**PREPARATION OF BIODIESEL FROM RBD PALM OIL AND WCO VIA ALKALINE TRANSESTERIFICATION PROCESS WITH THE AID OF NaOH AS CATALYST BY BATCH PROCESS**

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I declare that this thesis entitled "*Preparation of Biodiesel from RBD palm oil and WCO via alkaline Transesterification Process with the aid of NaOH as catalyst by Batch Process"* is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....................................................

Name : MOHD HAFIZ BIN KAMLUDIN @ YUSOF

Date : 28 APRIL 2009

Special Dedication of This Grateful Feeling to My…

Beloved father and mother;
***Kamludin @ Yusof Bin Salleh and Asmah Binti Isa***

Loving brothers and sisters;
***Suhaimi, Rahayu, Faridah, Zuraini, Zulkifli, Mohd Radhi, and Nurul Izzati***

Supportive friends

For Their Love, Support and Best Wishes.

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**ABSTRACT**

The fast depletion of fossil fuels, coupled with the increasing awareness of environmental issues, concern for increasing green house gas emissions and escalating petroleum prices, have led to concerted efforts in the search for renewable and environmentally friendly alternative energy sources. One of the alternative ways is by producing biodiesel. The purpose of this research is to examine the comparison on purity, yield and gas emission between RBD palm oil and waste cooking oil in the production of biodiesel by batch alkaline transesterification process. In the research, catalyst (NaOH) concentration of 0.25 wt% to 1.5 wt% was used. The temperature range used is fixed at 40°C and the time that be conducted is between 20 min to 60 min. The first parameter studied was catalyst concentration, where the highest value achieved was 0.75 wt% for RBD palm oil and 1.00wt% for WCO. 40 minutes was the highest reaction time obtained for RBD palm oil, while 50 minutes for WCO. The last parameter studied was the gas emission and the result showed that gas emission for biodiesel is better than gas emission produced by the fossil-based diesel. In comparison between RBD palm oil and WCO, WCO biodiesel produce more environmental friendly gases than RBD palm oil biodiesel.

# ABSTRAK

Penurunan hasil minyak yang semakin pantas, di tambah dengan kesedaran pentingnya isu alam sekitar, peningkatan gas-gas rumah hijau dan meningkatnya harga petroleum telah membawa kepada satu pencarian sumber tenaga yang baru dan mesra alam. Salah satu alternatif itu ialah dengan menghasilkan biodiesel. Tujuan kajian ini dijalankan adalah untuk mengetahui dan membuat perbezaan daripada segi ketulenan, penghasilan dan pengeluaran gas di antara minyak masak biasa dan miyak masak terpakai di dalam penghasilan biodiesel melalui proses transesterifikasi menggunakan alkali sebagai pemangkin. Di dalam kajian ini, kepekatan NaOH adalah di antara 0.25 wt% sehingga 1.5 wt%. Suhu ditetapkan pada 40°C dan masa tindak balas adalah antara 20 minit hingga 60 minit. Parameter pertama yang dikaji adalah kepekatan pemangkin dan nilai maksima yang dicapai untuk minyak masak biasa adalah 0.75wt% manakala 1.00wt% untuk minyak masak terpakai. 40 minit adalah masa tindak balas yang paling tinggi untuk minyak biasa, manakala 50 minit untuk minyak masak terpakai. Parameter terakhir yang dikaji pula adalah pengeluaran gas dan ia menunjukan bahawa biodiesel lebih mesra alam berbanding diesel biasa. Di antara minyak masak biasa dan terpakai pula, minyak masak terpakai lebih mesra alam berbanding dengan minyak masak biasa.

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| | |
|---|---|
| RBD | - refined, bleached and deodorized |
| NaOH | - Sodium hydroxide |
| ASTM | - American Society for Testing and Material |
| WCO | - Waste cooking oil |

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# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction

The fast depletion of fossil fuels, coupled with the increasing awareness of environmental issues, concern for increasing green house gas emissions and escalating petroleum prices, have led to concerted efforts in the search for renewable and environmentally friendly alternative energy sources.

Biofuel is one such fuel. In the global scene, especially on the European front, the use of methyl esters as diesel has achieved widespread acceptance. In fact, biodiesel made from rapeseed oil is already produced on a significant scale in Europe. The demand in the EU is projected to increase from 3 million tonnes in 2005 to 10 million tonnes in 2010. The United States, Brazil, India and Japan, have already embarked on their own biofuels programme, while other countries like Korea and Thailand have set specific targets for biofuels implementation.

As the world's largest palm oil producer and exporter, Malaysia is now looked upon as the pioneer palm biofuel producer. Malaysia has embarked on a comprehensive palm biofuel programme since 1982 and has successfully established the use of palm methyl esters and the blend of processed palm oil (5%) with petroleum diesel (95%) as a suitable fuel for the transport and industrial sectors. Homegrown indigenous palm biodiesel production technologies, including winter palm biodiesel, have also been successfully developed. These products and technologies can be further developed for the world market.

Another source for the producing of the biodiesel is from waste cooking oil (WCO). From a waste management standpoint, production of biodiesel from waste cooking oil is environmentally beneficial as it provides a cleaner means of disposing of these products than is typically used. The world consumes each year billions of litres of oil and land for frying foods, and much of the waste cooking oil is discarded into sewage systems, where it adds to the cost of treating effluent or pollutes waterways.

Basically, biodiesel is the name that has been given to an alternative fuel made from vegetable oil. It is a perfect alternative to traditional gasoline. Animal fat and vegetable oil go through a specific process called "transesterification" which turns it into esterified oil. Esterified oil can then be sued to power unmodified diesel engines. This biodiesel can also be used to treat regular diesel if desired.

## 1.2 Problem statement

The increasing industrialization and motorization of the world has led to a steep rise for the demand of petroleum-based fuels. Petroleum-based fuels are obtained from limited reserves. According to British Petroleum's Statistical Review of World Energy in 2007(Table 1.1), we can see that top twelve oil reserves in our world today will not stand its oil for more years. From the point of view of protecting the global environment and the concern for longterm supplies of conventional diesel fuels, it becomes necessary to develop alternative fuels comparable with conventional fuels.

**Table 1.1**: Summary of reserve data as 2007

| Country | Reserves [1] | | Production [2] | | Reserve life [3] |
|---|---|---|---|---|---|
| | $10^9$ bbl | $10^9$ $m^3$ | $10^6$ bbl/d | $10^3$ $m^3$/d | years |
| Saudi Arabia | 260 | 41 | 8.8 | 1,400 | 81 |
| Canada | 179 | 28.5 | 2.7 | 430 | 182 |
| Iran | 136 | 21.6 | 3.9 | 620 | 96 |
| Iraq | 115 | 18.3 | 3.7 | 590 | 85 |
| Kuwait | 99 | 15.7 | 2.5 | 400 | 108 |
| United Arab Emirates | 97 | 15.4 | 2.5 | 400 | 106 |
| Venezuela | 80 | 13 | 2.4 | 380 | 91 |
| Russia | 60 | 9.5 | 9.5 | 1,510 | 17 |
| Libya | 41.5 | 6.60 | 1.8 | 290 | 63 |
| Nigeria | 36.2 | 5.76 | 2.3 | 370 | 43 |
| United States | 21 | 3.3 | 4.9 | 780 | 11 |
| Mexico | 12 | 1.9 | 3.2 | 510 | 10 |
| **Total of top twelve reserves** | 1,137 | 180.8 | 48.2 | 7,660 | 65 |

**Notes:**

1 Claimed or estimated reserves in billions ($10^9$) of barrels (converted to billions of cubic metres). (Source: Oil & Gas Journal, January, 2007)

2 Production rate in millions ($10^6$) of barrels per day (converted to thousands of cubic metres per day) (Source: US Energy Information Authority, September, 2007)[11]

3 Reserve life in years, calculated as reserves / annual production. (from above)

Source: British Petroleum's Statistical Review of World Energy (2007)

In Malaysia, there has been interest in the utilization of palm oil and oil palm biomass for the production of environmental friendly biofuels. A biorefinery based on palm oil and oil palm biomass for the production of biofuels has been proposed. Malaysia, among the world's largest producer and exporter of palm oil today, produces about 47 per cent of the world's supply of palm oil. The palm oil industry is the backbone of rural development and the nation's political stability (Chandran, 2005). In producing biodiesel, cost is also playing an important role. The price of waste cooking oils (WCO) is 2–3 times cheaper than virgin vegetable oils. Consequently, the total manufacturing cost of biodiesel can be significantly reduced.

## 1.3 Objective of research project

The purpose of this research is to determine the best condition in producing biodiesel with high purity of methyl ester and environment friendly biodiesel from RBD palm oil and WCO using NaOH(as catalyst) via alkaline transesterification by batch process.

## 1.4 Scope of research project

The scopes of this research are:

1. To study the effect of catalyst concentration on yield and purity of biodiesel using batch transesterification process.
2. To study the combustion characteristic of biodiesel from both RBD palm oils and waste cooking oils using batch transesterification process and analyze the product using Gas Chromatography.

In the research that we conduct, we used the catalyst concentration of 0.25wt% to 1.5wt%. While the temperature range used is fixed at 40°C and the time that be conducted is between 20 min to 60 min.

## 1.5 Rational and significance

The rationale of this research is to get the higher yield and purity of biodiesel produced from the RBD palm oils while by using waste cooking oils, we can reduced the cost of raw material since it is cheap and available everyday (Freedman et al, 1984). Otherwise, we also want to protect the environment from continuously polluted by hazardous gases that produce from the vehicles every day, such as carbon monoxide, carbon dioxide and sulfur that will effect to the global warming by use biodiesel as the alternative way to replace the resource of conventional fuel such as crude petroleum diesel that running out day by day.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

It is estimated that in the coming years, the fossil oil price will increase because the oil production cannot meet the projected demand due to oil depletion (Association of Peak Oil and Gas, 2004). This is a result of overconsumption in the developed countries and overpopulation in the developing countries (Korbitz, 1999). The energy crisis in the mid 1970s coupled with the fast depleting energy reserves, increasing energy consumption and greater environmental awareness have led to an intensified search for viable alternate sources of energy globally. (Choo Yuen May *et al*., 2002). A lot of efforts have been carried out to develop an alternative fuel for the current energy and transportation vehicle system, i.e.: fuel cell, electric power, hydrogen or natural gas for internal combustion engines, etc. One of the promising alternatives that are applied in small scale production is biodiesel.

The term "biodiesel" has a specific, technical definition that has been agreed to through a process by members of industry and government which has received full approval by the American Society of Testing and Materials (ASTM), the premier standard setting organization for fuels and fuel additives. Generally, biodiesel is a domestic, renewable fuel for diesel engines derived from natural oils like soybean oil, and which meets the specifications of ASTM D 6751. Technically**,** biodiesel is a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM D 6751. In addition biodiesel blend is a blend of biodiesel fuel meeting ASTM D 6751 with petroleum-based diesel fuel, designated BXX, where XX represents the volume percentage of biodiesel fuel in the blend.

**Table 2.1**: ASTM D6751-07b Specification for Biodiesel (B100)

| Property | Method | Limit |
|---|---|---|
| Calcium & Magnesium, combined | EN 14538 | 5ppm maximum |
| Flash Point | D93 | 93 Degrees C minimum |
| Methanol | EN 14110 | .2 % volume maximum |
| Water & Sediment | D 2709 | 0.05 % volume maximum |
| Kinematic Viscosity | D 445 | 1.9 - 6.0 $mm^2$/sec |
| Sulfated Ash | D 874 | 0.02 % mass maximum |
| Sulfur | D 5453 | 0.0015 % mass (ppm) maximum |
| Copper Strip Corrosion | D 130 | No. 3 maximum |
| Cetane | D 613 | 47 minimum |
| Cloud Point | D 2500 | Degrees C Report |
| Carbon residue | D 4530 | 0.05 % mass maximum |
| Acid Number | D 664 | 0.50 mg KOH/g maximum |
| Free Glycerin | D 6584 | 0.020 % mass maximum |
| Total Glycerin | D6584 | 0.240 % mass maximum |
| Phosphorus Content | D 4951 | 0.001 % mass maximum |
| Distillation | D1160 | 360 Degrees C maximum |
| Sodium/Potassium, combined | EN 14538 | 5 ppm maximum |
| Visual Appearance** | D 4176 | 2 Mas |
| Oxidation Stability | EN 14112 | 3 hours minimum |

Source: Nasional Biodiesel Board (Alptekin E and Canakci M., 2008)

## 2.2 Raw material

A variety of oils can be used to produce biodiesel. These include virgin oil feedstock, waste cooking oil or from animal fats.

### 2.2.1 Virgin oil feedstock

Rapeseed and soybean oils are most commonly used, soybean oil alone accounting for about ninety percent of all fuel stocks in the US. It also can be obtained from field pennycress and Jatropha other crops such as mustard, flax, sunflower, palm oil, hemp and many other types of vegetables oils. The type of oil used is largely a factor of where the biodiesel is being produced and what type of oil is abundant there. Thus, rapeseed and sunflower oils are used in Europe, palm oil predominates in biodiesel production in tropical countries, and soybean oil is the major feedstock in the United States. Canada is a large producer of canola oil (1.6 Mt annually reported by the Canola Oil Council of Canada), which has the least amount of saturated fat of any vegetable oil, less than 7%; biodiesel from canola oil has excellent cold-flow properties ( B. Coleman, 2006).

### 2.2.2 Waste cooking oil (WCO)

Most restaurants and other frying-oil users have to pay a rendering or waste company to haul the greasy stuff away. Some used cooking oils are processed into animal feed, make up, or fertilizer, but for many years much of it has been dumped in landfills or sewers in some locations, causing a lot of headaches for sewage treatment plants. But used vegetable oil is a great low-cost resource for making biodiesel, and it is increasingly used for that purpose in numerous countries.

Many researchs have been studies in the past regarding making biodiesel from waste cooking oil. Biodiesel can also be produced from waste cooking oils (WCO) (Marchetti *et al*., 2007). It is being tested for diesel engine performance and has similar performance with biodiesel produced from fresh vegetable oils (M.P Dorado *et al*., 2003). One way of reducing the cost of biodiesel production is to employ low quality feedstocks such as waste cooking oils which are readily available and inexpensive, instead of neat vegetable oil (Watanabe *et al*., 2005).

### 2.2.2 Animal fats

Animal fat, a by-product of the animal rendering process, is the least expensive feedstock currently available for biodiesel production. Animal fats including tallow, lard, yellow grease, chicken fat, and the by-products of the production of Omega-3 fatty acids from fish oil. Fats originating from animals, which were previously investigated as raw materials for biodiesel production, include beef tallow, lard, and fish oil. Also, direct acid-catalyzed esterification and transesterification using animal waste products without previous fat extraction, has been reported ([Leung and Guo, 2006] and [Ma and Hanna, 1999]). With regard to their fatty acid compositions, animal fats have certain disadvantages with regard to quality. Biodiesel derived from animal fats with a high saturated fatty acid content evidence poor cold temperature properties, which can cause some problems in winter operation. On the other hand, the high degree of saturation inherent to biodiesel evidences excellent fuel properties, specifically with regard to heating value and cetane number ([Mittelbach and Remschmidth, 2004], [Kang and Kim, 2001], [Yang *et al*., 2007] and [Lang *et al*., 2001]).

## 2.3 Process

There are many ways to convert oils and fats into biodiesel. At least four ways have been created which are direct use and blending, micro-emulsion, pyrolysis (thermal cracking) and transesterification. Among the four ways, the transesterification is the best method to produce environmentally friendly fuel from vegetables oils.

### 2.3.1 Direct use and blending

Beginning in 1980, there was considerable discussion regarding use of vegetable oil as a fuel. Bartholomew (1981), addressed the concept of using food for fuel, indicating that petroleum should be the "alternative" fuel rather than vegetable oil and alcohol being the alternatives and some form of renewable energy must begin to take the place of the nonrenewable resources. The most advanced work with sunflower oil occurred in South Africa because of the oil embargo. Caterpillar Brazil, in 1980, used pre-combustion chamber engines with a mixture of 10% vegetable oil to maintain total power without any alterations or adjustments to the engine. At that point, it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% diesel fuel was successful. Some short-term experiments used up to a 50/50 ratio (Fangrui Ma, 1999)**.** 25 parts of sunflower oil and 75 parts of diesel were blended as diesel fuel (Ziejewski *et al*., 1986). The viscosity was 4.88 cSt at 40°C, while the maximum specified ASTM value is 4.0 cSt at 40°C. It was considered not suitable for long term use in a direct-injection engine. Direct use of vegetable oils and/or the use of blends of the oils have generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems.

### 2.3.2 Micro-emulsion

To solve the problem of the high viscosity of vegetable oils, micro emulsions with solvents such as methanol, ethanol and 1-butanol have been studied. A micro emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1–150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. Short term performances of both ionic and non-ionic micro emulsions of aqueous ethanol in soybean oil were nearly as good as that of No. 2 diesel, in spite of the lower cetane number and energy content (Goering *et al*., 1982b). The durabilities were not determined.

### 2.3.3 Pyrolysis

Pyrolysis, strictly defined, is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst. It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules (Weisz *et al*., 1979). Pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum. The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil. Since World War I, many investigators have studied the pyrolysis of vegetable oils to obtain products suitable for fuel. In 1947, a large scale of thermal cracking of tung oil calcium soaps was reported (Chang and Wan, 1947). Rapeseed oil was pyrolyzed to produce a mixture of methyl esters in a tubular reactor between 500 and 850°C and in nitrogen (Billaud *et al*., 1995). The equipment for thermal cracking and pyrolysis is expensive for modest throughputs. In addition, while the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal