DEVELOPMENT OF ULTRASONIC-ASSISTED METHYL ESTER PROCESS FROM PALM OIL USING ALKALINE EARTH METAL OXIDE CATALYSTS

by

HAMED MOOTABADI

Thesis submitted in fulfillment of the requirements for the degree of Master of Science

October 2010

ACKNOWLEDGMENTS

First, I would like to thank the Almighty God upon the accomplishment of my studies. I would like to express my genuine gratitude to my supervisor, deputy dean of School of Chemical Engineering, Assoc. Prof. Dr. Ahmad Zuhairi Abdullah for his wonderful supervision and the enormous time and effort he spent guiding and assisting me throughout my studies. I would also like to extend my gratitude to Prof. Dr. Subhash Bhatia for her brilliant comments and encouragement. I really was honored to have the opportunity to work under the supervision of both of you.

I would also like to express my appreciation to the Dean, Prof. Dr. Azlina Bt. Harun @ Kamaruddin and Deputy Deans, Assoc. Prof. Dr. Lee Keat Teong and Assoc. Prof. Dr. Mohamad Zailani Bin Abu Bakar for their continuous support and help rendered throughout my studies. My sincere thanks to all the respective lecturers, staff and technicians, School of Chemical Engineering for their cooperation and support. Thousand thanks to Mr. Shamsul Hidayat Shaharan and Mr. Mohd. Faiza Ismail for their valuable and kind help in laboratory works. I highly appreciate all the help and supports from Mrs. Aniza Abd. Ghani for her assistance in the official work during my studies. I am also indebted to School of Chemical Sciences and School of Material and Mineral Engineering in USM for AAS and SEM analysis. Very special thanks goes to Mr. Babak Salamatinia for his kind helps and support in forwarding this thesis.

I would like to show my deepest gratitude to all my adored friends, in Malaysia and in Iran for their unparalleled help, kindness and moral support towards me. Thank you for always being there for me. I hope we all have a very bright future undertaking ahead.

Last but definitely not least, my deepest and most heart-felt gratitude to my beloved mum, Mrs. Azra Asghari and my adored dad, Mr. Ahmad Mootabadi for their endless love and support. I would like to dedicate this Master thesis to them. To my wonderful sister, Moloud, my kind brother, Mahmood, for their love and care. To those who are directly and indirectly involved in this research, your contribution given shall not be forgotten. My appreciation to all of you.

Hamed Mootabadi

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF PLATES

LIST OF SYMBOLS

Symbols	Descriptions	Unit
A	Arrhenius factor (pre-exponential factor)	Dimensionless
C_{TG}	Concentration of triglyceride	(mol/dm^3)
$C_{TG,0}$	Concentration of initial triglyceride	(mol/dm^3)
C_{FAME}	Concentration of FAME	(mol/dm^3)
C_{TG} calc	Simulated data for triglyceride concentration	(mol/dm^3)
C_{TG} exp	Experimental data for triglyceride concentration	(mol/dm^3)
C_{MeOH}	Concentration of methanol	(mol/dm^3)
$-dC_{TG}/dt$	Differential of C_{TG} polynomial with respect to time (t)	$(mol/dm^3.h)$
dX/dt	Differential of conversion of triglyceride with respect to time	(mol/h)
Df	Dilution factor	Dimensionless
Ea	Activation energy	(kJ/mol)
k	Reaction rate constant	$(dm^3/mol.h)$
$[ME\ pure]_{SD}$	Concentration of ester in the standard references	(g/l)
m	Order of reaction	Dimensionless
n	Order of reaction	Dimensionless
N_A	Initial numbers of moles	(mol)
R	Gas constant	$(J/mol.K)$
R_{SD}	Ratio of peak area of ester to peak area of internal standard references	Dimensionless
R_{SP}	Ratio of peak area to peak area of internal standard in the sample	Dimensionless
$-r_A$	Rate of reaction	$(mol/dm^3.h)$
$-r_{TG}$	Rate of reaction of triglyceride	$(mol/dm^3.h)$
T	Reaction temperature	(K)
t	Reaction time	(h)
X	Conversion of triglyceride	Dimensionless
V	Total volume	(dm^3)

LIST OF ABBREVIATIONS

Al_2O_3	Aluminum oxide
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
BaO	Barium oxide
BET	Brunauer-Emmett-Teller
CaO	Calcium oxide
CCD	Central composite design
CCO	Coconut oil
CO_2	Carbon dioxide
CCRD	Central composite rotatable design
DF	Degree of freedom
DOE	Design of experiment
FAME	Fatty acid methyl ester
FID	Flame ionization detector
FFA	Free fatty acid
H_2O	Water
HNO_3	Nitric acid
ISO	International Standard Organization
KOH	Potassium hydroxide
MeOH	Methanol
MPOB	Malaysian Palm Oil Board
MPOC	Malaysian Palm Oil Council
MS	Mean square
NaOH	Sodium hydroxide

NO_X	Nitrogen oxides
PKO	Palm kernel oil
RPO	Refined palm oil
RSM	Response Surface Methodology
SEM	Scanning electron microscope
$SrCO_3$	Strontium carbonate
SrO	Strontium oxide
SS	Sum of square
TG	Triglyceride
UCO	Used cooking oil

PEMBANGUNAN PROSES BERBANTUKAN ULTRASONIK BAGI PENGHASILAN METHYL ESTER DARI MINYAK SAWIT MENGGUNAKAN MANGKIN OKSIDA LOGAM ALKALI BUMI

ABSTRAK

Biodiesel adalah sumber tenaga mesra alam untuk enjin diesel yang boleh disintesis melalui pengtransesteran minyak sayuran atau lemak haiwan dengan alkohol. Pengesteran minyak sawit berbantukan tenaga ultrabunyi dengan kehadiran mangkin oksida logam alkali bumi (CaO, SrO dan BaO) telah diselidik. Mangkin dicirikan dengan SEM, analisis permukaan, analisis AAS dan kaedah penunjuk Hammett. Proses kelompok pengesteran berbantukan tenaga ultrabunyi pada 20 kHz, dengan kekuatan maksimum 200 W, ini dilakukan untuk mengkaji kesan tempoh waktu tindak balas (10-60 minit), nisbah molar alkohol kepada minyak sawit (3:1-15:1), jumlah mangkin (0.5-3.0 %) dan variasi amplitud ultrabunyi (25-100 %). Aktiviti mangkin banyak dipengaruhi oleh kekuatan alkali manakala sifat fizikal memainkan peranan kecil. Aktiviti mangkin berada dalam turutan CaO <SrO <BaO. Selain itu, keputusan yang dicapai menggunakan yang dicapai ultrabunyi meningkat dari 5.5 % menjadi 77.3 % (CaO), 48.2 % menjadi 95.2 % (SrO), dan 67.3 % menjadi 95.2 (BaO), masing-masing dalam tempoh 60 minit. Penggunaan semula mangkin selepas beberapa kitaran berturut-turut juga dikaji. Pengurangan yang ketara dalam aktiviti pemangkinan dialami oleh mangkin BaO sedangkan penurunan sederhana ditunjukkan oleh SrO dan mangkin CaO. SrO disokong pada alumina juga dibangunkan untuk tindak balas pengesteran tersebut. Keadaan optimum sintesis dicapai pada dengan suhu pengkalsinan 500 °C dan pembebanan logam 35 %wt. Proses pengesteran berbantu tenaga ultrabunyi juga dijalankan untuk mengetahui pengaruh tempoh tindak balas (10 - 60 minit), nisbah molar alkohol terhadap minyak sawit (3:1-15:1), amaun mangkin (0.5-3 %wt) dan amplitud ultrabunyi pada tahap 50 % bagi mangkin SrO/Al_2O_3. Keputusan menunjukkan

peningkatan hasil dari 47.1 % menjadi 83.6 % untuk mangkin tersebut bagi sistem berbantukan ultrabunyi berbanding dengan sistem pengadukan magnet. Kajian penggunaan semula mangkin SrO/Al_2O_3 untuk tiga kitaran juga diselidiki. Hasil biodiesel telah digunakan sekitar 40 % selepas tiga kitaran penggunaan mangkin telah dicapai. Kaedah sambutan permukaan (RSM) telah digunakan untuk pengoptimuman proses penghasilan biodiesel dan untuk menilai interaksi antara pembolehubah pembolehubah proses. Keadaan optimum dengan hasil biodiesel sebanyak 80.2 % ditemui pada nisbah metanol terhadap minyak sebanyak 9.2:1, berat mangkin pada 1.6 wt %, masa tindakbalas 30.2 minit dan amplitud ultrabunyi pada tahap 69.7 %. SrO dan SrO/Al_2O_3 turut diuji bagi pengesteran berbantukan ultrabunyi bagi minyak masak terpakai. Peningkatan yang ketara telah dicapai bagi hasil biodiesel dalam tempoh tindakbalas selama 60 minit iaitu dari 35.1% menjadi 71.7 % untuk SrO/Al_2O_3 dan dari 38.8 % menjadi 75.7 % untuk mangkin SrO berbanding sistem pangadukan magnetik.

DEVELOPMENT OF ULTRASONIC-ASSISTED METHYL ESTER PROCESS FROM PALM OIL USING ALKALINE EARTH METAL OXIDE CATALYSTS

ABSTRACT

Biodiesel is an eco-friendly and alternative energy source for diesel engines that can be synthesized by transesterification of vegetable oil or animal fat with alcohols. Ultrasonic-assisted transesterification of palm oil in the presence of alkaline earth metal oxide catalysts (CaO, SrO and BaO) was investigated. The catalysts were characterized by SEM, surface analysis, AAS analysis and the Hammett indicator method. Batch transesterification process assisted by 20 kHz ultrasonic cavitation, with a maximum power of 200 W, was carried out to study the effects of reaction time (10–60 min), alcohol to palm oil molar ratio (3:1–15:1), catalysts loading (0.5–3 %) and variation of ultrasonic amplitudes (25-100 %). The activities of the catalysts were mainly related to their basic strength. The catalytic activity was in the sequence of CaO < SrO < BaO. Also, the yields achieved under ultrasonic increased from 5.5 % to 77.3 % (CaO), 48.2 % to 95.2 % (SrO), and 67.3 % to 95.2 (BaO) , respectively within a period of 60 minutes. Reuse of the catalysts after several successive cycles was also investigated. Significant reduction in catalytic activity was experienced by BaO catalyst while moderate decrease in the yield occurred for SrO and CaO catalysts. SrO supported over alumina was selected for the transesterification reaction. The optimum synthesis condition was achieved at 500 °C of calcinations temperature with 35 %wt of metal loading. Ultrasonic-assisted transesterification process was carried out to study the effect of reaction time (10–60 min), alcohol to palm oil molar ratio (3:1–15:1), catalysts loading (0.5–3 %) at 50 % of ultrasonic amplitude for the SrO/Al_2O_3 catalyst. The yield increased from 47.1 % to 83.6 % for the SrO/Al_2O_3 catalyst in ultrasonic-assisted system compare to that of the magnetic

stirrer system. The reusability study of the SrO/Al_2O_3 catalyst for up to three cycles was also studied. Biodiesel yield dropped by about 40 % after three cycles of use. Response surface methodology (RSM) was employed for the optimization process to achieve the highest biodiesel yield. The optimum condition with 80.2 % of biodiesel yield was found at a methanol to oil ratio of 9.2, 1.6 wt. % of catalyst, 30.2 min of reaction time and 69.7 % of ultrasonic amplitude power. SrO and SrO/Al_2O_3 catalysts were tested in the ultrasonic-assisted transesterification of used cooking oil. There was a significant increase in biodiesel yield for reaction time of 60 min from 35.1 % to 71.7 % for SrO/Al_2O_3 and 38.8 % to 75.7 for SrO catalyst in ultrasonic-assisted system compare to those of magnetically stirred system. Furthermore, low activation energy of 47.33 kJ/mol was obtained for the ultrasonic-assisted transesterification process.

CHAPTER 1

INTRODUCTION

1.1. Industrialization and Oil Consumption

Recently, the increase in the price of crude oil, limited resources of fossil oil and also environmental concerns have caused great impact on future energy senario. Majority of the worlds energy needs are supplied through non-renewable petroleum sources, coal and natural gases. With the exception of hydroelectricity and nuclear energy, all of these sources are finite and at current usage rates they will be consumed shortly. Due to diminishing petroleum reserves and the growing environmental concerns have made renewable fuels an exceptionally attractive alternative as a fuel for the future (Demirbas, 2009). Thus, the attraction for renewable energy resources has been increasing. The most feasible way to meet this growing demand is by utilizing alternative fuels. Biofuels, in particular, biodiesel as a fuel demonstrate a great potential (Fernando et al., 2006).

Economic growth is always accompanied by commensurate increase in the transportation. Transport vehicles are one of the largest consumers of oil based fuels and include jet fuel, engine fuel and diesel fuel. Due to these facts, a renewed focus on finding cheap fuel as a replacement for these fuels has been investigated. With the advent of cheap petroleum, appropriate crude oil fractions are refined to serve as fuel in diesel engines.

The high energy demand in the industrialized world as well as in the domestic sector and pollution problems is mainly due to the widespread use of fossil fuels to make it increasingly necessary to develop the renewable energy sources of limitless

duration and smaller environmental impact than the traditional ones. This has encouraged recent interest of the scientists to find alternative sources for petroleum-based fuels. The substitution fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available (Meher et al., 2006). For this purpose, the use of the esters from vegetable oils or animal fats appears to be the most promising alternative for petroleum-based diesel fuels under the name of "biodiesel" (Ma and Hanna, 1999, Stavarache et al., 2005, Meher et al., 2006).

1.2. Biodiesel

Biodiesel fuel is a mixture of mono-alkyl esters of long chain fatty acid methyl esters (FAMEs) derived from plant oils or animal fats. This fuel is increasingly available as a possible substitute for conventional diesel fuel (Shu et al., 2007). Biodiesel has variable physical properties due to the different sources of vegetable oils or animal fats. Production and consumption of biodiesel is somehow advantageous while it has its own disadvantages as well.

1.2.1. Advantages

There are different ways of producing biodiesel out of various types of raw material such as refined, crude or frying oils. One of the advantages of this fuel is that the raw materials used to produce it are natural and renewable. All these types of oils come from vegetable oil or animal fat which can make it biodegradable and also renewable (Marchetti et al., 2007). biodiesel has attracted considerable attention among many researches as an alternative fuel for diesel engines, due to the depleting fossil fuel resources and its favorable properties (Stamenković et al., 2007). The benefits of substation of this fuel are the biodegradability of these fuels due to its

biological source, non toxicity and low emission profiles as compared to petroleum based diesel fuel. Biodiesel can be blended at any level with petroleum diesel creating diesel blends. With little or no modification, biodiesel can be used in compression-ignition (diesel) engine (Kim et al., 2004). The use of bio-fuels in ignition compression engines can play a vital role in helping to reduce the environmental impacts of fossil fuels. The main target for the use of biodisel is to decrease the emissions of gaseous pollutants to the atmosphere, mainly CO_2 emissions (Coronado et al., 2009). Figure 1.1 shows the emission levels of the main polluting agents. The 100% is considered the emission level of the diesel engine. In the case of biodiesel combustion, the levels are very low (with the exception of NO_x).
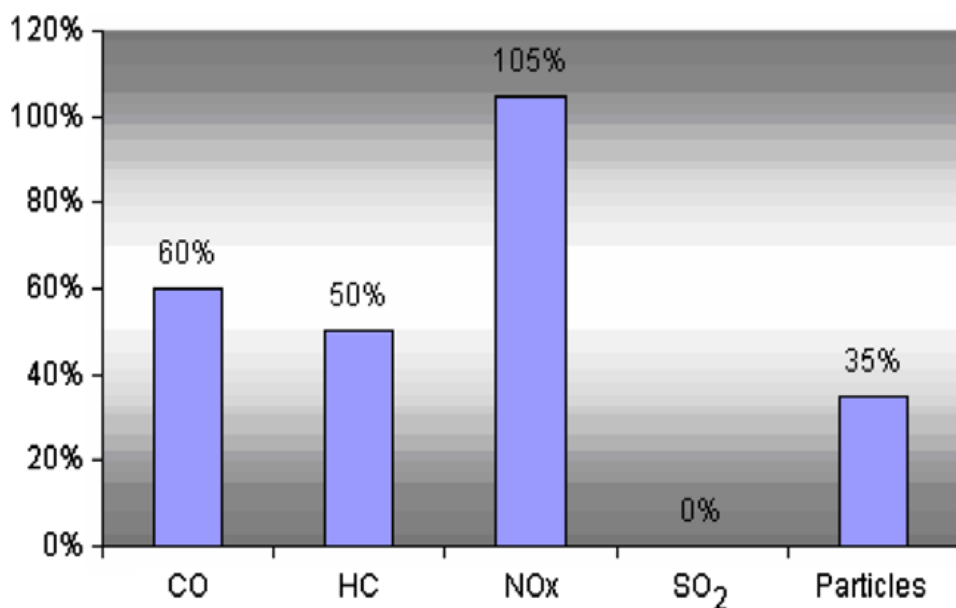
Figure 1.1 Pollutants emissions of the biodiesel combustion in an internal combustion engine (Coronado et al., 2009).

The economical advantages of biodiesel are that it reduces greenhouse gas emissions, helps to reduce a country's reliance on crude oil imports, and supports agriculture by providing new labor and market opportunities for domestic crops. In addition, it enhances lubrication and is widely accepted by vehicle manufacturers

(Demirbas, 2009). Figure 1.2 shows world production and capacity of the biodiesel in recent years. As can be observed in Figure 1.2 there is a significant increase in biodiesel production in last four years with roughly 50 % improvement of capacity of biodiesel production in each year.
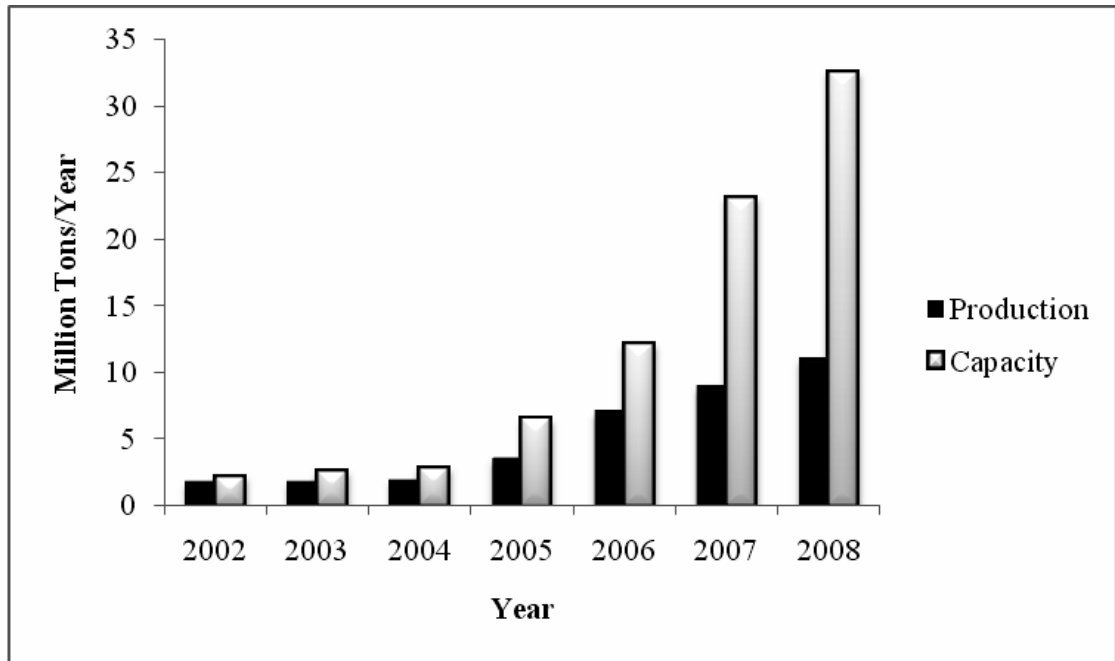
Figure 1.2 World production and capacity of the biodiesel in recent years
(Biodiesel 2020, 2008).

1.2.2. Disadvantages

One of the important fuel properties is viscosity, as it controls the characteristics of fuel injection in the injector (Yuan et al., 2005). The viscosity of biodiesel is approximately 1.5 times higher than that of fossil diesel (Tat and Van Gerpen, 1999). At low temperatures, this property of biodiesel fuel may thicken and might not flow properly, thereby affecting the performance of fuel lines, pumps and injectors (Meher et al., 2006). Thus, high viscosity is one of the main drawbacks of biodiesel. Pure biodiesel gels at 3 °C, and therefore it becomes difficult to use in diesel engines and home heating systems as it may clog filters and cause problems in pumping from the fuel tank to the engine or furnace burner (Joshi and Pegg, 2007).

Another disadvantage is higher iodine value implies higher tendency of the biodiesel to undergo chemical as well as microbial changes that will degrade the fuel (Joshi and Pegg, 2007).

1.3. Biodiesel Production

1.3.1. Direct use and Blending

In early 1980s, the use of vegetable oils as alternative fuels attracted a lot of discussion. At that point it was not practical to substitute 100 % of vegetable oil for diesel fuel, but a blend of 20 % of vegetable oil and 80 % of diesel are summarized. Physical properties of biodiesel blends with diesel were illustrated in Table 1.1. As observed in the table, increasing percentage of the biodiesel in the blend results in a reduction in calorific value with corresponding increase in other parameters such as acid number, viscosity and flash point. The reduction in calorific value for the biodiesel and its blends compared to diesel is due to the presence of oxygen in the biodiesel (Phan and Phan, 2008).

The advantages of vegetable oils as diesel fuels are (1) liquid nature-portability, (2) heat content (80% of diesel fuel), (3) ready availability and (4) renewability. There are also some disadvantages for the use of vegetable oils as fuel including (1) higher viscosity, (2) lower volatility and (3) the reactivity of unsaturated hydrocarbon chains. There are also some problems which only occur after a longer engine run using vegetable oils. These problems which mostly occur with direct-injection engines are (1) coking and trumpet formation on the injectors, (2) carbon deposits, (3) oil ring sticking and (4) thickening and gelling of the lubricating oil as a result of contamination by vegetable oils (Ma and Hanna, 1999).

Due to the disadvantages, the direct use of vegetable oils and/or use of blends of oils have generally been considered unsatisfactory and impractical for both direct and indirect diesel engines (Sharma et al., 2008).

Table 1.1 Physical properties of biodiesel blends with diesel (Phan and Phan, 2008).

Quantity	Unit	Samples							
		B5	B10	B15	B20	B25	B30	B50	B75
Density	g/ml	0.85	0.85	0.85	0.85	0.85	0.86	0.86	0.88
Viscosity at 40°C	mm^2/s	3.56	3.72	3.72	3.75	3.82	3.90	4.25	4.64
Cloud point	°C	0	0	0	0	0	0	0	0
Pour point	°C	-12	-11.5	-9.5	-9	-8.5	-8	-6	-4.5
Flash point	°C	74	80.5	81	82	85	86	91	106.5
Calorific value	kcal/kg	10845	10750	10683	10615	10545	10462	10180	10100
Water content	wt%	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Acid number	mg KOH/g	0.11	0.12	0.13	0.16	0.20	0.23	0.32	0.35

1.3.2.   Emulsification (Microemulsions)

A microemulsion 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 (Meher et al., 2006; Sharma et al., 2008).

1.3.3. Thermal Cracking (Pyrolysis)

Strictly defined, Pyrolysis is the conversion of one substance into another by means of heat or by heating with the aid of a catalyst. It involves heating in the

absence of air or oxygen and cleavage of chemical bonds to yield smaller molecules (Meher et al., 2006, Demirbas, 2009).

1.3.4. Transesterification (Alcoholysis)

The most commonly used method is the transesterification of vegetable oils and animal fats. This method is more suitable and the by-product (glycerol) has commercial value (Ma and Hanna, 1999). Transesterification (alcoholysis) is the chemical reaction between triglycerides and alcohol in the presence of catalyst to produce mono-esters. Transesterification process consists of a sequence of three consecutive reversible reactions. That is, conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides (Meher et al., 2006, Basha et al., 2008). The overall transesterification reaction can be represented by Figure 1.3.

$$
\begin{array}{ccccc}
CH_2-OOC-R_1 & & & R_1-COO-R' & CH_2-OH \\
| & & Catalyst & & | \\
CH-OOC-R_2 & + \ 3R'OH & \rightleftharpoons & R_2-COO-R' & + \ CH-OH \\
| & & & & | \\
CH_2-OOC-R_3 & & & R_3-COO-R' & CH_2-OH \\
\\
Glyceride & Alcohol & & Esters & Glycerol
\end{array}
$$
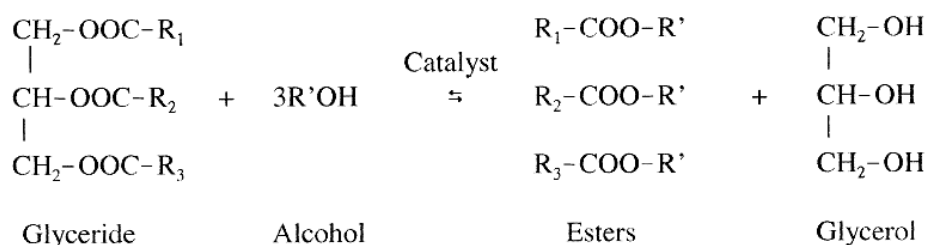
Figure 1.3 Transesterification of triglycerides with alcohol.

1.4. Catalyst for the Transesterification Process

Catalysts used for the transesterification of triglycerides are classified as alkali, acid, enzyme or heterogeneous catalysts. The alkalis include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Sulfuric acid, sulfonic acid and hydrochloric acid are usually used as acid catalysts. Lipases can also be used as biocatalysts (Meher et al., 2006). Transesterification process in

presence of alkali-catalyst is much faster than acid-catalyzed transesterification. Therefore, alkali-catalyzed transesterification is most often used because of the lower price compare to other alcohols. For an alkali-catalyzed transesterification, the glyceride and alcohol must be substantially anhydrous, as water makes the reaction partially change to saponification, which produces soap (Hideki Fukuda, 2009).

1.5. Heterogeneous Catalyst

The typical production method for biodiesel fuel is a base-catalyzed process with homogeneous catalysts. Nevertheless, these alkali compounds have some drawbacks. They must be neutralized giving rise to wastewaters and cannot be reutilized. Homogeneous catalysts are fully dissolved in the glycerin layer and moderately in the fatty acid methyl ester (FAME) layer, to make the product separation difficult (Singh and Fernando, 2008, Arzamendi et al., 2007). Large amount of wastewater is also produced in separating and cleaning the catalyst and the products (Ono, 2003, Xie et al., 2006a). Therefore, conventional homogeneous catalysts are expected to be replaced in the near future by environmentally friendly heterogeneous catalysts.

Heterogeneous catalysis is an economically and ecologically important field in catalysis research because these catalysts after many advantages. They are non-corrosive, environmentally benign and present fewer removal problems. They are also much easier to separate from liquid products and they can be designed to give higher activity, selectivity and longer catalyst lifetimes (Liu et al., 2007). A wide variety of solid bases have been examined for this purpose. Alkaline-earth metals oxides and hydroxides (Arzamendi et al., 2008), alkali metals (Na and K) hydroxides

or salts supported on γ-alumina (Arzamendi et al., 2007, Chen et al., 2008, Ebiura et al., 2005, Li et al., 2007a), zeolites (Suppes et al., 2004), hydrotalcites (Cantrell et al., 2005, Xie and Li, 2006, Georgogianni et al., 2009) have been investigated to date at different reaction conditions and with a variable degrees of success. One main group of catalyst used is single component alkaline earths metal oxide (BaO, SrO, CaO, MgO) which are among the well-researched heterogeneous catalysts as they have a higher basicity, lower solubility and higher biodiesel yield (Kawashima et al., 2009).

1.6.   Ultrasonic-assisted Biodiesel Production Process

As the oil and methanol are not completely miscible, mixing efficiency is identified as one of the most important factors affecting the yield of the transesterification. The reaction between these species can occur only in the interfacial region between the methanol, oil and catalyst, as alkaline catalysts are essentially insoluble in the oil phase. Vigorous mixing is required to increase the area of contact between the three phases (Mikkola et al., 2001, Stavarache et al., 2006).

Low frequency ultrasound is an efficient, time saving and economically functional, offering a lot of advantages over the conventional mechanical stirring method (Hanh et al., 2009b). Ultrasonic mixing produces smaller droplet sizes than conventional agitation, leading to more interfacial area for the reaction to occur (Wu et al., 2007). Because of improvement in mass transfer, the mixing requirement during the process is also significantly lowered, translating in reduced energy consumption (Mikkola et al., 2001; Stavarache et al., 2005). Another advantage of using ultrasonic energy is the retardation of catalyst deactivation. This is because

ultrasonic can 'grind' the catalyst into smaller particles, creating new active sites for the reaction. Thus, the solid catalyst is expected to last longer in the ultrasonic assisted process. Mikkola et al., (2001) found that the deactivation of catalyst decreased notably upon the use of ultrasonic energy.

The use of ultrasonic in this process can improve the efficiency of the biodiesel production by reducing the reaction time and improvement in the conversion. Also, by the use of ultrasonic process, the time spent for the reaction and the amount of catalyst in use reduce sharply which can lead to a cheaper production of biodiesel.

1.7.   Problem Statement

Major energy demand is fulfilled from the conventional energy resources such as coal, petroleum and natural gas. Petroleum-based fuels available only in certain regions of the world are limited. These sources are on the edge of getting finished. Therefore, alternative fuels for diesel engines have been becoming increasingly important (Demirbas, 2009). Recently, biodiesel has been receiving increasing attention due to its less polluting nature and renewable as compared to the conventional diesel, which is a fossil fuel leading to a potential exhaustion.

In the reaction process by means of homogeneous catalysts, removal of the base catalysts after the reaction is a major problem. Large amount of wastewater is also produced to separate and clean the catalyst and the products. Therefore, conventional homogeneous catalysts are needed to be replaced by environmentally friendly heterogeneous catalysts. Heterogeneous catalysts have many advantages such as, more environmentally friendly, fewer removal problems, less-corrosive, higher activity and selectivity and longer lifetimes. However, transesterification

process via heterogeneous catalysts has some drawbacks. They need long reaction time and have a low rate of biodiesel yield. As the heterogeneous catalysts are almost immiscible in the oil and methanol, vigorous mixing is required to increase the area of contact between the three phases (oil, alcohol and catalyst). Thus, some solutions need to be found so that the heterogeneous transesterification of biodiesel will become more efficient and economical.

Currently, new transesterification processes, either based on the use of cheaper feedstock or modifications with an aim of process intensification are being developed to produce biodiesel in large scale and at lower costs of production (Vishwanath et al., 2009). The use of ultrasonic-assisted reactors can favour the reaction chemistry and propagation by way of enhanced mass transfer and mixing between the phases and also can lower the requirement of the severity of the operating conditions in terms of temperature and pressure. This will reduce production costs and make biodiesel more competitive in price with fossil diesel fuel.

The synthesis and characterization of high performance heterogeneous catalyst, establishment of a suitable process set up for an ultrasonic-assisted transesterification of palm oil and optimization of the suitable method are important aspects that are worth further investigation. As an important aim in fuel industry, a high yield and low cost biodiesel can be produced by means of ultrasonic energy in the presence of heterogeneous catalyst which can be economically competitive with petroleum-based diesel.

1.8. Objectives

This research project is planned and carried out to address the following objectives:

1) To develop high performance heterogeneous catalyst system for the ultrasonic-assisted transesterification of palm oil and characterization of the catalyst in order to identify its properties in the transesterification process.

2) To identify the most suitable set of process variables for the enhancement in the production of biodiesel using the ultrasonic reactor.

3) To study the performance of used oil in the system developed and comparison with fresh oil.

4) To study the reaction kinetics in the ultrasonic-assisted biodiesel production process.

1.9. Scope of Study

In this study, the main objective is to develop a suitable ultrasonic-assisted heterogeneous transesterification process for converting palm oil which is readily available in Malaysia into a high quality biodiesel. For this purpose, an ultrasonic-assisted reactor was used to enhance the process. In this study, four different types of alkaline earth metal oxides, MgO, CaO, SrO and BaO were tested as heterogeneous catalysts in transesterification of palm oil in order to find out the most suitable catalyst for the process. These catalysts were tested in both ultrasonic assisted reactor and magnetic stirring reactor to study the effect of ultrasonic energy in biodiesel production from palm oil and to be compared with the conventional magnetic stirring reactor. The effects of reaction time, molar ratios of alcohol to palm oil, quantity of catalysts (wt of heterogeneous catalyst/wt of palm oil) and variation

in ultrasonic amplitude were thoroughly studied. The most suitable catalyst was loaded on alumina to synthesize supported alkaline earth metal oxide catalysts in order to increase the biodiesel yield.

Response surface methodology was employed to optimize the ultrasonic assisted biodiesel production. The variables for the optimization of the transesterification process were the time, molar ratios of alcohol to palm oil, quantity of catalysts and ultrasonic amplitude. For the optimization of alumina supported catalyst synthesis, the calcinations temperature and metal oxide loading on alumina were considered as the process variables. Characterizations of the catalysts were carried out using analytical instruments such as scanning electron microscope (SEM), surface area analyzer. Basic strengths of the catalysts (H-) were determined using Hammett indicator method.

The utilization of used cooking oil (UCO) in ultrasonic-assisted transesterification process was also investigated. SrO catalyst (as the best of three alkaline earth metal oxides) and SrO/Al_2O_3 (as supported catalyst) were selected to investigate the behavior and activity of the heterogeneous catalysts in both ultrasonic–assisted and non-ultrasonic transesterification. The effects of three variables i.e. reaction time, alcohol to oil molar ratio and catalyst mass ratio were investigated. The kinetic study for the reaction of fresh palm oil in presence of SrO/Al_2O_3 as the catalyst was studied using Arrhenius equation to obtain the reaction rate ($-r_A$) and order of reaction (n). The kinetics was studied in a time range varying between 10-60 min with an interval of 10 min at 65 °C.

1.10. Benefits towards Society

Recently, biodiesel has become more attractive because of its environmental benefits and the fact that it is made from renewable resources. Lately, because of increases in crude oil prices, limited resources of fossil fuels and environmental concerns, there has been a renewed focus on vegetable oils and animal fats to make biodiesel fuels. The use of ultrasonic in this process can improve the efficiency of the biodiesel production by reducing the reaction time and improvement in the conversion. Therefore, ultrasonic-assisted biodiesel production is an energy saving process compare with conventional methods. This process aims at a more cleaner and environment friendly process as compared with conventional methods. Also, by the use of ultrasonic process, the time spent for the reaction and the amount of catalyst in use could be significantly reduced which can lead to a cheaper production of biodiesel. The heterogeneous catalyst used in this reaction generates less waste, ending up to a cleaner environment. Because of the regeneration ability of heterogeneous catalyst as compared to other heterogeneous catalysts, used for this process will reduce the cost of the reaction. Therefore, this new method in conjunction with the abundance of crude palm oil in Malaysia seems to be a promising method for the production of biodiesel in Malaysia.

1.11. Organization of Thesis

This thesis contains four main chapters. The first chapter (Introduction) will briefly introduce the research project, the problem statement, and the scopes of the study. In the Literature Review section (Chapter 2), an overview of the reported results related to this study and the main basic knowledge about this project such as biodiesel production, transesterification process, heterogeneous catalyst, ultrasonic

energy, modeling and others are discussed in detail. Chapter Three (Material and Methods) includes descriptions on the materials, experimental procedures and instrumental analysis used in this project. The response surface methodology (RSM) designs used including the ranges and the codes are introduced and discussed in this section. This chapter is presented in great detail and arranged in such a way that it can be easily repeated by other researchers. Results and Discussions made in this project are given in Chapter Four. This chapter includes different parts such as effect of different parameters on production of biodiesel, synthesis of heterogeneous catalyst, catalyst characterization, optimization, kinetic and catalyst regeneration studies. In Chapter 5 (Conclusion and Recommendations), overall conclusions based on results and findings made in the present study are given in brief. The recommendations for future research based on the understanding and knowledge generated in the present study are also given in this chapter.

CHAPTER   2

LITERATURE REVIEW

2.1.   Biodiesel Production and Feed Stock

2.1.1. Introduction

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic has low emission profiles and is environmentally beneficial. Natural vegetable oils and animal fats are extracted or pressed to obtain crude oil or fat (Ma and Hanna, 1999). Biodiesel is a mixture of mono-alkyl esters of long chain fatty acid methyl esters (FAMEs) derived from plant oils or animal fats (Meher et al., 2006). The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics. Most biodiesel, are produced from refined/edible type oils using methanol and alkaline catalyst.

Biodiesel is the monoalkyl esters of long chain fatty acids derived from renewable feed stocks, such as vegetable oil or animal fats and it is for use in compression ignition engine. The unprocessed vegetable oil can be used in diesel engines, but it requires extensive engine adjustments and modifications. Unlike diesel fuel, vegetable oil consists mostly of saturated hydrocarbons and those of vegetable oils are triglycerides, consisting of glycerol and esters of fatty acids. The fatty acids vary in their carbon chain length and in the number of double bonds. To overcome these problems, the neat vegetable oils have to be modified to bring their combustion-related properties closer to those of petroleum diesel (Enweremadu and Mbarawa, 2009). Technical properties and general characteristics of biodiesel are listed in Table 2.1.

Table 2.1 Technical properties and general characteristics of biodiesel (ASTM D 6751)

Common name	Biodiesel (bio-diesel)
Common chemical name	Fatty acid (m)ethyl ester
Chemical formula range	C_{14}–C_{24} methyl esters or $C_{15\_25}H_{28\_48}O_2$
Kinematic viscosity range (mm^2/s, at 313 K)	3.3–5.2
Density range (kg/m^3, at 288 K)	860–894
Boiling point range (K)	>475
Flash point range (K)	420–450
Distillation range (K)	470–600
Vapor pressure (mm Hg, at 295 K)	<5
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

2.1.2. Biodiesel Properties

Biodiesels are characterized by their viscosity, density, cetane number, cloud and pour points, distillation range, flash point, ash content, sulfur content, carbon residue, acid value, copper corrosion, and higher heating value (HHV). The most important parameters affecting the ester yield during the transesterification reaction are the molar ratio of alcohol to vegetable oil and reaction temperature. The viscosity values of vegetable oil methyl esters decrease sharply after transesterification. Compared to D2 fuel, all of the vegetable oil methyl esters are slightly viscous. The flash point values of vegetable oil methyl esters are significantly lower than those of vegetable oils. There is a high regression between the density and viscosity values of

vegetable oil methyl esters. The relationships between viscosity and flash point for vegetable oil methyl esters are considerably regular (Demirbas, 2009).

These parameters are all specified through the biodiesel standard, ASTM D 6751. This standard identifies the parameters the pure biodiesel (B100) must meet before being used as a pure fuel or being blended with petroleum-based diesel fuel.

2.1.3. Biodiesel Feed Stock

Typical raw materials of biodiesel are rapeseed oil, canola oil, soybean oil, sunflower oil and palm oil. Beef and sheep tallow and poultry oil from animal sources and cooking oil are also possible sources of raw materials. There are various other biodiesel sources such as almond, andiroba (*Carapa guianensis*), babassu (*Orbignia sp.*), barley, camelina (*Camelina sativa*), coconut, copra, cumaru (*Dipteryx odorata*), Cynara cardunculus, fish oil, groundnut, *Jatropha curcas*, karanja (*Pongamia glabra*), laurel, *Lesquerella fendleri*, *Madhuca indica*, microalgae (*Chlorella vulgaris*), oat, piqui (*Caryocar sp.*), poppy seed, rice, rubber seed, sesame, sorghum, tobacco seed, and wheat (Pinto et al., 2005).

Vegetable oils are renewable fuels. They have become more attractive recently because of their environmental benefits and the fact that they are made from renewable resources. Vegetable oils are a renewable and potentially inexhaustible source of energy, with energy content close to that of diesel fuel. Global vegetable oil production increased from 56 million tons in 1990 to 88 million tons in 2000, following a below-normal increase. The source of this gain was distributed among

the various oils. Global consumption rose by 56–86 million tons, leaving world stocks comparatively tight (Demirbas, 2005).

Various oils have been in use in different countries as raw materials for biodiesel production owing to its availability. Soybean oil is commonly used in the United States, rapeseed oil is used in many European countries for biodiesel production while, coconut and palm oils are used in Malaysia and Indonesia (Demirbas, 2006; Ghadge and Raheman, 2006; Sarin et al., 2007). In India and Southeast Asia, also from Jatropha tree (*Jatropha cursas*) (Tiwari et al., 2007), Karanja (*Pongamia pinnata*) (Sharma et al., 2008) and Mahua (M. indica) (Ghadge and Raheman, 2006) are investigated the potential feedstocks.

Commonly accepted biodiesel raw materials include the oils from soy, canola, corn, rapeseed, and palm. New plant oils that are under consideration include mustard seed, peanut, sunflower, and cotton seed. The most commonly considered animal fats include those derived from poultry, beef, and pork (Usta, 2005).

Algae can grow practically anywhere where there is enough sunshine. Some algae can grow in saline water. All algae contain proteins, carbohydrates, lipids and nucleic acids in varying proportions. While the percentages vary with the type of algae, there are algae types that are comprised up to 40% of their overall mass by fatty acids. The most significant distinguishing characteristic of algal oil is its yield and hence its biodiesel yield. According to some estimates, the yield (per acre) of oil from algae is over 200 times the yield from the best-performing plant/vegetable oils (Sheehan et al., 1998). Microalgae are the fastest-growing photosynthesizing

organisms. They can complete an entire growing cycle every few days. Approximately 46 tons of oil/hectare/year can be produced from diatom algae. Different algae species produce different amounts of oil. Some algae produce up to 50% oil by weight. The production of algae to harvest oil for biodiesel has not been undertaken on a commercial scale, but working feasibility studies have been conducted to arrive at the above number. Specially bred mustard varieties can produce reasonably high oil yields and have the added benefit that the meal left over after the oil has been pressed out can act as an effective and biodegradable pesticide (Pinto et al., 2005). The difficulty of alkaline-esterification of non-edible oils and fats is that they often contain large amounts of free fatty acids. This leads to quick reaction with the alkaline catalyst that will produce soap and inhibits the separation of ester and glycerin (Gerpen, 2005).

2.2. Palm Oil-Based Biodiesel

The source for biodiesel production is usually chosen according to the availability in each region or country. In Brazil, biodiesel production has been adjusted to the available crop in each region. In the north, palm kernel and soybean are the most popularly used oil sources while in the northeast, castor bean, palm oil, palm kernel, babassu, soybean and cotton seed are more popular. In the central west, soybean, cotton seed, castor bean and sunflower seed are more preferred while in the southeast, soybean, castor bean, cotton seed and sunflower seed are more suitable (Abdullah et al., 2009b; Pinto et al., 2005). There are different oil sources reported in scientific articles showing their suitability in biodiesel production. Soybean oil (Kim et al., 2004), sunflower oil (Stamenković et al., 2007), rubber seed oil (Ramadhas et al., 2005), palm kernel oil (Chongkhong et al., 2007), canola oil (Strayer et al.,

1983), rapeseed oil ; (Rashid and Anwar, 2008; Strayer et al., 1983), coffee oil (Oliveira et al., 2008), are some examples of oil sources investigated for biodiesel production.

Figure 2.1 summarizes the number of technical reports on various vegetable oils that have been used to produce biodiesel and mostly soy, sunflower and rapeseed oils have been reported to be the feedstock (Pinto et al., 2005). Life cycle analysis (LCA) conducted on various biodiesels revealed that palm oil-based biodiesel can reduce the current emission rate of greenhouse gases (GHG) by 62 % as compared to that of soy-based (40 %), rapeseed-based (45 %) and sunflower-based (58%) (Sani, 2009). Thus, leading producers of palm oil like Malaysia are looked upon to be the anchors to produce palm oil-based biodiesel and exported to other regions of the world. To ensure the success, comprehensive biodiesel programs have to be put in place from the very beginning while home-grown indigenous palm biodiesel production technologies should be further developed for the world market (Policy, 2006).

The European Standard Specifications for Biodiesel (EN 14214) and the American Standard Specifications for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels (ASTM 6751) are tabulated for comparison in Table 2.2 besides the Malaysian palm diesel specifications and Malaysian petroleum diesel standards (Foon et al., 2005). As can be observed in Table 2.2, the typical palm biodiesel properties for both normal point and low pour point can fully meet the European Standards and ASTM without much difficulty. Currently, Malaysia is using blended diesel (B5) with the specifications as can be seen in Table 2.2. Although the specifications can fit to biodiesel standards to some extents, high percentage of

petroleum diesel in this blend causes the comparison meaningless. Thus, its properties are compared with the Malaysian Standards for diesel fuel and generally, they are not much different (Abdullah et al., 2009b).
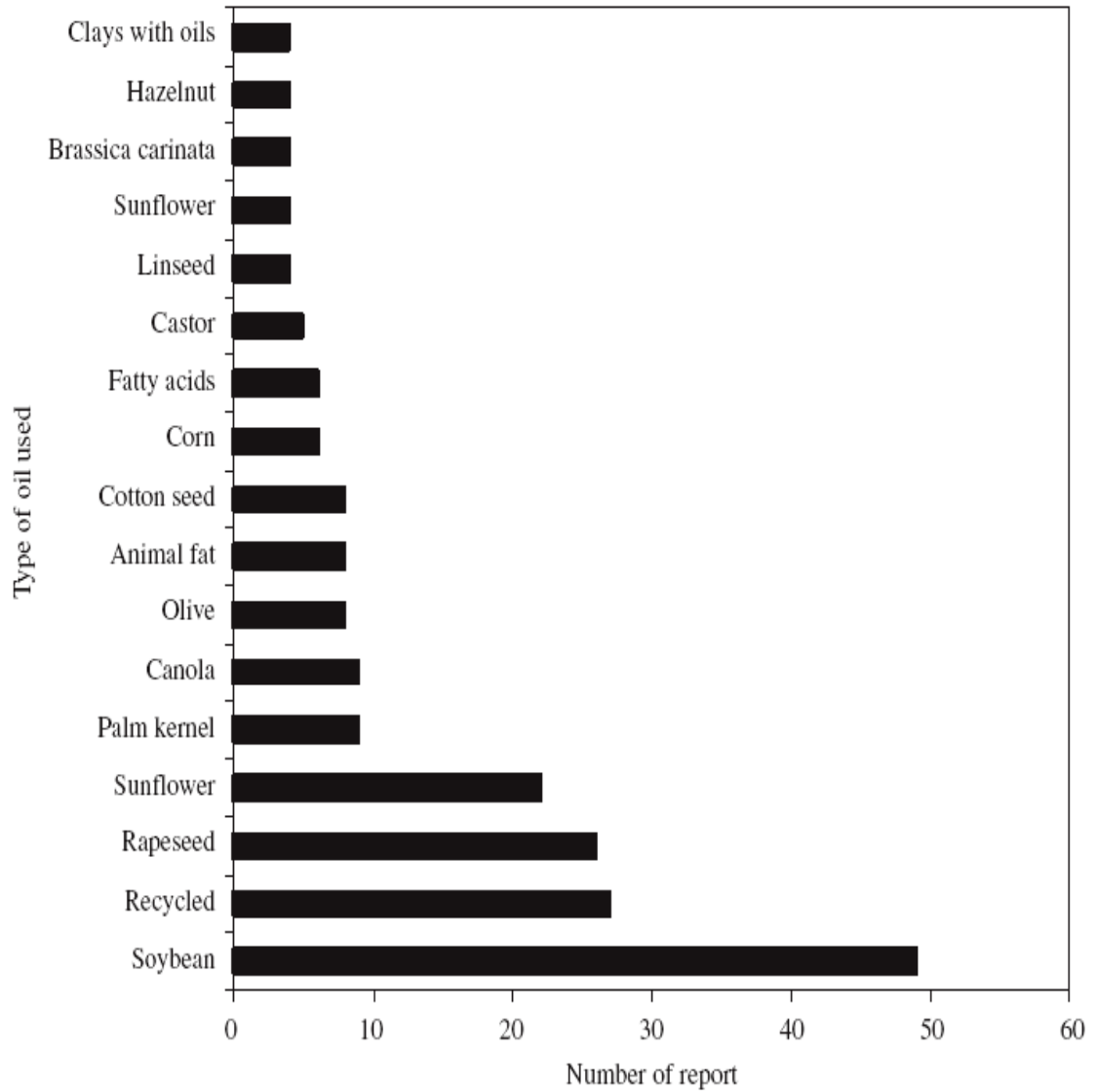

Figure 2.1 Number of scientific articles in 2005 on oils used as feedstock for biodiesel production (Pinto *et al.*, 2005).

Table 2.2 Different standards and typical specifications for palm biodiesel (Foon et al., 2005).

Property	Unit	Biodiesel standards		Biodiesel standards Palm biodiesel			
		EN14214	ASTM D6751	Normal point	Low pour point	PLPO/PDB5[a]	MS123:1993[b]
Ester content	% (m/m)	96.54>	-	98.50	99.5	-	-
Density at15 1C	Kg/m3	860-900	-	878.3	870-890	841.9–845.9	-
Viscosity at40 1C	mm2/s	3.5-5.0	1.9-6.0	4.415	4-5	4.136–4.549	1.5-5.8
Flash point	°C	120<	130<	182	150-200	75–81	60<
Cloud point	°C		Report[c]	15.2	-18 to 0	14–16	18
Pour point	°C			15	-21 to 0		15
Carbon residue (on 10% distillation residue)	% (m/m)	0.3>	0.50>	0.02	0.02-0.03	0.2	0.2>
Acid value	mg KOH/g	0.5>	0.80>	0.08	0.3>	-	-
Cetane index	-	51<	47<	58.3	53.0-59.0	51-57	47<
Sulphur content	% (m/m)	0.001>	0.0015>	0.001>	0.001>	0.00017–0.00018	0.005>
Sulphated ash content	% (m/m)	0.02>	0.020>	0.01>	0.01>	-	-
Water content	mg/kg	0.05>	0.05>	0.05>	0.05>	0.001>	0.001>
Copper strip corrosion (3 h at 50°C)	Rating	1a	3a>	1a	1a	1a	1a
Iodine value	-	120>	-	52	56-83	-	-
Linolenic acid methyl ester	% (m/m)	12>	-	0.5>	0.5>	-	-
Polyunsaturated ($\geq$ 4 doublebonds) methylesters	% (m/m)	1>	-	0.1>	0.1>	-	-
Methanol content	% (m/m)	0.2>	-	0.2>	0.2>	-	-
Monoglyceride content	% (m/m)	0.8>	-	0.4>	0.4>	-	-
Diglyceride content	% (m/m)	0.2>	-	0.2>	0.2>	-	-
Triglyceridecontent	% (m/m)	0.2>	-	0.1>	0.1>	-	-
Free glycerol	% (m/m)	0.02>	0.02>	0.01>	0.01>	-	-
Total glycerol	% (m/m)	0.25>	0.24>	0.01>	0.01>	-	-
Phosphorous content	mg/kg	10>	10>	-	-	-	-
Distillation temperature (90% recovered)	°C	-	360>	-	-	363.7–367.8	370

[a] PLPO/PD B5:5% processed liquid palm oil (PLPO)+95% petroleum diesel (PD).

[b] MS123:1993: Malaysian Standard for Diesel Fuel (Malaysia Biodiesel Standard, 2007).

[c] The cloud point of biodiesel is generally higher than that of petroleum based diesel and should be taken into consideration when blending.

In view of the positive results obtained from the evaluation of palm biodiesels and PLPO/PD blends, establishing individual standards for each of the palm biofuels that is acceptable to diesel engine manufacturers sounds to be essential. Having standards is important to control the quality and assure the engine manufacturers and end-users (Abdullah et al., 2009b). The European and American standards on biodiesel are good references for biodiesel based on palm oil methyl esters (Rashid and Anwar, 2008). Meanwhile, the Malaysian Standard for Diesel Fuel can be used as a close reference for the PLPO/PD blends in our effort in working towards Malaysian Biodiesel Standards. It should be timely for Malaysia to setup national biodiesel standard which complements with the European and American standards. Meanwhile, these standards should first be practical for the intended applications (Foon et al., 2005; Sani, 2009).

2.3.   Transesterification

Transesterification (alcoholysis) is the chemical reaction between triglycerides and alcohol in the presence of catalyst to produce mono-esters. Transesterification process consists of a sequence of three consecutive reversible reactions. That is, conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides (Meher et al., 2006). The glycerides are converted into glycerol and yielding one ester molecule in each step (Ma and Hanna, 1999). The overall transesterification reaction can be represented by Figure 2.2.
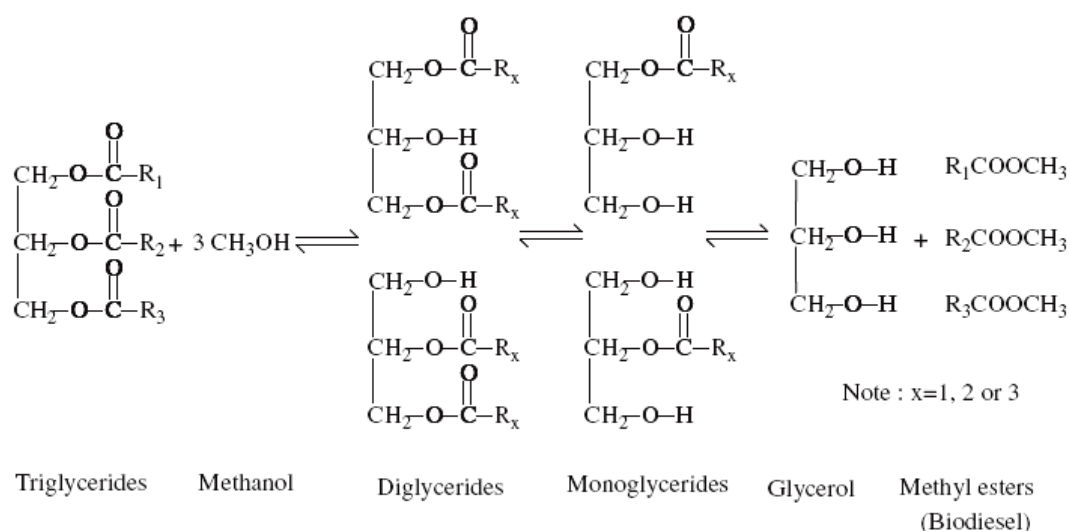
Figure 2.2 Transesterification of triglycerides with alcohol (Abdullah et al., 2007).

Stoichiometrically, three moles of alcohol are required for each mole of triglyceride, but in practice a higher molar ratio is employed in order to displace the equilibrium for getting greater ester production. Though esters are the desired products of the transesterification reactions, glycerin recovery is also important due to its numerous applications in different industrial processes such as CP glycerol, USP glycerol and dynamite glycerol. Glycerol is separated by gravitational settling or centrifuging. Commonly used short chain alcohols are: methanol, ethanol, propanol and butanol (Meher et al., 2006).

2.4. Transesterification Mechanism

The mechanism of acid catalyzed transesterification of vegetable oil (for a monoglyceride) is shown in Fig. 2.3. However, it can be extended to di- and tri-glycerides. The protonation of carbonyl group of the ester leads to the carbocation, after which a nucleophilic attack of the alcohol produces a tetrahedral intermediate.