

**TRANSESTERIFICATION OF VIRGIN AND WASTE COOKING PALM  
OIL USING CALCIUM OXIDE CATALYST SUPPORTED ON ACTIVATED  
CARBON**

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CARBON**

**by**

**WAN ZURAIDA BINTI WAN KAMIS**

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## LIST OF SYMBOLS

$\alpha$	Alpha (axial distance from center point which makes the design rotatable)
$\dot{A}$	Amstrong
$\beta_0$	Constant coefficient
$\beta_i$	Coefficient for the linear effect
$\beta_{ii}$	Coefficient for the quadratic effect
$\beta_{ij}$	Coefficient for the interaction effect
$\varepsilon$	Error
$R^2$	Coefficient of determination

## LIST OF ABBREVIATIONS

AC	Activated Carbon
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
CCD	Central Composite Design
B5	5% Biodiesel
B20	20% Biodiesel
BET	Brunauer-Emmett-Teller
CCD	Central Composite Design
VPO	Virgin cooking Palm Oil
cSt	centistokes
DG	Diglyceride
DOE	Design of experiment
EDX	Energy Dispersive X-ray
ESG	Eruca sativa Gars
EU	European Union
ME	Fatty acids methyl ester
FFAs	Free Fatty Acids
FTIR	Fourier Transform Infrared
GC	Gas chromatography
H <sub>-</sub>	Hammett Function
HT	Hydrotalcites
MSDS	Material Safety Data Sheet
NO <sub>x</sub>	Nitrogen oxide
RSM	Response surface methodology

SEM	Scanning Electron Microscopy
SO <sub>x</sub>	Sulfur oxide
WPO	Waste cooking palm oil
wt%	Weight percent



# **TRANSESTERIFIKASI MINYAK MASAK KELAPA SAWIT BARU DAN SISA MENGGUNAKAN PEMANGKIN KALSIUM OKSIDA DISOKONG OLEH KARBON TERAKTIF**

## **ABSTRAK**

Dalam penyelidikan ini, metil ester (ME) telah dihasilkan daripada minyak masak kelapa sawit yang baru (VPO) dan sisa (WPO) dengan menggunakan sejenis pemangkin yang baru dijana iaitu kalsium oksida disokong oleh karbon teraktif (CaO/AC) sebagai pemangkin heterogen. Kaedah permukaan sambutan (RSM) berdasarkan rekabentuk komposit berpusat (CCD) telah digunakan untuk mengoptimumkan aktiviti pemangkin dengan cara mengkaji kesan parameter iaitu jumlah CaO yang dimuatkan di atas karbon teraktif, suhu dan masa kalsinasi. Keadaan yang optimum untuk aktiviti pemangkin dalam proses transesterifikasi VPO adalah seperti berikut: 13.18 peratusan berat CaO dimuatkan di atas karbon teraktif, suhu 540 °C dan tempoh masa 2 jam untuk proses kalsinasi yang telah menghasilkan kandungan ME sebanyak 77.35%. Kajian tentang keadaan yang optimum untuk proses transesterifikasi VPO dan WPO telah dijalankan menggunakan kaedah RSM. Keadaan yang optimum untuk proses transesterifikasi VPO yang dicapai adalah: 1 jam 21 minit masa tindakbalas, 15:1 nisbah molar metanol kepada minyak, 190 °C suhu tindakbalas dan 5.5 jumlah peratusan pemangkin berdasarkan berat minyak. Manakala, keadaan yang optimum untuk proses transesterifikasi WPO yang dicapai adalah: 2 jam 22 minit masa tindakbalas, 15:1 nisbah molar metanol kepada minyak, 170 °C suhu tindakbalas dan 5.5 jumlah peratusan pemangkin berdasarkan berat minyak. Keputusan menunjukkan jumlah kandungan ME adalah 80.98% bagi VPO dan 77.32% bagi WPO. Kajian tentang kebolehan untuk diguna semula pemangkin yang terpakai telah menunjukkan penurunan daripada segi aktiviti pemangkin di

mana kandungan ME adalah 79.80%, 57.92% dan 41.17% untuk kitaran yang pertama, kedua dan ketiga bagi transesterifikasi VPO. Corak yang serupa telah ditunjukkan dalam transesterifikasi WPO dengan penurunan kandungan ME kepada 76.30%, 43.98% dan 31.26% bagi kitaran yang pertama, kedua dan ketiga. Kajian tentang penjanaan semula pemangkin telah menunjukkan bahawa pencapaian pemangkin dapat dikekalkan selepas dua kitaran proses transesterifikasi VPO di mana kandungan ME adalah 80.98%, 80.91% dan 65.32% bagi setiap kitaran. Manakala penurunan aktiviti pemangkin yang ketara telah dilihat dalam transesterifikasi WPO dengan penurunan kandungan ME dari 77.32%, 57.02% dan 52.48% bagi setiap kitaran. Hasil kajian transesterifikasi VPO dan WPO menggunakan pemangkin CaO/AC telah menunjukkan bahawa pemangkin ini mempunyai potensi yang bagus untuk digunakan di dalam penghasilan biodiesel. Kajian juga menunjukkan ME yang diperolehi dari transesterifikasi VPO dan WPO mempunyai ciri-ciri bahan bakar yang mencapai standard ASTM D6751 dari segi kelikatan dan ketumpatan. Kaedah penghasilan pemangkin yang ringkas, kos bahan mentah yang murah, pemisahan produk dan pemangkin yang mudah dan warna ME yang cerah serta glycerol tanpa warna yang dihasilkan adalah antara kelebihan pemangkin heterogen yang telah dihasilkan di dalam kajian ini.

# **TRANSESTERIFICATION OF VIRGIN AND WASTE COOKING PALM OIL USING CALCIUM OXIDE CATALYST SUPPORTED ON ACTIVATED CARBON**

## **ABSTRACT**

In this present study, methyl ester (ME) was produced by transesterification of virgin cooking palm oil (VPO) and waste cooking palm oil (WPO) using newly developed calcium oxide catalyst supported on activated carbon (CaO/AC) as a heterogeneous catalyst. Response surface methodology (RSM) based on central composite design (CCD) was used to optimize the catalytic activity by investigating the effect of CaO loading amount on AC, calcination temperature and calcination time. The optimum conditions for catalyst activity in VPO transesterification was obtained as follows: 13.18 wt% of CaO precursor on AC, 540 °C calcination temperature and 2 h calcination time which produce the ME content of 77.35%. The study on the optimum conditions for transesterification of VPO and WPO were conducted using RSM. The optimum conditions for VPO transesterification are: 1 h 21 min reaction time, 15:1 methanol to oil molar ratio, 190 °C reaction temperature and 5.5 wt% catalyst amount. On the other hand, the optimum conditions for WPO transesterification are: 2 h 22 min reaction time, 15:1 methanol to oil molar ratio, 170 °C temperature, 5.5 wt% catalyst amount. The results show the ME content was 80.98 % for VPO and 77.32 % for WPO. Catalyst reusability studies indicated a reduction in catalytic activity with ME content of 79.80%, 57.92% and 41.17% in the first, second and third cycles respectively for VPO transesterification. Similar trend was observed for WPO transesterification with ME content of 76.30%, 43.98% and 31.26% in the first, second and third cycles respectively. Catalyst regeneration studies indicated that the catalyst performance was sustained for two cycles in the

VPO transesterification with ME content of 80.98%, 80.91% and 65.32% respectively for each cycle. However, significant catalyst deactivation was observed in the WPO transesterification with reduction in ME content of 77.32%, 57.02% and 52.48% respectively for each cycle. The studies on the transesterification of VPO and WPO using CaO/AC have discovered a good potential for this heterogeneous catalyst in biodiesel production. The ME obtained from VPO and WPO transesterification meet the selected fuel properties of ASTM Biodiesel Standard D6751 in terms of viscosity and density. The simple method of catalyst preparation, comparatively low cost of raw materials, ease of catalyst separation from the products and the light colored ME and colorless glycerol obtained are among the advantages of the heterogeneous catalyst developed in this study.

## CHAPTER 1

### INTRODUCTION

#### 1.1 Energy Demand

The use of energy is crucial for human to pursue economic growth and maintain standard of living. Energy resources play a critical role in human lives and the future of our planet. Most of human energy needs are supplied by finite sources such as petroleum, coal and natural gases. These sources will eventually be depleted particularly due to the tremendous increase of worldwide energy consumption in the last century (Srivastava and Prasad, 2000). Fossil fuels remain the largest contributor to meet the global energy demand (Kulkarni and Dalai, 2006). In 2006, more than 83% of the world total primary energy productions are contributed from these sources, whereas remaining 17% from other sources such as nuclear and hydroelectric (EIA, 2008). In Malaysia, 95% of total primary energy productions are contributed from fossil fuels. The trend is expected to continue for the next 20 years as Malaysia is a rapidly developing country (IEA, 2006).

As the demand for energy grown, the adverse environmental effect of its production also increases. The main causes of atmospheric pollution are due to CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub> emission from fossil fuels combustion. The effects of these greenhouse gases are predicted to cause disastrous global consequences to life on this planet such as drastic climate changes, acid rain and smog (Jegannathan *et al.*, 2009). It is predicted that the total world emissions of greenhouse gases by fossil fuels will increase from 29 billion metric tonnes in 2006 to projections of 40.4 billion metric tonnes by 2030 (Lim and Teong, 2010). The total CO<sub>2</sub> emissions from fossil fuels in Malaysia have increase over 37% from 1998 to 2006 (EIA, 2006). It is also reported

that total CO<sub>2</sub> emissions from coal fired power plants are projected to grow at 4.1% per year to reach 98 million tonnes in 2020 (Othman *et al.*, 2009). In addition, detrimental effects to our ecology system are the results of energy intensive activities such as harvesting, processing and distributing fossil fuels (Lim and Teong, 2010)

## **1.2 Renewable Energy**

As well known, the world today is confronted with the crisis of fossil fuel depletion and environmental degradation. Biofuel is an alternative source of energy that is sustainable and environmental friendly. This renewable energy can be produced from vegetable oils, sugar beets and organic wastes that can be obtained locally, therefore reduce dependency on fuel imports (Malca *et al.*, 2006). Global biofuel production has tremendous growth from 4.8 billion gallons in 2000 to 16 billion gallons in 2007, for which the U.S and Brazil contributed 75% of world's productions (Licht, 2006). The three main biofuel technologies are biodiesel, bioethanol and biogas. There are several drawbacks in the production of biogas and bioethanol. The biogas technology is a relatively slow and unstable process, which requires large volumes of digester that are costly (Yadvika *et al.*, 2004), whereas bioethanol technology requires high temperature process, generates toxic wastewater and produces fuel that is corrosive. Biodiesel has been touted as the most likely technology capable of large-scale production in a controlled and cost effective manner (Jegannathan, 2009).

Renewable energy from biodiesel has become important in recent decades as the most promising alternative for petroleum-derived fuel. It has physical properties and energy content close to those of petroleum diesel therefore it can function

efficiently in diesel engine without modification. Biodiesel production capacity continues to increase around the world. The world biodiesel production output is about 11 million metric tonnes in 2008 and estimated by 2010, the production can be as high as 20 million tonnes (Lim and Teong, 2010).

Biodiesel is a clean-burning fuel that is nontoxic and biodegradable. It has low emission of unburned hydrocarbons, carbon monoxide, sulfur and particulate matter which makes it suitable for use in marine areas, national parks and heavily polluted cities. Biodiesel has higher flash point than diesel fuel thereby making it safe during storage and transportation. In addition, it serves as a better lubricant, which increases engine performance and life span (Vasudevan and Briggs, 2008).

Biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. ASTM D 6751 standard covers pure biodiesel (B100) intended for blending with petrodiesel up to 20% by volume (B20). ASTM (American Society for Testing and Materials) is an international standards organization that develops and publishes technical standards for a wide range of materials, products, systems, and services. Biodiesel that meets the ASTM standards is assured to have trouble free engine operation. From the studies, there have been over 45 million miles of successful, trouble-free, real-world operation with B20 blends in various type of engines, climates, and applications (Van Gerpen *et al.*, 2007; NBB, 2008).

### **1.3 Biodiesel Industry in Malaysia**

Vegetable oil has been the major feedstock for biodiesel production. As one of the main palm oil producer in the world, Malaysia is looked upon as the pioneer palm biofuel producer. Malaysia contributes about 51% of world palm oil production and 62% of world exports. Malaysia has undertaken research and development on palm based biofuel since 1982. Since then it 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. In 1992, research on palm oil biodiesel has successfully developed winter-grade biodiesel production technology that enabled its usage under cold condition and near freezing temperature. The palm oil biodiesel from Malaysia meet the international biodiesel standard ASTM D 6751 (MPOC, 2008).

In domestic production, there are currently 10 active biodiesel plants with a total annual biodiesel installed capacity of 1.2 million tonnes. To date, there are 91 biodiesel licenses that have been issued by Malaysia's Ministry of Plantation Industries and Commodities, which implies a tremendous potential in biodiesel industries. Exports of biodiesel increased by 24.9% to 0.23 million tonnes in 2009 compared to 0.18 million tonnes recorded in 2008. The EU is the largest biodiesel export market, which accounts for 52.4% of total biodiesel exports, followed by U.S.A with 17.4% (MPOB, 2009).

The Malaysia National Biofuel Policy was launched in 2006. The primary aim is to reduce the country's dependency on fossil fuels by focusing on alternative energy sources, which are environmentally friendly, sustainable and to promote palm



oil demand. The short term policy implementation includes establishing the Malaysian standard specification for B5 diesel and utilizing it on selected government department vehicle. The medium term plans include establishing Malaysian standard specification on palm oil based biodiesel for domestic use and export, implementation of legislation to mandate the use of biodiesel in transport vehicle and pioneering the establishment of palm biodiesel plants. The long term plans are to gradually increase the proportion of processed palm oil in the diesel blend and to promote greater uptake of biofuels technology by Malaysian and foreign companies (MPOC, 2006).

Foreign investments have been remarkable in ensuring continuous growth of biodiesel industries in Malaysia. Among them are Middle East Dubai Group USD 49.5 million investments in Malaysia's biodiesel company, Japanese Yanmar biodiesel research facility in Malaysia and Carotech Bio-Fuel Sdn. Bhd.'s USD 57 million contract with Swiss-based company to supply 60,000 to 84,000 tonnes of biodiesel a year to Europe. In addition, a venture involving Malaysia, Uganda and Libya had been secured to construct a 250,000 tonne-capacity plant in Negeri Sembilan to be completed in late 2010 (Lim and Teong, 2010).

#### **1.4 Waste Cooking Oil**

The Malaysian government is faced with several challenges to advocate the development of palm biodiesel to a greater height. High cost feedstocks, controversial issues on fuel versus food debate, limited land availability, and clearance of rainforests are among the challenges. The high cost of virgin vegetable oils significantly impacts the process profitability due to at least 75% of the

production cost is from the feedstock cost (Vasudevan and Briggs, 2008). The price of crude palm oil has been on increasing trend from RM996/tonnes in year 2000 to RM2777/tonnes in 2008 (MPOB, 2008).

Low cost feedstock such as waste cooking oil and animal fats are some of the alternatives to reduce the production cost. Huge quantities of these waste are available throughout the world. In the U.S.A, it is estimated that some 100 million gallons of waste cooking oil is produced per day. The U.K. produces over 200,000 tonnes per year of waste cooking oil (Chhetri *et al.*, 2008).

The waste cooking oils are cheap and abundant but are disposed of inadequately. Malaysia and most countries are lack of proper waste oil collection process from restaurants and households. Most of uncollected waste oil is being dumped into sewage system, drain system or landfill sites thereby generating additional waste disposal problem. Utilizing waste cooking oil in the production of biodiesel contributes to the lower production cost and most importantly helps to save the environment from health and environmental hazards. Waste cooking oil and grease poured down the drains can build up in pipes causing blockage at home, streets and the storm drain system which resulted in overflows and therefore pollution (Kulkarni and Dalai, 2006; EBMUD, 2010).

However, the production process poses many challenges such as the need to handle a wider range of process parameters and impurities to produce high quality biodiesel which meets international standards such as ASTM D6751 and EN 14214. Low cost feedstock contains high free fatty acids and water content that results in

soap formation. Additional steps required in the purification process that causes an increase in the production cost (Meng *et al.*, 2008).

## **1.5 Heterogeneous Catalytic Transesterification**

At present, biodiesel are commonly produced by transesterification of triglyceride with mono-alkyl alcohols, such as methanol and in the presence of homogeneous base or acid catalysts. The base catalysts are most often used commercially due to higher catalytic activity compared to acid catalysts, which are also more corrosive. Nevertheless, the purification process for homogeneous catalyzed process is costly and produces a large amount of toxic wastewater due to its high basicity (Xie and Li., 2006). The development of effective heterogeneous catalyzed process can simplify the downstream purification process by removing the neutralization and washing steps, thus more environmental friendly.

Advantages of heterogeneous or solid catalysts are their reusability, better product separation and eco-friendly nature (Venkat *et al.*, 2006). A lot of studies have been conducted in search for ideal solid catalysts with high stability, strong active sites, mesoporous and low cost (Lotero *et al.*, 2005). The development of solid catalysts loaded on support or carrier is very promising and has shown good conversion results in transesterification of vegetable oils. Previous researches include  $\text{KNO}_3/\text{Al}_2\text{O}_3$  (Vyas *et al.*, 2009),  $\text{La}_2\text{O}_3/\text{ZrO}_2$  (Sun *et al.*, 2010),  $\text{K}_2\text{CO}_3$  on alumina/silica support ( Lukic *et al.*, 2009) and  $\text{KNO}_3/\text{KL}$  zeolite and  $\text{KNO}_3/\text{ZrO}_2$  (Jitputti *et al.*, 2006). Basically, porous materials are favored as the catalyst support due to their high surface area per volume. CaO is one of the most attractive catalyst

among the alkali earth metal oxides because of its high transesterification activity (Granados *et al.*, 2007; Ngamcharussrivichai *et al.*, 2008; Kawashima *et al.*, 2009).

## **1.6 Problem Statement**

The world today is faced with the problems of diminishing fossil fuel reserves, growing emissions of combustion-generated pollutants and environmental degradation. Biodiesel can be a viable alternative because of its many benefits such as its renewability, reduction of green house gas emissions and it offers the same performance and engine durability as petroleum diesel fuel.

The limiting factors of biodiesel industry are feedstock prices, production costs and crude oil prices. The high price of biodiesel is largely due to the high price of feedstock. Biodiesel can cost more than twice the petroleum diesel and this can vary depending on the geographic area, variability in crop production between seasons, the price of crude petroleum and other factors (Demirbas, 2009). Low cost feedstock such as waste cooking oil is one of the most economical choices to produce biodiesel. In addition, waste cooking oils are abundant and contribute to environmental hazards without proper disposal process.

The use of conventional homogeneous base and acid catalysts in the transesterification of vegetable oils poses several problems such as its solubility in reaction mixture that contributes to costly separation and purification process and environmental hazards (Xie *et al.*, 2006b). Various side reactions are formed with feedstocks contain high free fatty acid (FFA) and water that lead to soap formation, thus complicates the products separation. Heterogeneous catalyzed process is more

promising due to its many benefits such as catalyst reusability, lower operation cost and environmental friendly (Yan *et al.*, 2010).

In this present study, the potential of activated carbon as catalyst support for biodiesel production is explored. Activated carbon has porous structure that contains large specific surface area and widely used in industrial and environmental applications for purifying and decolorizing products due to its strong adsorption capabilities such as gas purification, water purification and food decolorization (Adinata *et al.*, 2007). Activated carbon was also found to be highly effective catalyst support in the production of Dipropyl carbonate (Fan and Zhang, 2007). In addition, activated carbon structure is stable at high temperature (above 1000 K) and the cost of activated carbon supports is usually lower than conventional supports such as alumina and silica (Hameed *et al.*, 2009a).

CaO is a type of alkaline earth metal oxides that have been selected as active species for biodiesel production in previous research (Zhu *et al.*, 2006; Liu *et al.*, 2008a; Gotch *et al.*, 2009). It possesses basicity as high as barium and strontium oxide and its sources such as calcium carbonate and calcium nitrate are cheaper and less toxic (Zabeti *et al.*, 2009a). CaO has shown low solubility in methanol and less corrosion compared to alkali metals such as sodium and potassium that makes it suitable as heterogeneous catalyst. It also showed a high tolerance to water and free fatty acid that is present in waste oil feedstocks (Yan *et al.*, 2010). However, CaO existed in the reaction mixture in a form of suspensoid due to its poor mechanical strength, which can be resolved by supporting it onto carriers (Yan *et al.*, 2008).

Hence, in this research, the potential of activated carbon loaded with CaO catalysts will be examined for the transesterification of virgin cooking palm oil and waste cooking palm oil.

### **1.7 Research Objectives**

The purpose of this research is to study the transesterification of virgin cooking palm oil (VPO) and waste cooking palm oil (WPO) using the synthesized calcium oxide catalyst supported on activated carbon (CaO/AC) for methyl ester (ME) production. The objectives are:

1. To prepare CaO/AC catalyst and optimise the effect of catalyst preparation variables, such as catalyst loading amount on support, calcination time and calcination temperature.
2. To characterize the synthesized solid catalyst in terms of surface morphology, elemental compositions, surface area, pore volume, pore size and functional groups.
3. To study the effects of transesterification reaction variables (reaction time, methanol to oil molar ratio, reaction temperature and catalyst amount) of VPO and WPO using the synthesized catalyst and to characterize the methyl ester obtained.
4. To investigate the reusability and regeneration of the used catalyst in the transesterification of VPO and WPO.

## **1.8 Research Scope**

This study focused on the development of CaO/AC as the heterogeneous catalyst for ME production from VPO and WPO. The effect of catalyst preparation conditions such CaO loading amount on AC, calcination temperature and calcination time on the catalyst performance was investigated. The characterization of the developed catalyst was performed using SEM, EDX, BET and FTIR. The process optimization for transesterification of VPO and WPO was also investigated by studying the effect of reaction time, molar ratio of methanol to oil, reaction temperature and catalyst amount. Additionally, the characterization of ME obtained from VPO and WPO transesterification was performed based on selected fuel properties given in ASTM D6751 specifications. Finally, the stability of the solid catalyst was investigated by performing reusability studies and regeneration studies on the used catalyst in the transesterification of VPO and WPO.

## **1.9 Organization of Thesis**

This thesis is organized into five chapters as follows;

**Chapter 1** describes overview on global energy demand, renewable energy, palm oil and biodiesel industries in Malaysia, waste cooking oil and heterogeneous catalyzed transesterification process. This chapter also discusses the problem statement, scope and objectives of the research.

**Chapter 2** describes literature review from other researches and references on the topic of vegetable oils, biodiesels, transesterification of vegetable oils, homogeneous and heterogeneous catalysts, effect of variables in catalyst preparation and

transesterification process. It also discusses biodiesel feedstocks such as palm oil and waste cooking oil and statistical design of experiment using response surface methodology (RSM).

**Chapter 3** describes the methods and analysis required for the catalyst preparation and transesterification process, the chemical requirements and equipments used throughout this study.

**Chapter 4** presents the result obtained from each experimental runs and discusses the findings.

**Chapter 5** presents the conclusion of this research and provides the recommendation for improvement in future research.



## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.0 Introduction**

This chapter provides the literature review of vegetable oil and biodiesel in terms of its composition, properties and performance as diesel fuel. Biodiesel feedstocks such as palm oil and waste cooking oil are also discussed. Next, the various methods for biodiesel production particularly transesterification process are presented. The following section reviews various homogeneous and heterogeneous catalysts used in transesterification of vegetable oils. The study of variables affecting transesterification reaction such as reaction time, alcohol to oil molar ratio, reaction temperature and amount of catalyst are also presented. Various types of heterogeneous catalysts for biodiesel production are reviewed. Next, the effect of catalyst preparation variables affecting transesterification reaction such as calcinations time, calcinations temperature and loading amount of catalyst on support are discussed. Finally, literature review on the statistical tools to perform design of experiment and data analysis is also presented followed by a summary.

#### **2.1 Vegetable Oil**

The use of vegetable oils as diesel substitute has long been discovered. As early as 1900, Rudolf Diesel demonstrated a prototype engine that used peanut oil at the World's Exhibition in Paris. By 1920's petroleum diesel becomes the fuel of choice over vegetable oil due to cheaper price, higher availability and government subsidies. The higher market demand for petroleum diesel led to the alteration of diesel engine by manufacturers in order to utilize the lower viscosity petroleum diesel. However, in the late 1970's during the OPEC oil embargo, the fuel shortages

have revived interests in research and development for alternative petroleum diesel. The ASAE's (American Society of Agricultural Engineers) conference in 1982 has published a 400-page proceeding which were contributed by leading researches around the world in which many of the articles discussed potential of raw oils as fuel (Van Gerpen *et al*, 2007).

Many researches of vegetables oils as diesel fuel were reported since the 1980s. In the United States, the use of sunflower oil, soybean oil, peanut oil and used frying oil as diesel fuel in agricultural vehicle and public transportation were reported. Vegetable oil has become more attractive in recent decades due to many advantages such as its availability, renewability, lower sulfur and aromatic content and biodegradability (Demirbas, 2009).

### 2.1.1 Composition of Vegetable Oil

The main component of vegetable oil is triglyceride, which is an ester composed of a glycerol bound to three molecules of fatty acids. The fatty acids vary in their carbon chain length and the number of double bonds. The chemical structure is shown in Figure 2.1 (Barnwal and Sharma, 2005).

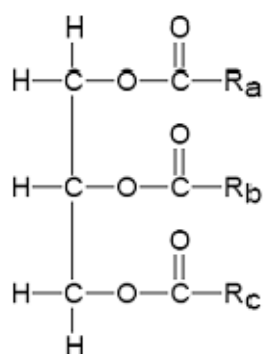


Figure 2.1: Chemical structure of triglycerides

Vegetable oil also contains some minor components such as mono- and diglycerides, free fatty acids, phosphatides and pigments. The free fatty acid content of vegetable oil varies widely based on the source (Karmakar *et al.*, 2010). Table 2.1 shows the composition of various fatty acids present in vegetable oils.

Table 2.1: Fatty acid composition of various oil sources (Ma and Hanna, 1999)

Fatty acid	Formula	Soybean	Cottonseed	Palm	Coconut
Lauric	$C_{12}H_{24}O_2$	0.1	0.1	0.1	46.5
Myristic	$C_{14}H_{28}O_2$	0.1	0.7	1.0	19.2
Palmitic	$C_{16}H_{32}O_2$	10.2	20.1	42.8	9.8
Stearic	$C_{18}H_{36}O_2$	3.7	2.6	4.5	3.0
Oleic	$C_{18}H_{34}O_2$	22.8	19.2	40.5	6.9
Linoleic	$C_{18}H_{32}O_2$	53.7	55.2	10.1	2.2
Linolenic	$C_{18}H_{30}O_2$	8.6	0.6	0.2	0.0

Chemically, the oil consists of 90-98% triglycerides which contains substantial amount of oxygen in their structures. Simple triglycerides are the ones with three fatty acids that are identical, whereas mixed triglycerides are those with fatty acids which are not identical. Mixed triglycerides fatty acids can be fully saturated with hydrogen and may not contain double bonds. Monounsaturated fatty acids may have only one double bond or triple bond per molecule. Polyunsaturated fatty acids have more than one double or triple bond per molecule. Fully saturated triglycerides lead to excessive carbon deposits in engines (Demirbas, 2003; Singh and Singh, 2010).

### 2.1.2 Properties and Performance of Vegetable Oil as fuel

Table 2.2 listed the fuel properties for various types of vegetable oils compared to pure diesel.

Table 2.2: Fuel properties of vegetable oils (Barnwal and Sharma, 2005)

Vegetable oil	Kinematic viscosity, 38°C (mm <sup>2</sup> s <sup>-1</sup> )	Heating value (MJkg <sup>-1</sup> )	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kgL <sup>-1</sup> )
Corn	34.9	39.5	-1.1	-40	277	0.9095
Cottonseed	33.5	39.5	1.7	-15	234	0.9148
Linseed	27.2	39.3	1.7	-15	241	0.9236
Peanut	39.6	39.8	12.8	-6.7	271	0.9026
Rapeseed	37.0	39.7	-3.9	-31.7	246	0.9115
Safflower	31.3	39.5	18.3	-6.7	260	0.9144
Sesame	35.5	39.3	-3.9	-9.4	260	0.9133
Soya bean	32.6	39.6	-3.9	-12.2	254	0.9138
Sunflower	33.9	39.6	7.2	-15.0	274	0.9161
Palm	39.6	NA	31.0	NA	267	0.9180
Pure Diesel	3.06	43.8	NA	-16	76	0.8550

NA- not available

All vegetable oils are extremely viscous with viscosities ranging from 10-13 times greater than diesel fuel. The higher viscosity is due to their larger molecular mass ranging from 600-900 depending on the oil source, which is about 20 times greater than diesel fuel. The flash point of vegetable oil is higher, about 3 times greater than diesel fuel whereas the heating value is about 10% lower than diesel fuel (Barnwal and Sharma, 2005).

The use of vegetable oils in conventional diesel engine leads to many short term and long term problems as obtained from engine tests conducted by earlier researchers. The high viscosity of vegetable oil intervenes with the injection process

which led to poor fuel atomization. The inefficient mixing of fuel and air causes incomplete combustion. The high flash point and lower volatility of vegetable oil contributes to carbon deposit formation, ring sticking, lubricating oil thickening and degradation. The high viscosity and low volatility of vegetable oil also causes poor cold engine start up and ignition delay. Polyunsaturated fatty acids are very susceptible to polymerization and gum formation caused by oxidation during storage. It can also be caused by complex oxidative and thermal polymerization at higher temperature and pressure of combustion (Srivastava and Prasad, 2000).

## **2.2 Biodiesel**

Biodiesel is defined as the mono alkyl esters (methyl and ethyl esters) of long chain fatty acids derived from vegetable oils or animal fats. Biodiesel can be a viable alternative to petroleum diesel fuel because of its many benefits. It is produced from renewable resources such as vegetable oils and animal fats. Biodiesel is also cleaner for the environment compared to diesel fuel as it is biodegradable, non toxic and free of sulfur and aromatics (Fukuda *et al.*, 2001).

The use of biodiesel or its blends would result in a less offensive exhaust odor and reduction of pollutants such as carbon dioxide. Studies on the lifecycle production and use of biodiesel showed that it produces between 80-100% less carbon dioxide and close to 100% less sulphur dioxide emissions. Biodiesel also provides significant reduction in particulates and carbon monoxide than petroleum diesel fuel (The Mill Biofuels, 2008).

Biodiesel has many advantages in the fuel injection engines. It can run in a conventional unmodified diesel engine and can be used alone or blends with petroleum diesel. Biodiesel is able to extend engine life because of its excellent lubricating properties. In terms of safety, biodiesel has a higher flash point of about 125 °C compared to 76 °C for petroleum diesel making it safe to handle and transports (Al-Zuhair, 2007; The Mill Biofuels, 2008).

Vegetable oil has been the major feedstock for biodiesel production. Various oil were used in biodiesel production includes soybean oil (Kim *et al.*, 2004; Suppes *et al.*, 2004; Furuta *et al.*, 2004; Xie and Li, 2006), sunflower oil (Ramos *et al.*, 2008; Granados *et al.*, 2007), canola oil (D'Cruz *et al.*, 2007), rapeseed oil (MacLeod *et al.*, 2008), coconut oil (Jitputti *et al.*, 2006) and palm oil (Zabeti *et al.*, 2009b). Malaysia has the potential to be one of the main producers of biodiesel in the world. Malaysia currently contributes 51% of world palm oil production and 62% of world exports (MPOB, 2008).

### **2.2.1 Properties of Biodiesel**

The properties of biodiesel are close to diesel fuel therefore it is suitable to replace diesel fuel if the need arises. The fuel properties of biodiesel are dependent on the amount of each fatty acid present in the feedstock. The free fatty acid (FFA) content is the amount of fatty acid in oil which is not connected to triglyceride molecule. Heating of oil can cause breakage of long carbon chain and leads to formation of FFAs (Karmakar, 2010). The properties of biodiesel from various oil sources and diesel fuels are compared in Table 2.3.

Table 2.3: Properties of biodiesel and diesel fuel (Barnwal and Sharma, 2005)

Vegetable oil methyl ester (biodiesel)	Kinematic viscosity (mm <sup>2</sup> /s)	Heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Cetane no.	Density (kg/L)
Peanut	4.9	33.6	5	NA	176	54	0.883
Soya bean	4.5	33.5	1	-7	178	45	0.885
Babassu	3.6	31.8	4	NA	127	63	0.875
Palm	5.7	33.5	13	NA	164	62	0.880
Sunflower	4.6	33.5	1	NA	183	49	0.860
Tallow	NA	NA	12	9	96	NA	NA
Pure Diesel	3.06	43.8	NA	-16	76	50	0.855
20% biodiesel blend	3.2	43.2	NA	-16	128	51	0.859

NA- not available

The kinematic viscosity of biodiesel is close to diesel fuel. By converting triglycerides to methyl esters through transesterification process, it reduces the molecular weight to one-third of the triglyceride, and reduces its viscosity. Biodiesel contains 10 to 11 % oxygen by weight, which encourages more combustion than hydrocarbon based fuels in an engine. Biodiesel has about 12% lower volumetric heating value but higher cetane number and flash point compared to diesel fuel (Barnwal and Sharma, 2005; Srivastava and Prasad, 2000). The heating value is a measure of energy content of the oil. Fuels with greater saturation have higher energy content (Singh and Singh, 2010).

Biodiesel have pour point that is 8 to 25 °C higher than diesel fuel, thereby less suitable to be used in cold climate. The pour point is the temperature below which the fuel unable to flow therefore filters will clog and stop the engine unless changes made to the fuel to prevent gelling. Addition of anti-gel additives or a fuel line heater can be done to increase the temperature (Biodiesel in Winter, 2010).

### **2.2.2 Palm Oil as Biodiesel Feedstocks**

In Malaysia, biodiesel production is synonymous to palm oil. The thriving plantation of palm oil is the main driving force towards developing biodiesel production and technology. In comparison with other countries such as U.S.A, the main source is soybean oil whereas Europe utilizes rapeseed oil. The advantage of using oil-palm plant is that it produces high yield of vegetable oil. One hectare of oil palm can produce approximately five tonnes of palm oil, which is about 5 times and 10 times higher yield than rapeseed and soybean respectively with the same area of land (Lim and Teong, 2010). Palm oil is known to be an efficient biodiesel source in which, the average yield of approximately 6000 liter of palm oil per hectare can produce 4800 liter of biodiesel (Karmakar, 2010).

#### **2.2.2.1 Properties of Palm Oil**

Palm oil, which is from the fibrous mesocarp consists mainly of triglycerides, mono and diglycerides. It also contains free fatty acids, moisture, dirt and unsaponifiable matter (non oil fatty matter). Palmitic acid (saturated) and oleic acid (unsaturated) are the two major fatty acids in palm oil. In the palm oil refinery, the oil is fractionated into liquid and solid components. The liquid fraction is palm olein whereas the solid fraction is palm stearin. Palm olein is widely used as cooking oil especially for frying food because it has good resistance to oxidation and formation of breakdown products which are undesirable due to its harmful health effects. It is known that palm olein is one of the most widely used frying oil and considered the gold standard in frying. Palm stearin, which is the solid fraction, is widely used as natural hard fat component for products such as shortening and margarines (MPOC, 2008). The typical fatty acid compositions of palm oil are summarized in Table 2.4.