of ester and glycerol as well as water washing increasingly difficult (Song *et al.*,2007).Thus, low free fatty acids (FFAs) content in vegetable oil is required for alkali-catalyzed transesterification. In the acid-catalyzed process, the presence of water and FFAs have a significant effect on the FAME production as well as in the alkali catalysis.

A. Alkali catalyst

Either sodium hydroxide (NaOH) or potassium hydroxide (KOH) can be used with methanol or ethanol and the chosen oil. It is best to produce the alcoxy before the reaction to obtain a better global efficiency. The alcoxy reaction is shown in Equation 2.5.

$R2CH2OH + NaOH \square H2O + R2CH2ONa$

Equation (2.5)

The alcohol–oil molar ratio that should be used varies from a ratio of 1:1–6:1. However, 6:1 is the most used ratio, leading to an important conversion for the alkali catalyst without using an immense amount of alcohol. The types of alcohol considered are usually methanol and ethanol. Methanol has fewer safety problems because it is less toxic compared to ethanol, thus its usage would have significantly smaller safety issues. The amount of catalyst that should be added to the reactor varies from 0.5 to 1 wt % (J.M. Marchetti *et al.*, 2003). The alkali process is more efficient and less corrosive than the acid process.

Base-catalyzed transesterification of vegetable oils takes place at a faster rate than the acid-catalyzed reaction (Freedman *et al.*,1986; Freedman *et al.*, 1984). This reason, and the fact that alkaline catalysts are less corrosives than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides (Freedman *et al.*,1986; Freedman *et al.*, 1984; Schwab, *et al.*, 1987) and hydroxides (Aksoy *et al.*, 1990; Tanaka *et al.*, 1981; Gaskoks-Vertrieb 1989; Wimmer *et al.*, 1993) as well as sodium or potassium carbonates (Graille *et al.*, 1985; Filip *et al.*, 1992; Bajwa *et al.*, 1987).

Equation 2.6 shows the transesterification of vegetable oils, while Figure 2.1 shows the mechanism of the base-catalyzed transesterification of vegetable oils.

			ROCOR'		
H ₂ C – OCOR'		catalyst	+		H ₂ C-OH
HC-OCOR"	+ 3 ROH		ROCOR"	+	нс-он
			+		
$H_2C = OCOR^*$			ROCOR'''		h ₂ C=0H
triglyceride	alcohol		mixture of alkyl esters		glycerol
					Equation (2.6)


Figure 2.1 : Mechanism of the Base-catalyzed Transesterification of Vegetable Oils.

In Figure 2.1, the first step (1) is the reaction of the base with the alcohol, that produces an alkoxide and the protonated catalyst. A tetrahedral intermediate is formed out of the nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride (2) (Taft *et al.*1950; Guthrie *et al.*, 1991), from which the alkyl ester and the corresponding anion of the diglyceride are formed (3). The catalyst is deprotonated, thus regenerating the active species (4), which reacts with a second molecule of the alcohol, starting another catalytic cycle.

Alkaline metal alkoxides such as CH3ONa for methanolysis are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 min) even at low molar concentrations (0.5 mol%). Alkaline metal hydroxides such as potassium hydroxide,KOH and sodium hydroxide, NaOH are cheaper than metal alkoxides, but less active. However, high conversions of vegetable oils can be obtained by increasing the catalyst concentration to 1 or 2 mol% (Freedman *et al.*, 1984).

B. Acid catalyst

In this process, the triglycerides are used with the alcohol. In this case, instead of a base an acid is used. The most common acid used is sulfuric acid sometimes sulfonic acid. This catalyst gives a very high yield in esters but the reaction occurs very slowly. It normally takes more than a day to finish. If an excess of alcohol is used in the experiment, a better conversion of triglycerides is obtained. However, recovering glycerol becomes more difficult, which is why an optimal relationship between the alcohol and raw material should be determined experimentally considering each process as a new problem. The operation condition is usually in the form of a molar ratio of 30:1. The amount of catalyst that should be added to the reactor varies from 0.5 to 1 mol% (Song *et al.*,2007).

In acid catalyzed transesterification processes, the transesterification process is catalyzed by Bronsted acids, preferably by sulfonic (Stern *et al.*, 1990) and sulfuric acids (Freedman *et al.*, 1986; Harrington *et al.*, 1985; Graille *et al.*, 1986) These catalysts give high yields in alkyl esters, but the reactions are slow, requiring temperatures above 100 °C and more than 3 hours to complete (Freedman *et al.*, 1984; Freedman *et al.*, 1986).

The methanolysis of soybean oil, in the presence of 1 mol% of sulphuric acid, H2SO4, with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50 hours for complete conversion of the vegetable oil (> 99%), while the butanolysis at 117 °C and ethanolysis at 78 °C, using the same quantities of catalyst and alcohol, take 3 hours and 18 hours respectively. A main factor influencing the transesterification process is the alcohol/vegetable oil molar ratio. Excess alcohol favors the product formation. However, excessive of alcohol complicates the recovery of the glycerol. Thus, the ideal alcohol/oil ratio has to be established empirically, considering each individual process.



Figure 2.2 : Intramolecular Transesterification Reactions, forming Lactones or Macrocycles.



Figure 2.3 : Mechanism of the Acid-catalyzed Transesterification of Vegetable Oils.

The mechanism of the acid-catalyzed transesterification of vegetable oils applies for a monoglyceride. It may be extended to di- and triglycerides (Stoffel *et al.* 1959). Carbocation II is formed by the protonation of the carbonyl group of the

ester. After a nucleophilic attack of the alcohol, the tetrahedral intermediate III is produced, which eliminates glycerol to form the new ester IV. The regeneration of the catalyst H+ then follows. This mechanism suggests that carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. Thus, an acid-catalyzed transesterification process should be carried out in the absence of water to avoid the competitive formation of carboxylic acids. The formation of carboxylic acids reduce the yields of alkyl esters.

C. Lipase Catalyst

Lipases are enzymes used to catalyze reactions such as the hydrolysis of glycerol, alcoholysis and acidolysis. It can also be used as catalyst for transesterification and esterification reactions as well. Biocompatibility, biodegradability and environmental acceptability are important properties to be considered in determining its feasibility of use.

A few advantages of using lipases include the possibility of regeneration and reuse of the immobilized residue, because it can be left in the reactor if the reactive flow is kept (Song *et al.*,2007). The use of enzymes in reactors allows the usage of high concentration and that makes for a longer activation of the lipase. There is also a bigger thermal stability of the enzyme due to its native state. The immobilization of the lipase could protect it from the solvent that is used in the reaction and this will prevent the enzyme particles from getting close together. This catalyst will also allow for easier product separation.

The negative aspects of this enzyme include, that one can loose some initial activity due to the volume of the oil molecules, the number of support enzymes may not be uniform as well as the biocatalyst tends to be more expensive that the natural enzyme. Since the reaction yields as well as the reaction times are still unfavorable compared to the base-catalyzed reaction systems, this process is currently not economically feasible.

D. Non- Ionic Base Catalyst

Organic bases are used as catalysts or reactant for organic syntheses to obtain milder reaction conditions and to simplify manipulations. These bases include amines such as triethylamine (Resck at al., 1994; Hofle *et al.*, 1978), piperidine (Resck *et al.*, 1994), 1,2,2,6,6-pentamethylpiperidine (Resck *et al.*, 1994; Schewesinger *et al.*, 1985), pyridine (Resck *et al.*, 1994; Hofle *et al.*, 1978 Schwesinger *et al.*, 1985), 2.6di-tertbutylpyridine (Resck *et al.*, 1994; Schwesinger *et al.*, 1985) and 4-dimethyaminopyridine (Otera *et al.*, 1993) (DMAP); amines such as 1,8diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diabicyclo[4.3.0]non-5-ene (Oediger *et al.*, 1972) (DBN). These are frequently used in organic synthesis

In the usage of such non-ionic bases as catalysts for the transesterification of vegetable oils, it was observed that TBD even if applied at only 1 mol%, produces more than 90% of methyl esters after 1 hour. The other bases, under the same experimental conditions, produced yields not higher than 66%. The order of the catalytic activity is not directly related to the relative basicity of these compounds. The superior performance of TBD, when compared to BEMP and Me7P, is related to its kinetic activity. Having an unshared electron pair of the sp2 N, its catalytic site, is almost unhindered, allowing easy access of the methanol for proton transfer (Ulf Schuchardta *et al.*, 1998).

2.3.4.4 Glycerine washing and methanol recovery

The transesterification reaction between oil and an alcohol such as methanol to produce biodiesel yields glycerine as a byproduct. This glycerine needs to be separated out of the product and the methanol recovered. Since the methanol used in the reaction is in excess to allow for sufficient reaction, a considerable amount of methanol can be recovered for reuse. Among the methods available for the removal of methanol are vacuum evaporation, distillation, and water washing. An economical method of methanol removal would be the water washing method since it acquires a relatively low cost. The glycerine can be removed from the product by decantation.



Figure 2.4 : Process flow schematic for biodiesel production

2.4 Byproduct of biodiesel production

Glycerine, a byproduct form the transesterification reaction to produce biodiesel, is a colorless, odorless, viscous liquid that is widely used in pharmaceutical formulations. It also goes by the names, glycerol and glycerin. Glycerine is a sugar alcohol of sweet-taste and low toxicity. It has three hydrophilic alcoholic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. Its substructure is a central component of many lipids. Figure 2.5 shows a typical molecule of glycerine.



Figure 2.5 : Glycerine molecule

Identifying new or alternative uses for glycerin is of high priority due to the overabundance of crude glycerin that is available in current markets. This excess in crude glycerin is a result of biodiesel processing. If a plant finds it difficult to identify a market for this material, it may be faced with disposal fees. Interest is growing to use crude glycerin to produce energy. This material can be used as a fuel source for industrial boilers (Norris *et al.*, 2007). However, compliance must be met by applying for, and obtaining, an emissions permit from the government prior to the regulatory review and actual demonstration of the fuel. The energy value contained in the crude glycerin shows the need of using a blend of crude glycerin with another source fuel.

2.5 Catalyst Comparison

2.5.1 Hydroxides and Alcoholates

The types of hydroxide catalysts used are such as sodium hydroxide, NaOH and potassium hydroxide, KOH. The high performance alcoholate catalysts are such as sodium methylate with a 30% methanol solution, sodium ethylate with a 21% ethanol solution, and potassium methylate with a 32% methanol solution (Zadra *et al.*, 2005).

Based on the comparison given in the table below, hydroxides are good choice as they are a more feasible immediate solution to tackle the surge in energy demand. Even though the usage of high performance alcoholates requires lower capital investment, the relatively high cost of the catalyst levels its playing field with the feasible usage of hydroxides amidst the capability of hydroxides in generating job opportunities alongside energy security.

Hydroxides		High performance alcoholates		
1.	Relatively cheaper	1.	Relatively expensive	
2.	Strong price variation	2.	Stable price	
3.	Higher capital investments in terms	3.	Lower capital investment in terms of	
	of the equipment needed for catalyst		the storage tank required.	
	preparation. This includes tanks with	4.	Less manpower is required for liquid	
	cooling systems, and pumps.		handling	
4.	Manpower is needed for big bag	5.	There is no contact with the product	
	handling and catalyst preparation.		produced.	
5.	There is potentially dangerous	6.	No mixing is needed in the process.	
	handling of sodium hydroxide or	7.	Less than 0.2% water is present in	
	potassium hydroxide catalysts.		the catalyst.	
6.	Exothermic reactions occur with	8.	Relatively low purification costs.	
	alcohol.			
7.	There is 11-13% water content in the			
	self made alcoholate.			
8.	Relatively high purification costs.			

Table 2.2 : A comparison between hydroxides and high performance

alcoholates

2.5.2 Homogenous and Heterogenous Catalysts

2.5.2.1 Homogenous Catalysts

In homogenous catalysis of the production of biodiesel, potassium hydroxide, KOH or sodium hydroxide, NaOH is used as the catalyst upon being dissolved in an alcohol such as methanol. After the transesterification reaction, processing steps are required so that the fuel produced meets fuel standards. Soaps and other salts that are formed during the transesterification must be removed from the product biodiesel, and the byproduct glycerine (Croker *et al.*, 2006).

Potassium hydroxide is more easily dissolved in methanol as compared to sodium hydroxide. Sodium hydroxide tends to make the glycerin byproduct turn into a gel or even solid. This may cause equipment problems if the solidified glycerine is still in the processor or plumbing. Since potassium hydroxide is a heavier molecule than sodium hydroxide, more potassium hydroxide is used in catalyzing the production of biodiesel compared to sodium hydroxide. 1.4 times as much of potassium hydroxide is used compared to sodium hydroxide. 5 grams per liter for sodium hydroxide is used as opposed to 7 grams per liter of potassium hydroxide.

2.5.2.2 Heterogeneous Catalysts

There has been a significant amount of research on solid acid or basic catalysts that could be used in a heterogeneous catalyzed process (Stern *et al.*, 1999; Stern *et al.*, 2000; Vogel *et al.*, 1984; Gelbard *et al.*, 1995). In a new continuous process using a completely heterogeneous catalyst, the catalyst consists of a mixture of oxides of zinc and aluminium which removes catalyst loss (Bournay *et al.*, 2005). The reaction occurs at a relatively high temperature and pressure compared to a reaction using homogeneous catalysis. It is carried out with excess methanol. Two successive stages of reaction and glycerol separation is required in order to meet European specifications.

2.5.2.3 Comparison between Homogenous and Heterogenous Catalysts

Both homogenous and heterogeneous catalysts are used to catalyze the transesterification reaction, which is used widely in the process of manufacturing biodiesel. Table 2.3 and 2.4 summarize the advantages and disadvantages of both types of catalysts.

Homogeneous Catalysts		Heterogeneous Catalysts				
1.	Higher reaction rate	1.	Relatively environment friendly,			
2.	Relatively cheaper	giving fewer disposal problems.				
3.	High conversion is achieved with	2.	The catalyst is non-corrosive.			
	minimal undesired reactions.	3.	Its separation from the reaction			
4.	High solubility in alcohol		mixture is less complicated.			
		4.	Relatively high catalytic activity.			
		5.	The catalyst has higher selectivity			
			and a longer life span.			
		6.	The catalyst can be regenerated.			

 Table 2.3 : The advantages of homogeneous and heterogeneous catalysts

Table 2.4 : The disadvantages of homogeneous and heterogeneous catalysts

Homogeneous Catalysts		Heterogeneous Catalysts		
1.	Basic catalysts must be neutralized.	1. The alcohol may corrode certain		
2.	Acidic catalysts have a lower	types of catalysts.		
	reaction rate compared to basic	2. The surface of catalysts may face		
	catalysts.	deterioration.		
3.	Saponification occurs as a side	3. The catalyst is relatively less stable.		
	reaction forming emulsions, making	4. The catalyst has a short life span.		
	the separation process more	5. A relatively high cost is required for		
	complicated.	catalyst regeneration.		
4.	High sensitivity towards water and			
	free fatty acids.			
5.	The catalyst can not be reutilized.			

2.6 Solvent

Methanol and ethanol are the most considered solvents in the transesterification of oil to produce biodiesel. However, methanol is favoured since it is significantly less toxic, and lower priced compared to ethanol.

The yield of methyl esters is highly dependent on the methanol to oil molar ratio. The transesterification of vegetable oil requires three moles of methanol per mole of triglyceride, in theory. Since the transesterification of triglyceride is a reversible reaction, excess methanol shifts the equilibrium towards the direction of ester formation. In order to shift the equilibrium forward, the use of high molar ratios of oil to alcohol such as 1:40 and even 1:275 have been reported. An increase in oil to alcohol molar ratios from 1:6 to 1:18 results in a significant effect on ester yield. The yield of methyl esters increased from 81 to 98 wt. % corresponding to a FFA content of about 1 wt. % after 10 h reaction time. Excess methanol used can be collected by distillation and reused (K. Jacobson *et al.*,2008).

2.7 Ultrasonic Transesterification

The usual type of reactor used in the production of biodiesel is the batch and continuous stirred tank reactors that use heat and mechanical mixing as its energy input. Although large amounts of product are produced using these reactors, the lengthy reaction time required for production incurs high cost and maintenance in the long term. This long term negative economic impact makes the conventional reactor less favourable compared to newer methods.

A new and more successful biodiesel production method would be the ultrasonic reactor (Stavarache *et al.*, 2004). An ultrasonic in-line reactor can be designed to fit any scale of power and size for different capacities and applications such as for biodiesel production, homogenization of liquids or liquid suspensions, emulsification of processing foods, pharmaceuticals as well as cosmetics, dissolving solids in solvents and sonochemistry.

Ultrasonication increases the rate of the transesterification reaction of the chosen oil into biodiesel as well as significantly reduces the amount of excess alcohol required for processing. It also increases the purity of the glycerin formed. This allows for a change from the production from batch processing into continuous flow

processing. Apart from this, the usage of the ultrasonic reactor on an industrial scale can also achieve a biodiesel yield of over 97%.

Ultrasonic cavitational mixing achieves a better degree of mixing on a commercial scale. This makes it possible for the usage of reduced amounts of catalyst and alcohol by 15-35% due to increased chemical activity through cavitation. Ultrasonic mixing is an effective means to achieve better mixing levels in commercial processing. It provides the activation energy needed for the industrial transesterification process. Power ultrasonic reactors have been used to produce biodiesel through the methanolysis of soybean with sodium hydroxide as a catalyst.

2.8 Product Analysis

2.8.1 Gas Chromatography

Gas chromatography (GC) is a type of chromatography in which the mobile phase is a carrier gas. This carrier gas is usually an inert gas such as helium or an unreactive gas such as nitrogen. The stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside glass or metal tubing, called a column. The instrument used to perform gas chromatographic separations is called a gas chromatograph.

Fuels are the most important type of hydrocarbon mixtures which require characterization and analysis in almost all the steps of fuel preparation. This statement holds true in the case of biodiesel as well. Biodiesel must be properly analyzed to ensure that it is appropriate to suit diesel engine operation. Analysis is presently carried out by a few GC based methods, that are currently still challenging in view of the complexity of diesel fuels, the high analysis temperatures involved as well as the required long analysis time (Fialkov *et al.*, 2008). A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample such as a sample of newly produced biodiesel. A gas chromatograph uses a column, through which different chemical constituents of a sample pass in a gas stream at different rates depending on their various chemical and physical properties and their interaction with the stationary phase. The chemicals are identified and detected electronically as they exit the end of the column. The stationary phase functions to separate different components causing each one to exit the column at different retention times. The carrier gas flow rate, as well as temperature can also be used to alter the order or time of retention.

2.8.2 Combustion Analysis

Research has shown that combustion tests on biodiesel have yielded findings that nitrogen oxide, NO emissions are reduced by about 20% using a biodiesel and low sulfur blend, compared to that of fossil diesel (Batey *et al.*, 2003). The combustion stability of the biodiesel blend is relatively favourable due to its low levels of carbon monoxide emissions that is similar to conventional fuel oil. sulfur oxide, SO emissions are reduced by 83% while smoke numbers were shown to be significantly lower compared to fossil oil with the same burner air setting (Batey *et al.*, 2003). Fuel oil and combustion odors were also better with the biodiesel and low sulfur oil blend.

The carbon monoxide, CO emission of a combusted fuel is an essential aspect to consider and determine in deciding if or not the fuel concerned is environmentally acceptable. B20, which is a blend of 20% biodiesel and 80% fossil diesel, has similar CO emissions to conventional fuel oil (Batey *et al.*, 2003). It also has similar CO versus excess air emission profiles. This shows that B20 and the fuel oil have similar combustion stabilities.

CHAPTER 3

MATERIALS AND EXPERIMENTAL METHODS

3.1 Materials

The materials used in this study were waste cooking oil (WCO) collected by the Faculty of Chemical Engineering and Natural Resources (FKKSA) of University Malaysia Pahang (UMP) and Refined- Bleached-Deodorized (RBD) palm oil of the brand Buruh, potassium hydroxide in granular form, and methanol. Fossil diesel was also used to make a comparative analysis on the combustion characteristics of the biodiesel produced.

3.2 Process details

The experiment was divided into two stages in which one variable was fixed while the other was varied to study the experimental results. The variable fixed in the first stage was the reaction time, at 40 minutes, while the catalyst concentration was varied. In the second stage, the catalyst concentration was fixed at a level at which maximum purity was obtained in the first stage while the reaction time was varied. The temperature was fixed at 40°C. The experiment was carried out on two levels, that is, firstly with WCO and secondly with RBD palm oil as the feedstock.

The steps outlined below were conducted using an ultrasonic reactor. Once the optimum catalyst concentration and reaction time had been determined, another sample of biodiesel was prepared according to these optimal conditions. A Gas Chromatographic analysis was conducted after each run, while a combustion analysis was carried out on the product produced at optimal catalyst concentration and reaction time to determine the efficiency of the fuel produced.



Figure 3.1 : Process Flow Diagram

3.2.1 Prefiltration

The WCO used is filtered in bulk using the filter press method. The WCO can only be used once it has been filtered. Prefiltration was omitted in the case of RBD palm oil, where by the next step was carried out without prior prefiltration.

3.2.2 Preheating of WCO

The WCO was heated using an electric heater in order to speed up the transesterification reaction that followed. Without preheating, the transesterification reaction using WCO as the feedstock would take significantly longer. This step was omitted in the case of RBD palm oil.

3.2.3 Catalyst Preparation

This study was conducted using a base catalyzed reaction using potassium hydroxide (KOH) as the catalyst. The methanol and the catalyst were mixed and the amount of methanol used was approximately 20% the volume of the oil. The methanol was poured first, followed by the KOH. When the particles of KOH were no longer seen in the solution, the catalyst was considered to be ready. It was then added to the oil which was readily poured into a solvent vessel and placed inside the ultrasonic reactor. The transesterification reaction should begin.

Properties	Methanol	RBD Palm Oil	WCO
Density	0.79 g/cm^3	0.880 g/cm^3	0.90 g/cm^3
Molecular weight	32.02 g/mol	847.3 g/mol	856 g/mol
Molar ratio	6 x 32.04	1x847.3	1x856
	= 192.24 g/mol	=847.3 g/mol	=856 g/mol
Methanol volume	-	252.7 cm^3	255.9 cm^3

Table 3.1 : Methanol, RBD palm oil and WCO preparation

Catalyst concentration	Mass of KOH (g)			
(wt %)	RBD Palm oil	WCO		
0.75	4.4	4.5		
1.00	6.6	6.75		
1.5	8.8	9.0		
1.75	13.2	13.5		

Table 3.2 : KOH catalyst preparation

3.2.4 Transesterification

The reaction between the methanol, potassium hydroxide, KOH, catalyst, and the raw oil was carried out in an ultrasonic water bath. First, the desired volume of methanol was measured into a conical flask. After measuring the desired weight of KOH, the catalyst was mixed with the alcohol in the conical flask. This was done using a magnetic stirrer until the KOH was fully dissolved in the methanol.

While this step was being carried out, the ultrasonic water bath with a frequency of 60 H was set at the desired temperature of 40 0C to prepare it for the first transesterification reaction. When the temperature of the water bath was stable at 400C, the catalyst and methanol mixture was added into 1L of raw oil. The electric stirrer used was set to a speed of 800 rpm. Once the transesterification reaction was completed, the sample was left for 24 hours to make way for the gravitational settling of glycerine.

3.2.5 Draining of Glycerine

After the transesterification reaction, the solvent vessel was left untouched for approximately 24 hours, to enable the glycerol to settle at the bottom of the vessel. This occurred since glycerol is more dense than biodiesel. After 24 hours elapsed, the glycerol that had settled at the bottom of the container was drained off using the decantation technique.

3.2.6 Methanol Removal

The biodiesel was placed in a rotary evaporator to separate out excess methanol. The temperature was set at 800C to enable the methanol to evaporate out of the fuel. The rotary evaporator was then left to run for approximately 3 hours. Once the rotary evaporation was completed, a Gas Chromatographic analysis of the sample was carried out for the first and second stages of research.

3.2.7 Washing Process

The methyl ester product was washed with warm deionized water that was boiled to a temperature of 800C. This is conducted several times until the wash water was made clear. This step was carried out to remove methanol, glycerol, catalyst and soap residue. Water was used as a washing reagent since water is hydrophilic while biodiesel is hydrophobic, and this enables it to attract the water molecules within the sample.

The biodiesel was then separated form the wash water using a separator funnel. The sample was then heated to a temperature of 100 0C for about half an hour to remove moisture. After being collected and its volume measured, the biodiesel was analyzed using gas chromatography (GC) analysis to determine the purity of the product formed.

3.3 Equipment

The ultrasonic water bath was used as the reactor in which the base-catalyzed transesterification was carried out. The water bath was of the brand Elmasonic and had a frequency of 60 H. The temperature settings available were from 350C to 800C. The time range for ultra sonic wave transmission through the water within it had specified settings with the option of an unspecified amount of time, depending on the user.



Figure 3.2 : Ultrasonic water bath



Figure 3.3 : Rotary evaporator

The rotary evaporator used was the Büchi Rotavapor R-200 that was invented by Lyman C. Craig. It had a vertical water condenser assembly and a digital heating bath with a motorised lifting jack. It was used to separate out methanol form the samples produced. The heating oil used had a boiling point temperature of about 1800C which enabled it to withstand evaporation while methanol was being evaporated out at 800C.

3.4 Analysis of sample

The methods of analysis used in this research were gas chromatography, and combustion analysis.

3.4.2 Gas chromatography

Gas chromatographic analysis was carried out on each product produced during the experiments conducted at different combinations of catalyst concentration and reaction time. The analysis was carried out during stages 1 and 2 of this research to determine the purity of the products.



Figure 3.4 : Agilent 6890 Gas Chromatograph

Biodiesel sample was weighed into a 10ml volumetric flask, and its weight was measured at approximately and not exceeding 110 mg. 5ml of standard solution was then added to the weighed sample and the volumetric flask was shaken to allow the sample to dissolve in the standard solution. The prepared sample was then injected into a 1.5 ml gas chromatography vial using a 10ml syringe with a 0.25 μ m filter attached to it.

The column used in the analysis of the biodiesel samples was the HT-5, DBwax column and HPLC grade heptanes was used in the GC analysis. The ovenramping setting was chosen and the analysis was carried out with hold times of 1 minute for 500C, 3 minutes for 750C as well as 2000C, and 18 minutes for 2300C. The injector used was of the 1 μ lid type while the detector was set at a temperature of 2800C.

3.4.3 Combustion analysis

A combustion analysis was carried out on the product produced at optimum conditions of catalyst concentration and reaction time, in order to compare its combustion characteristics with that of fossil diesel.



Figure 3.5 : Gas Analyzer

Approximately 2 L of sample was used in each combustion analysis of the biodiesel samples. The parameter that was emphasized was the amount of carbon monoxide, CO, emissions of each sample in parts per million, ppm. This value was then compared to that obtained from the combustion analysis of fossil diesel.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This research project was carried out over a duration of one year. The experimental data collected was analyzed using Gas Chromatography in order to determine the best potassium hydroxide, KOH, catalyst concentration and reaction time needed to produce biodiesel of high purity. It also shows that the usage of different raw materials namely, Refined-Bleached-Deodorized palm oil and Waste Cooking Oil, affects the purity of biodiesel.

The gas analyzer was used to observe the combustion properties of biodiesel obtained from the best conditions of catalyst concentration and reaction time. Although current standards for biodiesel are in the form of blends with fossil diesel, this research was carried out using samples of B-100 that were not mixed with fossil diesel. This is because the combustion properties of B-100 made from RBD palm oil relative to that of WCO would be similar to that of comparing the combustion properties of blends that were mixed with biodiesel made from the said raw materials.

4.2 Effect of catalyst concentration

The effect of catalyst concentration was the first parameter studied in the first stage of this transesterification process in producing biodiesel. The objective of this stage was to determine the optimal catalyst concentration required in the reaction for biodiesel produced from both WCO and RBD palm oil biodiesel. The concentration of potassium hydroxide, KOH catalyst used was in the range of 0.75 to 1.75 wt%. The temperature of the reaction was fixed at 40 0C while the reaction time was fixed at 40 minutes through out the experiment.

Figure 4.1 shows the of KOH catalyst concentration on the production of biodiesel from WCO and RBD pal oil in terms of purity of methyl ester



Figure 4.1: Effect of KOH catalyst concentration on methyl ester amount for WCO and RBD palm oil biodiesel

The purity of methyl ester in the biodiesel produced was determined by Gas Chromatography, GC analysis. Based on the analysis carried out, the best concentration of KOH to catalyze the transesterification process was 1.75 wt% for biodiesel produced by both WCO and RBD palm oil. From the results in Figure 4.1, the purity of methyl ester increased with increasing catalyst concentration. This occurs because increasing the catalyst concentration increases the degree of conversion of triglycerides that react with the methanol to produce methyl esters and glycerine (Meng *et al.*, 2008). The reaction occurs according to Equation 4.1.

$H_2C - OCOR'$ $H_2C - OCOR' + 3 ROH$ $H_2C - OCOR''$		catalyst	ROCOR' + ROCOR" + ROCOR'''	+	H ₂ C-ОН HC-ОН H ₂ C-ОН	
triglyceride	alcohol		mixture of alkyl esters		glycerol	
					Equation (4)	.1)

Although the methyl ester content in the samples increased with higher catalyst concentration, a corresponding increase in soap formation was also observed. This occurs because increased concentrations of KOH gives rise to the selectivity of triglycerides in the saponification reaction rather than transesterification (Phan *et al.*, 2008).

The results obtained for biodiesel production from WCO and RBD palm oil show that RBD palm oil has higher methyl ester content with increasing catalyst concentration as compared to that of WCO. This occurs because the free fatty acid, FFA content of WCO is relatively higher than that contained in RBD palm oil (Lou *et al.*, 2008). The relatively high FFA content in WCO causes a higher selection towards the conversion of FFA into soap rather than that of triglycerides into methyl ester. For this reason, biodiesel produced by RBD palm oil gives a relatively higher methyl ester content compared to that produced by WCO for a given catalyst concentration.

4.3 Effect of reaction time

The effect of reaction time was the parameter studied in the second stage of this transesterification process to produce biodiesel. The objective of this stage was to determine the optimal reaction time required for the production of biodiesel from both WCO and RBD palm oil biodiesel. The reaction times used were in the range of 20 to 50 minutes. The concentration of KOH catalyst used was fixed at 1.75 wt% for both transesterification reactions using WCO and RBD palm oil as this was the optimal catalyst concentration determined in the previous stage.

Figure 4.2 shows the results obtained for the effect of reaction time on the production of WCO biodiesel, followed by that of RBD palm oil biodiesel, and lastly a comparison between that of WCO and RBD palm oil biodiesel.



Figure 4.2 : Effect of reaction time on the purity of methyl ester of WCO and RBD palm oil biodiesel

The optimum reaction time for the transesterification reaction to produce biodiesel form both WCO and RBD palm oil was 50 minutes. The highest methyl ester content was obtained in both WCO and RBD palm oil biodiesel that was produced by 50-minute reactions. The lower reaction times of 20, 30, and 40 minutes yielded lower methyl ester content because the conversion of triglycerides into methyl ester did not have sufficient time to be completed. Longer reaction time gives rise to the percentage of methyl ester produced (Hanh *et al.*, 2009).

In using an ultrasonic water bath to carry out the reaction, it was expected that a relatively lower reaction time would prove sufficient in producing biodiesel of high methyl ester content. However, an optimal reaction time of 50 minutes was obtained. The reason why this occurred was due to the fact that instead of subjecting the reaction mixture itself to ulltrasonication, the reaction mixture was placed in a beaker which was subsequently placed into water in which ulltrasonication was being carried out. A higher optimal reaction time was obtained than that expected with an ultrasonic reactor because the reaction mixture was not directly exposed to ultrasonic waves for better mixing. Better mixing would lead to a higher reaction rate, thus further shortening the reaction time needed to produce biodiesel with an optimal methyl ester content (Hanh *et al.*, 2009).

The effect of reaction time on methyl ester content for biodiesel produced form both WCO and RBD palm oil showed the same trend and almost the same results based on GC analysis. This shows that the optimal reaction time to produce biodiesel from the transesterification reaction catalyzed by KOH is not significantly dependent on the FFA content of the raw material used. At 50 minutes, the methyl ester content for WCO biodiesel and RBD palm oil biodiesel were 82.33% and 83.46 % respectively. RBD palm oil showed a higher methyl ester content of only 1.37% relative to WCO. Thus, in terms of reaction time, it can be said that WCO and RBD palm oil show approximately the same level of methyl ester content for a given reaction time.

4.4 Combustion Test

Combustion tests were carried out on RBD palm oil biodiesel, WCO biodiesel and fossil diesel. The data obtained from the combustion of these samples were used to make comparisons with respect to the extent of emissions of carbon monoxide and carbon dioxide. The emissions produced by both biodiesel samples were compared to fossil diesel as well as to each other. This was done to demonstrate the differences between fossil diesel and biodiesel as well as between using RBD palm oil and WCO as the raw material for biodiesel production in terms of environmental advantage.



Figure 4.3 : Carbon monoxide emission levels upon combustion.

When both samples of biodiesel were compared to fossil diesel in terms of carbon monoxide emissions, it was observed that biodiesel has significantly lower emissions of carbon monoxide compared to fossil diesel (Peng *et al.*, 2008). The carbon monoxide emission of WCO biodiesel was lower than that of fossil diesel by 76.33% while RBD palm oil biodiesel emission was lower than that of fossil diesel by 70.74%. This is due to the higher oxygen content in biodiesel as compared to fossil diesel, allowing for the occurrence of complete combustion at a relatively greater extent (Ghobadian *et al.*, 2008). Complete combustion yields carbon dioxide while incomplete combustion yields carbon monoxide. When complete combustion increases, incomplete combustion decreases. Thus, the amount of carbon monoxide emissions from biodiesel were significantly lower than that of fossil diesel (Lin *et al.*, 2007). This shows that with respect to poisonous carbon monoxide emissions, biodiesel is more favourable than fossil diesel.

In the comparison between experimental data obtained from the combustion tests for RBD palm oil biodiesel and WCO biodiesel, it was observed that WCO biodiesel has lower emissions of carbon monoxide compared to RBD palm oil biodiesel. The carbon monoxide emission of WCO biodiesel was significantly lower than that of RBD palm oil biodiesel by 19.1%. The reason why this occurs is that WCO had already been burnt prior to its collection to be a raw material in this

research, implying that some of its carbon had already been combusted to form carbon dioxide before it was used to synthesize biodiesel. On the other hand, RBD palm oil had not been combusted prior to its usage as a raw material for biodiesel production and retains its relatively high amount of carbon. Thus, the carbon monoxide emissions from WCO biodiesel is far lower than that of RBD palm oil biodiesel This implies that with respect to air pollution by carbon monoxide, WCO biodiesel is better than RBD palm oil biodiesel.



Figure 4.4 : Carbon dioxide emission levels upon combustion.

When both samples of biodiesel were compared to fossil diesel in terms of carbon dioxide emissions, it was observed that RBD palm oil biodiesel had the same extent of emissions with fossil diesel at 8.7%. The carbon dioxide emission of WCO biodiesel was only slightly higher than that of RBD palm oil and fossil diesel by just 2.3%. The amount of carbon dioxide released upon combustion signifies the extent to which combustion had taken place. These results show that both RBD palm oil biodiesel and WCO biodiesel have approximately the same fuel compatibility with fossil diesel. Therefore, although biodiesel gives out lower emissions of poisonous carbon monoxide upon combustion, it still achieves complete combustion at the same extent as fossil diesel. However, in terms of carbon dioxide from biodiesel upon combustion would still be significantly lower than that of fossil diesel (Cheng *et al.*, 2008).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research has shown a clear comparison on the effect of catalyst concentration and reaction time in producing biodiesel from both Refined-Bleached-Deodorized (RBD) palm oil and waste cooking oil (WCO) using ultrasonic transesterification. It has also provided a strong basis in comparing the emissions of each type of biodiesel upon combustion.er and also with conventional fossil diesel.

The best potassium hydroxide catalyst concentration for transesterification to occur was the same for RBD palm oil biodiesel and WCO biodiesel, at 1.75 wt %. The synthesis of both types of biodiesel also required the same reaction time of 50 minutes. In conclusion, with respect to catalyst concentration and reaction time, both RBD palm oil and WCO are on par with one another.

In terms of purity of biodiesel, RBD palm oil biodiesel has shown to have slightly higher purity compared to WCO biodiesel for a given catalyst concentration and reaction time. The synthesis of RBD palm oil biodiesel and WCO biodiesel at 0.75 wt % catalyst concentration and 50 minutes reaction time had a difference of only 1.37%.

Both RBD palm oil biodiesel and WCO biodiesel had significantly lower emissions of carbon monoxide upon combustion compared to fossil diesel. However, WCO biodiesel had lower emissions of carbon monoxide compared to RBD palm oil biodiesel upon combustion. The emissions of carbon dioxide of all three types were approximately the same. This shows that with respect to environmental friendliness, both types of biodiesel are more favorable than fossil diesel, but WCO biodiesel is more favorable than RBD palm oil biodiesel.

5.2 **Recommendations**

This research project was carried out in the best possible manner, utilizing the equipment and raw materials supplied by the Chemical Engineering & Natural Resources Lab of Universiti Malaysia Pahang. There were a few setbacks in terms of equipment availability and suitability which are discussed below, along with recommendations on how to improve further research into biodiesel and its various raw materials.

Despite using an ultrasonic water bath in which transesterification was allowed to occur, the best reaction time obtained for both RBD palm oil and WCO was 50 minutes. The reaction mixture was not directly exposed to ultrasonic waves but placed in a beaker within the ultrasonic water bath. For future research, it is advisable to use small-scale ultrasonic reactors that are specifically designated for biodiesel synthesis. This is so that the ultrasonic waves may be passed directly through the reaction mixture for better mixing and a shorter reaction time.

The combustion test that was carried out using the gas analyzer was only sufficient to determine the amount of emissions of poisonous gases such as carbon monoxide and carbon dioxide. To enable a better comparative analysis of the environmental detriments of biodiesel relative to fossil diesel and between different types of biodiesel, a more sensitive gas analyzer is required. It is therefore, advisable to upgrade and install more sensors in the gas analyzer used.

These recommendations would facilitate the growth and depth of research on biodiesel by providing more data, so that additional factors may be considered in comparing the effects of raw materials on the quality of production of biodiesel. With these recommendations, more knowledge can be garnered on the road to produce biofuels for energy security.

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APPENDIX A

A.1 Calculations for raw materials and solvent

A.1.1 Waste cooking oil

Volume of waste cooking oil used in each experiment = 500 cm^3

Density of waste cooking oil, $\rho_{WCO} = 900 \text{ kg/m}^3$ = (900 kg/m³) x (1000 g/1 kg) x (1 m³/10⁶ cm³) = 0.900 g/ cm³

Mass of waste cooking oil = $\rho_{WCO} \times V_{oil}$ = 0.900 g/ cm³ x 500 cm³ = 450 g

Mass of catalyst used in each experiment using waste cooking oil

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 \begin{array}{l} m \ _{KOH \ @ \ 0.75 wt\%} = 0.75/100 \ x \ 450 \ g \\ = \ 3.375 \ g \\ m \ _{KOH \ @ \ 1.00 wt\%} = 1.00/100 \ x \ 450 \ g \\ = \ 4.5 \ g \\ m \ _{KOH \ @ \ 1.5 wt\%} = 1.50/100 \ x \ 450 \ g \\ = \ 6.75 \ g \\ m \ _{KOH \ @ \ 1.75 wt\%} = 1.755/100 \ x \ 450 \ g \\ = \ 7.785 \ g \\ \end{array}
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The molar ratio of methanol to oil is 6:1. In order to find the mass of waste cooking oil and methanol that must be used, manual calculations were carried out according to Table A.1.

Table A.1: Calculations for Methanol for transesterification with Waste Cooking Oil

Properties	Methanol	Waste cooking oil
Density, p	0.791 g/ cm^3	0.900 g/ cm^3
Molecular Weight, MW	32.02 g/mol	856 g/mol
Molar Ratio	6 x 32.02 g/mol	1 x 856 g/mol

	= 192.24 g/mol	= 856 g/mol
Scale Down	= <u>192.24 g/mol</u>	For waste cooking oil
	1.902	amounts of 450 g.
	= 101.073 g Methanol	450 g = 856 g/mol/X
	$V_{\text{methanol}} = 101.073/0.791$	X = 1.902
	$= 127.94 \text{cm}^{3}$	

A.1.2 RBD Palm Oil

Volume of RBD palm oil used in each experiment = 500 cm³ Density of RBD palm oil, $\rho_{WCO} = 880 \text{ kg/m}^3$ = (880 kg/m³) x (1000 g/1 kg) x (1 m³/ 1x10⁶ cm³) = 0.880 g/ cm³

Mass of RBD palm oil = $\rho_{WCO} \ge V_{oil}$ = 0.880 g/ cm³ x 500 cm³ = 440 g

Mass of catalyst used in each experiment using RBD palm oil

m KOH @ 0.75wt% = 0.75/100 x 440 g= 3.3 g m KOH @ 1.00wt% = 1.00/100 x 440 g= 4.4 g m KOH @ 1.5wt% = 1.50/100 x 440 g= 6.6 g m KOH @ 1.75wt% = 1.75/100 x 440 g= 7.7 g

The molar ratio of methanol to oil is 6:1. In order to find the mass of RBD Palm oil and methanol that must be used, manual calculations were carried out according to Table A.2.

Properties	Methanol	RBD Palm oil
Density, p	0.791 g/ cm^3	0.880 g/ cm^3
Molecular Weight, MW	32.02 g/mol	847.3 g/mol
Molar Ratio	6 x 32.02 g/mol	1 x 847.3 g/mol
	= 192.24 g/mol	= 847.3 g/mol
Scale Down	= <u>192.24 g/mol</u>	For waste cooking oil
	1.926	amounts of 440 g.
	= 99.813 g Methanol	440 g = <u>847.3 g/mol</u>
	$V_{\text{methanol}} = \underline{99.813}$	X
	0.791	X = 1.926
	$= 126.346 \text{ cm}^3$	

Table A.2: Calculations for Methanol for transesterification with RBD Palm Oil

APPENDIX B

B.1 Calculations of methyl ester purity

The calculations for methyl ester purity according to gas chromatography were carried out using Equation B.1.

$$C = \underbrace{(\sum A) - A_{E1}}_{A_{E1}} x \underbrace{C_{E1} x V_{E1}}_{M} x 100\%$$
 (Equation B.1)

 $\sum A$ = total peak area of methyl ester in C₁₄ to C_{24:1}

 A_{E1} = peak area corresponding to methyl ester

 C_{E1} = concentration (mg/ml) of methyl ester stock solution

 V_{E1} = volume (ml) of methyl ester solution being used

M = mass of sample (mg)

C = methyl ester purity

In the sample preparation for gas chromatographic analysis, C_{E1} and V_{E1} were fixed at 10 g/ml and 5 ml respectively for each sample. Using equation ****, the data for methyl ester purity for different catalyst concentrations and reaction time were calculated according to Tables B.1 and B.2.

Table B.1: Methyl ester purity at varying catalyst concentrations

Catalyst concentration	WCO		RBD palm oil	
(weight %)	M (mg)	Methyl ester	M (mg)	Methyl ester
		(%)		(%)
0.75	101.0	79.47	102.6	86.37
1.00	102.6	87.38	105.3	91.99
1.5	104.8	88.76	103.9	94.02
1.75	101.5	89.10	100.9	94.31

Reaction time	WCO		RBD palm oil	
(minutes)	M (mg)	Methyl ester	M (mg)	Methyl ester
		purity (%)		purity (%)
20	100.6	72.6	100.2	73.72
30	100.7	78.64	108.6	78.61
40	100.7	81.92	101.0	82.73
50	104.5	82.33	105.8	83.46

Table B.2: Methyl ester purity at varying Reaction times

B.2 Combustion analysis

B.2.1 Carbon monoxide emissions

Table B.3: Amount of carbon monoxide emitted

Type of diesel fuel	Amount of carbon monoxide emission (ppm)
Fossil diesel	222
RBD palm oil biodiesel	110
WCO biodiesel	89

B.2.2 Carbon dioxide emissions

Table B.4: Amount of carbon dioxide emitted

Type of diesel fuel	Amount of carbon dioxide emission (%)
Fossil diesel	8.7
RBD palm oil biodiesel	8.7
WCO biodiesel	8.9

APPENDIX C

C.1 Gas Chromatogram for Standard Methyl Ester



Figure C.1: Standard Methyl Ester for Gac Chromatography Analysis

C.2 Gas Chromatograms for Biodiesel produced from RBD Palm Oil

C.2.1 Analysis for Best Potassium Hydroxide (KOH) Concentration



Figure C.2: Gas Chromatography Results for 0.75 wt % KOH Concentration in RBD Palm Oil



Figure C.3: Gas Chromatography Results for 1.00 wt % KOH Concentration in RBD

Palm Oil



Figure C.4: Gas Chromatography Results for 1.50 wt % KOH Concentration in RBD Palm Oil



Figure C.5: Gas Chromatography Results for 1.75 wt % KOH Concentration in RBD Palm Oil

C.2.2 Analysis for Best Reaction Time



Figure C.6: Gas Chromatography Results for 20 minutes Reaction Time of 1.75 wt % KOH Concentration in RBD Palm Oil



Figure C.7: Gas Chromatography Results for 30 minutes Reaction Time of 1.75 wt % KOH Concentration in RBD Palm Oil



Figure C.8: Gas Chromatography Results for 40 minutes Reaction Time of 1.75 wt% KOH Concentration in RBD Palm Oil



Figure C.9: Gas Chromatography Results for 50 minutes Reaction Time of 1.75 wt

% KOH Concentration in RBD Palm Oil

C.3.1 Analysis for Best Potassium Hydroxide (KOH) Concentration



Figure C.10: Gas Chromatography Results for 0.75 wt % KOH Concentration in WCO



Figure C.11: Gas Chromatography Results for 1.00 wt % KOH Concentration in WCO



Figure C.12: Gas Chromatography Results for 1.50 wt % KOH Concentration in WCO



Figure C.13: Gas Chromatography Results for 1.50 wt % KOH Concentration in WCO

C.3.2 Analysis for Best Reaction Time



Figure C.14: Gas Chromatography Results for 20 minutes Reaction Time of 1.75 wt % KOH Concentration in WCO



Figure C.15: Gas Chromatography Results for 30 minutes Reaction Time of 1.75 wt % KOH Concentration in WCO



Figure C.16: Gas Chromatography Results for 40 minutes Reaction Time of 1.75 wt % KOH Concentration in WCO



Figure C.17: Gas Chromatography Results for 50 minutes Reaction Time of 1.75 wt % KOH Concentration in WCO

C.4 Combustion Analysis Results using the Gas Analyzer

*** TEL BONN- *** TEMPELL 168 V3.3 DATE 3 21-93-09 TIME 0 148141 HEREYALL 1 AMBIE 1 0 STACK 0 NETT 28 693 664 9.4 9.0012 02 RATIO CO CO2 . 11 XAIR , 8 58. 41. DRY L 0.1 WET ico i 0.0 Prs. NO NOx H2S REF.

Figure C.18: Gas Emissions Results of RBD Palm Oil Biodiesel

TELEGAN *** 551 100 V3.3 11-03-09	ii:i4:10. EAVY OIL	ENT C 51	X 9.1 0 0.0010 PPM 89 X 8.9 X 140 59.6 -055 X 40.4 -055 X 9.0 -055 X 9.0 -055 X 9.0 -055 X 9.0 -0.02 -0
**** TI - PTE[IPE	TIME HEI	AMBIE STACK NETT	02 200 002 200 002 20 20 20 20 20 20 20

Figure C.19: Gas Emissions Results of WCO Biodiesel