OIL PALM ASH AS SOLID CATALYST FOR PALM OIL-BASED TRANSESTERIFICATION TO BIODIESEL: OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY

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by

CHIN LIP HAN

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LIST OF SYMBOLS

		Unit
Å	Angstrom	-
cSt	centistokes	mm^2s^{-1}

LIST OF ABBREVIATIONS

2FI	Two-Factor Interaction
AC	Activated Carbon
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
B5	5% Biodiesel
BET	Brunauer-Emmett-Teller
CCD	Central Composite Design
CPO	Cooking Palm Oil
CSAC	Coconut Shell Activated Carbon
DG	Diglyceride
EDX	Energy Dispersive X-ray
EPA	Environmental Protection Agency
EU	European Union
FFAs	Free Fatty Acids
FTIR	Fourier Transform Infrared
$H\_$	Hammett Function
HT	Hydrotalcites
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
MeOH	Methanol
MG	Monoglyceride
MSDS	Material Safety Data Sheet
OPA	Oil Pam Ash
PKO	Palm Kernel Oil
PORIM	Palm Oil Research Institute of Malaysia
Rpm	Revolutions per Minute
RSM	Response Surface Methodology
SBO	Soybean Oil
SEM	Scanning Electron Microscopy
TG	Triglyceride

| TGA | Thermogravimetric Analysis |
| WPO | Waste Palm Oil |

ABU KELAPA SAWIT SEBAGAI MANGKIN PEPEJAL UNTUK TRANSESTERIFIKASI BERASASKAN MINYAK SAWIT KEPADA BIODIESEL: PENGOPTIMUMAN MENGGUNAKAN KAEDAH RESPON PERMUKAAN

ABSTRAK

Biodiesel adalah satu bahan api alternatif untuk enjin diesel yang semakin mendapat perhatian dari segi kesusutan sumber bahan api fosil seluruh dunia dan juga keinginan mengurangkan kesan rumah hijau yang disebabkan oleh karbon dioksida. Dalam proses konvensional penghasilan biodiesel, trigliserida dalam minyak ditukar kepada biodiesel dengan menggunakan mangkin homogen. Walau bagaimanapun, penggantian mangkin homogen kepada cara heterogen telah menarik perhatian sebab proses ini dapat menyenangkan langkah perpisahan dan penulenan mangkin. Oleh itu, pengenalan mangkin pepejal heterogen dalam penghasilan biodiesel boleh mengurangkan harga dan juga menjadikan biodiesel persaingan kepada diesel dari segi aspek ekonomi. Oleh demikian, pengajian ini bertujuan untuk menyiasat kebolehlaksanaan abu kelapa sawit, bahan sisa dari kilang pemprosesan kelapa sawit yang mengandungi peratus berat kalium yang tinggi, sebagai mangkin pepejal untuk transesterifikasi berasaskan minyak sawit kepada biodiesel. Transesterifikasi minyak masak sawit (CPO), minyak sawit sisa (WPO) dan minyak sawit isirung (PKO) kepada biodiesel dikaji dalam proses berkelompok dan tindak balas dijalankan pada tekanan 10 bar. Mangkin OPA dicirikan dengan mikroskop electron imbasan, tenaga serakan X-ray, luas permukaan dan spektrometrik inframerah jelmaan Fourier. Kaedah respon permukaan digunakan untuk mengkaji kesan masa tindak balas, nisbah molar metanol kepada minyak, suhu tindak balas dan jumlah mangkin pada transesterifikasi. Kesan lima-aras-empat faktor dan salingan interaksi turut ditaksir. Kesan masa tindak balas didapati tidak memberi

kesan pada transesterifikasi CPO dan WPO tetapi memberi kesan yang bererti untuk transesterifikasi PKO. Keadaan optimum didapat dari transesterifikasi adalah 0.5-1.19 jam, 6.26-18, 60-175°C, 1.67-8.22 berat%, masing-masing untuk masa tindak balas, nisbah molar metanol kepada minyak, suhu tindak balas dan jumlah mangkin untuk transesterifikasi CPO, WPO dan PKO. Penghasilan biodiesel optimum adalah 89.90±10%, 60.07±10%, 67.53±10% bagi CPO, WPO, PKO masing-masing. Tambahan pula, mangkin pepejal OPA terbukti berkesan dalam pembuatan biodiesel berkualiti sesuai dengan speksifikasi ASTM. Keputusan ini menunjukkan bahawa OPA dapat digunakan sebagai mangkin bes pepejal dalam penghasilan biodiesel.

OIL PALM ASH AS SOLID CATALYST FOR PALM OIL-BASED TRANSESTERIFICATION TO BIODIESEL: OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY

ABSTRACT

Biodiesel is an alternative fuel for diesel engines that is gaining attention in terms of the depleting fossil fuel resources of the world and the mitigating of greenhouse effects due to carbon dioxide. In a conventional process for biodiesel production, triglycerides in oils are converted to biodiesel by using homogeneous catalyst. However, replacement of the homogeneous catalysis with a heterogeneous route has received much attention since the process can be simplified by facilitating the catalyst separation and purification steps. Hence, introduction of a solid heterogeneous catalyst in biodiesel production could reduce its price, also becoming competitive with diesel from a financial point of view. Therefore, this study aims to investigate the feasibility of oil palm ash (OPA), a waste material from oil palm mills which contains high weight percent of potassium, as solid catalyst for palm oil-based transesterification to biodiesel. Transesterification of cooking palm oil (CPO), waste palm oil (WPO) and palm kernel oil (PKO) to biodiesel was studied in a batch process and the reaction was carried out at 10 bars. OPA catalyst was characterized by scanning electron microscopy, energy dispersive X-ray, surface area and fourier transform infrared spectrometry. Response surface methodology was used to study the effect of reaction time, methanol to oil molar ratio, reaction temperature and amount of catalyst on the transesterification and the effects of five-level-four factors as well as their reciprocal interactions were assessed. The effect of reaction time was found to be not significant for the transesterification of CPO and WPO, but significant for the transesterification of PKO. The optimum conditions obtained for

transesterification were 0.5-1.19 h, 6.26-18, 60-175°C, 1.67-8.22 wt%, respectively for reaction time, methanol to oil molar ratio, temperature and amount of catalyst for transesterification of CPO, WPO and PKO. The optimum biodiesel yields of 89.90±10%, 60.07±10%, 67.53±10% were found for CPO, WPO, PKO, respectively. Moreover, the OPA solid catalyst proves to be effective in producing the appropriate quality of biodiesel as per the ASTM specification. The results indicate that OPA can be used in biodiesel production as a low cost solid base catalyst.

CHAPTER ONE

INTRODUCTION

The depletion of fossil fuels (Bardi, 2005), coupled with the increasing awareness of environmental protection, has led to concerted and escalating efforts in search for a renewable and environmentally friendly alternative energy source. As we all know, many initiatives have been taken today to address issues and problems pertaining to global warming and the greenhouse gas effects (Rotmans and Swart, 1990; McNeff *et al.*, 2008). The main agenda of deliberation was on the need to reduce the amount of atmospheric CO_2, a cause of global warming, emitted from the automobiles (Singh *et al.*, 2008). In view of the fact that much of this greenhouse gas effect is caused by the combustion of fossil fuel, many countries particularly the more advance ones are making a switch to exploit and utilize other alternative source of energy supply that are renewable and greatly contribute toward the improvement of the environment. Although economically, the utilization of these renewable energy such as biofuel may not appear to be as attractive as the conventional energy, that should not prevent its widespread use in the future as the concern towards depletion of the fossil fuel and drastically rising of fuel price and environmental factors becomes more and more pressing (Figure 1.1) (NRC, 2008).

In the global scene, especially on the European front, the use of methyl esters as diesel fuel has achieved widespread acceptance. In fact, biodiesel made from rapeseed oil is already produced on a significant scale in Italy, France, Germany, Austria and Czechoslovakia (Chin Peter, 2004). Between 2000 and 2005, worldwide production and consumption of biodiesel grew an average of 32%, and

forecast is for stronger growth annually of 115% in capacity and 101% for demand to 2008 and beyond (LaFond, 2006).
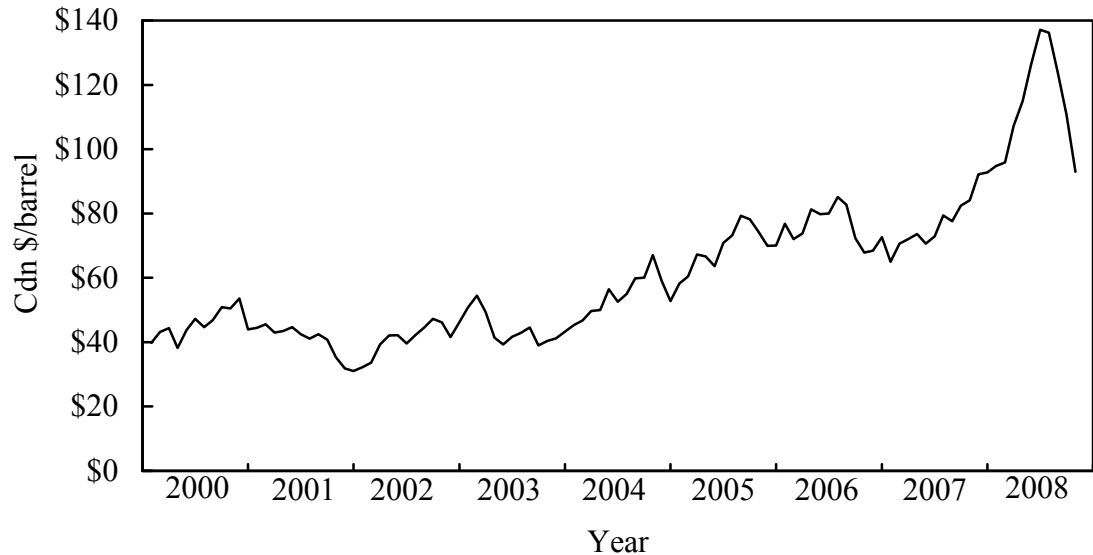
Figure 1.1   WTI NYMEX Chicago crude oil prices per barrel (2000-2008) (NRC, 2008).

In any case, biodiesel offers the environmental advantage of reducing greenhouse gas emissions compared with the use of fossil fuels, especially in resort areas, marine parks and highly polluting cities in terms of air quality. New legislation and government incentives strongly support the use of biofuel particularly biodiesels that have been introduced. In Germany, the last ten years production and consumption of biodiesel have increased several-fold, with the introduction of the statutory tax exemption until the end of 2009 (UFOP, 2005). Besides, in 2004, an estimated 476 million liters were sold at German filling stations, 32% more than in the previous year. This is enough to satisfy the annual requirement of approximately 300,000 cars (UFOP, 2005). Biodiesel is available at 1900 filling stations across Germany, which means that it is in some regions no longer an inconvenience to use biodiesel as a pure fuel. However, many drivers do not know that they are using

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biodiesel. With the petroleum tax-exempt and non-labeled additions of up to 5 % biodiesel (B5), petroleum companies such as Shell, ARAL/BP, OMV, Total and Orlen "dilute" their diesel and this is found in almost every diesel pump in Germany (UFOP, 2005).

On the other hand, the United States has increased its production from 2 million gallons in 2000 to an estimated 250 million gallons in 2006 (NBB, 2008). While 250 million gallons is smaller than the European Union production (Germany alone estimates its 2006 production at about 690 million gallons), it represent significant growth (Carriquiry, 2007). In US, biodiesel is registered as a fuel and fuel additive with the Environmental Protection Agency (EPA) and meets clean diesel standards established by the California Air Resources Board. The Department of Energy and the US Department of Transportation have designated neat biodiesel as an alternative fuel. In the Far East, Japan, Korea, China and Thailand have also expressed interest in biodiesel in the last few years. All of these developments underscore the environmental benefits in terms of lesser green house gas emission, reduced dependence on the fossil fuel imports and positive impact on agriculture.

Technically palm biodiesel project has been proven viable but it is not viable to use palm biodiesel in Malaysia, as our petroleum is still cheap. Now diesel price is less than RM2 per liter. It is very feasible for the oversea market where the petroleum diesel is very expensive. For example, In European Union (EU), the petroleum diesel is sold at about RM5 per liter. This makes palm biodiesel very competitive (MPOB, 2005).

Factors driving the growth in demand for biodiesel and others biofuel include increasing efforts to find alternatives to fossil fuels and to combat global warming. Intelligent and sustainable solutions are being sought to meet rising standards of living around the world lead to increased numbers of cars being bought. Biofuel such as biodiesel provide a key alternative to petroleum-based fuels for reducing carbon dioxide emissions in automotive applications. Developments in biofuel production technology have led to processes that are proving to be economically viable (Lurgi, 2005).

Biodiesel is normally manufactured from edible plant oils. The carbon dioxide (CO_2) emissions resulting from its combustion in vehicle engines are reabsorbed through photosynthesis when the next crops of plants are grown. There are therefore few net emissions of CO_2 or other greenhouse gases from the use of biodiesel in vehicle engines. The only net emissions are those resulting from its harvesting and manufacture which uses some petroleum fuels and electricity. Using biodiesel leads to lower levels of greenhouse gases being released into the atmosphere than conventional diesel. Biodiesel can be made from all normal plant oils. Rapeseed oil is most common in Europe, soybean oil in North America and palm oil in Southeast Asia (Demirbas, 2007b). As an alternative fuel, biodiesel can provide power similar to conventional petro diesel and this can be used safely in diesel engines without any modification of the currently used diesel engines, like Mercedez, Daimler Chrysler and VW Group (Sinha, 2005; NBP, 2006).

However, one of the important criteria for any vegetable oil to be used as biofuel is availability at competitive price. Palm oil meets this criterion perfectly. It is already common knowledge within the world of oils and fats that the development

of the oil palm industry in Malaysia has been remarkable. Malaysia takes pride of the fact that within a relatively short period of time, have become the world's largest producer and exported of palm oil products in the international oils and fats market (MPOB, 2006a). Also, 33 million tones of palm oil produced in year 2005 in the world and was also the largest production of 17 oils and fats (Table 1.1) in the world (MPOB, 2006b).

Table 1.1   World production of 17 oils and fats: 2000-2005 (TONNES) (MPOB, 2006b).

No	Oils/Fats	2000	2001	2002	2003	2004	2005
1	Palm Oil	21,867	23,984	25,392	28,111	30,909	33,326
2	Palm Kernel Oil	2,698	2,947	3,042	3,339	3,568	3,906
3	Soybean Oil	25,563	27,828	29,861	31,288	30,713	33,287
4	Cottonseed Oil	3,850	4,052	4,234	3,995	4,417	5,033
5	Groundnut Oil	4,539	5,141	5,181	4,511	4,746	4,509
6	Sunflower Oil	9,745	8,200	7,624	8,962	9,402	9,681
7	Rapeseed Oil	14,502	13,730	13,307	12,660	14,904	16,027
8	Corn Oil	1,966	1,962	2,016	2,015	2,015	2,099
9	Coconut Oil	3,261	3,499	3,145	3,286	3,037	3,143
10	Olive Oil	2,540	2,761	2,718	2,903	3,055	2,903
11	Castor Oil	497	515	438	430	492	539
12	Sesame Oil	705	747	822	782	828	823
13	Linseed Oil	705	648	585	597	623	607
14	Butter	5,967	6,010	6,188	6,274	6,351	6,521
15	Tallow	8,202	7,693	8,073	8,029	8,239	8,196
16	Fish Oil	1,411	1,131	934	989	1,077	1,054
17	Lard	6,739	6,780	7,006	7,210	7,363	7,545
	Total	114,757	117,628	120,566	125,381	131,739	139,199

The advantage which palm oil holds over other oils and fats lies in its productivity, yield and efficiency factors. Oil palm is the most productive oil-bearing plant species known. The yield of palm oil per unit area is 5 to 10 times higher than rapeseed and soybean oil, respectively (De Lima Montenegro Duarte *et al.*, 2007). Considering the comparative yields of various oil-bearing crops, oil palm is clearly

the most efficiently produced oil in the world today. When the world is looking at vegetables oil as renewable fuel, palm oil will undoubtedly stand out among other vegetables oils. This yield factor alone is adequate for the world to decide which vegetable oil should be produced to meet the expanding requirement for "Greener and Cleaner Energy" for its growing population (MPOB, 2005).

Anyway, one of the obstacles for the future growth of palm biodiesel is understandably the high cost of vegetable oil and cheap petroleum price in our country. This may not be true anymore due to the current escalation of petroleum price (Figure 1.1). Furthermore, with the anticipated depletion of petroleum reserves, palm oil fuel will become more economically attractive. We feel that it is timely now to introduce the palm biodiesel in our country for a clean and healthy environment (MPOB, 2005).

Currently, palm biodiesel is being used in Europe. One company in Germany is using palm biodiesel as fuel in commercial trains and positive feedback has been received. For example, one of the most exhaustive field trials on the use of palm biodiesel as diesel fuel was conducted by Mercedes-Benz in collaboration with PORIM and Cycle & Carriage. A fleet of 30 Mercedes-Benz buses covered mileages of up to 300,000 to 350,000 km each showed that buses, which have been actually designed for operation with diesel fuel, could as well be operated with palm biodiesel or a blend of palm biodiesel and petroleum diesel. This applies both to the engine performance and long-term operation (MPOB, 2005).

1.1 Problem Statement

The need for energy is increasing continuously, because of increases in industrialization and population. The basic sources of this energy are petroleum, natural gas, coal, hydro, and nuclear (Varese and Varese, 1996). Petroleum diesel continues to be a major fuel worldwide (Kulkarni and Dalai, 2006). The global consumption is 934 million tones of diesel fuel per year (Holbein *et al.*, 2004). Malaysia consumes 8.67 million tones of diesel and half of this is utilized in the transportation sector alone (Toscano, 2006). The major disadvantage of using petroleum-based fuels is that, day by day, the fossil fuel reserves are decreasing. Another disadvantage is atmospheric pollution created by the use of petroleum diesel. Petroleum diesel combustion is a major source of greenhouse gas. Apart from these emissions, petroleum diesel is also major source of other air contaminants including NO_x, SO_x, CO, particulate matter, and volatile organic compounds (VOCs) (Klass, 1998). The decreasing fossil fuel reserves, and the atmospheric pollution created by petroleum-based fuels, have necessitated the need for an alternative source of energy (Kulkarni and Dalai, 2006).

The use of vegetable oils as alternative fuels has been around for 100 years when the inventor of the diesel engine Rudolph Diesel first tested peanut oil, in his compression ignition engine (Shay, 1993). He stated, "The use of vegetable oils for engine fuels may seem insignificant today. But such oils may in course of time be as important as petroleum and the coal tar products of the present time". However, due to cheap petroleum products, such non-conventional fuels never took off (Meher *et al.*, 2006c).

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Vegetable oils occupy a prominent position in the development of alternative fuels although, there have been many problems associated with using it directly in diesel engine (especially in direct injection engine). These include (Meher *et al.*, 2006c);

- Coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or even prevented as a result of plugged orifices,

- Carbon deposits,

- Oil ring sticking,

- Thickening or gelling of the lubricating oil as a result of contamination by vegetable oils, and

- Lubricating problems.

Other disadvantages to the use of vegetable oils and especially animal fats are the high viscosity (about 11-17 times higher than diesel fuel) (Table 1.2), lower volatilities that causes the formation of deposits in engines due to incomplete combustion and incorrect vaporization characteristics (Meher *et al.*, 2006c). These problems are associated with large triglyceride molecule and its higher molecular mass and avoided by modifying the engine less or more according to the conditions of use and the oil involved. The modified engines built by Elsbett in Germany and Malaysia and Diesel Morten und Geraetebau GmbH (DMS) in Germany and in USA show a good performance when fuelled with vegetable oils of different composition and grades (Srivastava and Prasad, 2000).

Table 1.2   Properties of vegetable oils compare to diesel (SEA, 1996; Goering *et al.*, 1982).

Vegetable oil	Kinematic viscosity at 38°C (mm^2s^{-1})	Cetane no. (°C)	Heating value ($MJkg^{-1}$)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kgL^{-1})
Corn	34.9	37.6	39.5	-1.1	-40.0	277	0.9095
Cottonseed	33.5	41.8	39.5	1.7	-15.0	234	0.9148
Crambe	53.6	44.6	40.5	10.0	-12.2	274	0.9048
Linseed	27.2	34.6	39.3	1.7	-15.0	241	0.9236
Peanut	39.6	41.8	39.8	12.8	-6.7	271	0.9026
Rapeseed	37.0	37.6	39.7	-3.9	-31.7	246	0.9115
Safflower	31.3	41.3	39.5	18.3	-6.7	260	0.9133
Sesame	35.5	40.2	39.3	-3.9	-12.2	254	0.9138
Sunflower	33.9	37.1	39.6	7.2	-15.0	274	0.9161
Palm	39.6	42.0	-	31.0	-	267	0.9180
Babassu	30.0	38.0	-	20.0	-	150	0.9460
Diesel	3.06	50	43.8	-	-16	76	0.855

Currently, biodiesel are usually produced by transesterification of triglyceride with mono-alkyl alcohols, such as methanol. This reaction is commonly carried out in the presence of homogeneous base or acid catalysts. The catalytic activity of a base is higher than that of an acid and acid catalysts are more corrosive, the base catalysis is preferred to acid catalyzed routes, and is thus most often used commercially (Xie *et al.*, 2006b). Nevertheless, in the conventional homogeneous manner, removal of the base catalysts after reaction is a major problem, since aqueous quenching resulting in the formation of stable emulsion and saponification, making separation of the methyl esters difficult, and a large amount of wastewater was produced to separate and clean the catalyst and the products. For that reason, conventional homogeneous catalysts are expected to be replaced in the near future by environmentally friendly heterogeneous catalysts mainly because of environmental constraints and simplifications in the existing processes (Xie *et al.*, 2006b).

This study aims to investigate the feasibility of oil palm ash (OPA), a waste from palm oil mills as a solid catalyst for transesterification of cooking palm oil (CPO), waste palm oil (WPO), and palm kernel oil (PKO) to produce biodiesel.

1.2 Research Objectives

The purpose of this research was to examine the performance of the oil palm ash (OPA) as solid catalyst for the production of biodiesel from cooking palm oil (CPO), waste palm oil (WPO) and palm kernel oil (PKO). The objectives were focused to:

i) Study the feasibility of oil palm ash as catalyst for transesterification of CPO, WPO and PKO to biodiesel.

ii) Characterize the OPA in terms of surface morphology, energy dispersive X-ray, surface area, pore volume, pore size and fourier transform infrared spectrometry.

iii) Optimize the reaction parameters such as reaction temperature, amount of catalyst, reaction time and methanol to oil molar ratio in the transesterification of CPO, WPO and PKO using response surface methodology (RSM).

1.3 Organization of the Thesis

There are five chapters in this thesis. An overview on biodiesel usage and viability of biodiesel production from palm oil are outlined in Chapter One.

Chapter Two presents a review of the literature. It is divided into seven major sections. The first section gives a review about the properties and chemical compositions of vegetable oils as well as fuel properties of biodiesel. This is

followed by explanation on different methods for biodiesel production in section two. Detailed information on the transesterification reaction is also presented in the section. Comparison between homogeneous and heterogeneous catalysts is provided in section three. Then, review on different raw or processed vegetable oils for biodiesel production is given in section four. Section five focuses on the technical aspect of biodiesel production by transesterification using heterogeneous catalyst. Section six focuses on the statistical approach used for response surface methodology. Lastly, a short summary on the literature review is presented in section seven.

Chapter Three covers the methodology for the experimental work done in this research. This chapter is divided into four sections. The first section presents the materials such as vegetable oils and chemicals used in the experiments. The second section gives a general description experimental set-up while the third section provides brief explanation on the experimental procedure in this study. On the other hand, the fourth section is a general description of the characterization of the biodiesel product.

Chapter Four presents all the acquired results and discusses on the findings. It is grouped into five main sections. Section one presents the results and discussion on preliminary runs on a few prepared solid catalysts and modification done on the chosen solid catalyst. Section two characterization of solid catalyst while section three presents the statistical analysis done based on response surface methodology in order to investigate the significance of several main operating conditions to the biodiesel production and interaction between the factors as well as the final regression model obtained from ANOVA. In section four, reusability of solid catalyst

is presented while section five presents the characterizations of palm oil and biodiesel product.

Finally, Chapter Five gives the conclusion and some recommendations for future research. The conclusions are written according to the finding found in Chapter Four. Based on the conclusion, recommendations for future work are suggested.

CHAPTER TWO

LITERATURE SURVEY

This chapter provides the literature review of the properties and chemical compositions of vegetable oils in addition to fuel properties of biodiesel in section one. Section two provides an outline of different methods for biodiesel production. After that, comparison between homogeneous and heterogeneous catalysts is presented, followed by review on different raw or processed vegetable oils for biodiesel production. The technical aspect of biodiesel production by transesterification using heterogeneous catalyst is presented in section five. Literature review on statistical tools used to analyzed data is presented in section six and lastly, a short summary on this chapter is provided in section seven.

2.1   Properties of Vegetable Oils and Biodiesel

2.1.1   Properties of Vegetable Oils as Fuel

The fuel properties of vegetable oils as listed in Table 1.2 indicate that the kinematics viscosity of vegetable oils varies in the range of 30-40 cSt at 38°C. The high viscosity of these oils is due to their large molecular mass in the range of 600-900, which is about 20 times higher than that of diesel fuel. Besides, the flash point of vegetable oils is very high (above 200°C). The volumetric heating values are in the range of 39-40 MJkg^{-1}, as compared to diesel fuels (about 45MJkg^{-1}). This slight difference is due to the presences of chemically bound oxygen in vegetable oils which lower their heating values by about 10% (Barnwal and Sharma, 2005).

2.1.2 Chemical Compositions of Vegetable Oils

Vegetable oils, also known as triglycerides, have the chemical structure given in Figure 2.1 comprise of 98% triglycerides and small amounts of mono- and diglycerides. Triglycerides are esters of three molecules of fatty acids and one of glycerol and contain substantial amounts of oxygen in their structure. The fatty acids vary in their carbon chain length and in the number of double bonds (Barnwal and Sharma, 2005).

$$
\begin{array}{l}
\underset{\substack{| \\ H}}{\overset{\substack{H \\ |}}{H-C}}-O-\overset{\substack{O \\ \|}}{C}-(CH_2)_{\overline{ses}}-CH_a \\[4pt]
H-C-O-\overset{\substack{O \\ \|}}{C}-(CH_2)_{\overline{7}}-CH{=}CH\ \{CH_2\}_7CH_a \\[4pt]
H-C-O-\overset{\substack{O \\ \|}}{C}-(CH_2)_{\overline{7}}-CH{=}CHCH_2CH{=}CH(CH_2)_4CH_a
\end{array}
$$
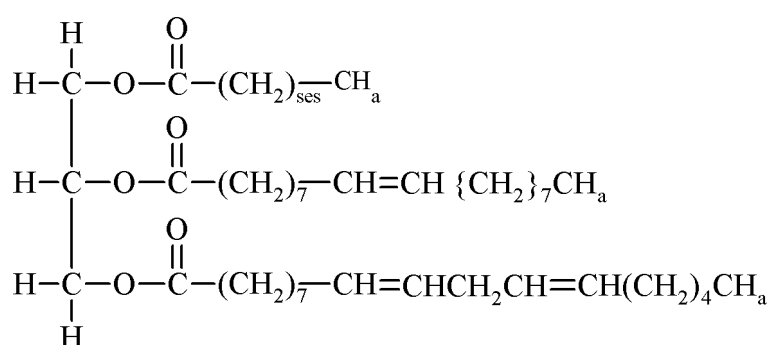
Figure 2.1   Structure of a typical triglyceride molecule (Barnwal and Sharma, 2005).

Besides, different types of oils have different types of fatty acids. The empirical formula and structure of various fatty acids present in vegetable oils are given in Table 2.1.

In addition, the plant oils usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Because of these, the oil cannot be used as fuel directly. To overcome these problems the oil requires slight chemical modification mainly transesterification, pyrolysis or microemulsification. Among these, the transesterification is the key and foremost important step to produce cleaner and environmentally safe fuel from vegetable oils (Meher *et al.*, 2006c).

Table 2.1   Chemical structure of common fatty acids (Marckley, 1960).

Name of fatty acid	Chemical name of fatty acids	Structure ($xx{:}y$)	Formula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$
Oleic	*cis*-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	*cis*-9,*cis*-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	*cis*-9-,*cis*-12,*cis*-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Erucle	*cis*-13-Docosenoic	22:1	$C_{32}H_{42}O_2$

xx indicates number of carbons, and *y* number of double bonds in the fatty acid chain.

Biodiesel is the monoalkyl esters of long chain fatty acids derived from renewable feed stocks, such as vegetable oil or animal fats, for use in compression ignition engine. Biodiesel, which is considered as a possible substitute of conventional diesel fuel is usually, composed of fatty acid methyl esters that can be prepared from triglycerides in vegetable oil by transesterification with methanol. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics (Meher *et al.*, 2006c) (Table 2.2). Moreover, biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content and biodegradability (Ma and Hanna, 1999).

2.1.3   Fuel Properties of Biodiesel

The properties of biodiesel and diesel fuels, as given in Table 2.2, show many similarities, and therefore, biodiesel is rated as a strong candidate as an alternative to diesel. This is due to the fact that the conversions of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one-third, reduces the viscosity by about one-eight, and increase the volatility marginally. Biodiesel contains 10-11% oxygen (w/w), thereby enhancing

the combustion process in an engine (Barnwal and Sharma, 2005). It has also been reported that the use of tertiary fatty amines and amides can be effective in enhancing the ignition quality of the biodiesel without having any negative effect on its cold flow properties (Barnwal and Sharma, 2005). However, starting problems persist in cold conditions. Furthermore, biodiesel has low volumetric heating values (about 12%), a high cetane number and a high flash point. The cloud points and flash points of biodiesel are 15-25°C higher than those of diesel.

Table 2.2   Properties of biodiesel from different oils (Feuge and Gros, 1949; Rao and Gopalakrishnan, 1991; Ali *et al.*, 1995; Dunn and Bagby, 1995; Chang *et al.*, 1996).

Vegetable oil methyl esters (biodiesel)	Kinematic viscosity at 38°C (mm^{2}s^{-1})	Cetane no. (^{o}C)	Lower heating value (MJkg^{-1})	Cloud point (^{o}C)	Pour point (^{o}C)	Flash point (^{o}C)	Density (kgL^{-1})
Peanut	4.9	54	33.6	5	-	176	0.833
Soya bean	4.5	45	33.5	1	-7	178	0.885
Babassu	3.6	63	31.8	4	-	127	0.875
Palm	5.7	62	33.5	13	-	164	0.880
Sunflower	4.6	49	33.5	1	-	183	0.860
Tallow	-	-	-	12	9	96	-
Diesel	3.06	50	43.8	-	-16	76	0.855
20%				-	-16	128	0.859
biodiesel blend	3.2	51	43.2				

If the biodiesel valorized efficiently at energy purpose, so would be benefit for the environmental and the local population, job creation, provision of modern energy carriers to rural communities, avoid urban migration and reduction of CO_2 and sulfur levels in the atmosphere (Demirbas, 2007a).

2.2 Transesterification Reaction for Biodiesel Production

Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. The overall transesterification reaction (Otera, 1993) is given by three consecutive and reversible equations as below:

$$\text{Triglyceride} + \text{ROH} \overset{\text{catalyst}}{\Longleftrightarrow} \text{Diglyceride} + \text{R}'\text{COOR}$$

$$\text{Diglyceride} + \text{ROH} \overset{\text{catalyst}}{\Longleftrightarrow} \text{Monoglyceride} + \text{R}''\text{COOR} \qquad (1.1)$$

$$\text{Monoglyceride} + \text{ROH} \overset{\text{catalyst}}{\Longleftrightarrow} \text{Glycerol} + \text{R}''\text{COOR}$$
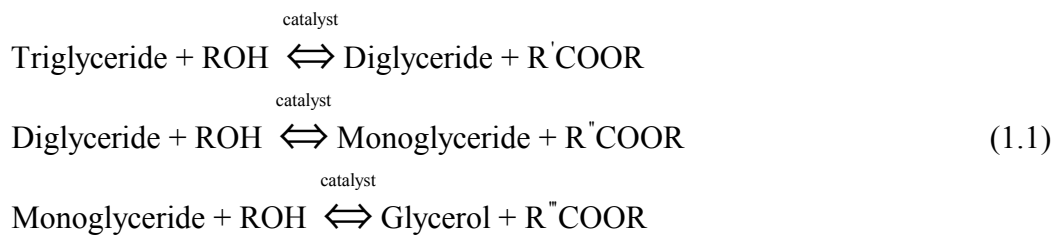
The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and of monoglycerides to glycerol, yielding one methyl ester molecule per mole of glyceride at each step (Freedman *et al.*, 1986; Noureddini and Zhu, 1997). The overall chemical reaction of the transesterification process is shown in Figure 2.2 where R', R'' and R''' are long-chain hydrocarbons which may be the same or different with R = $-CH_3/C_2H_5$.
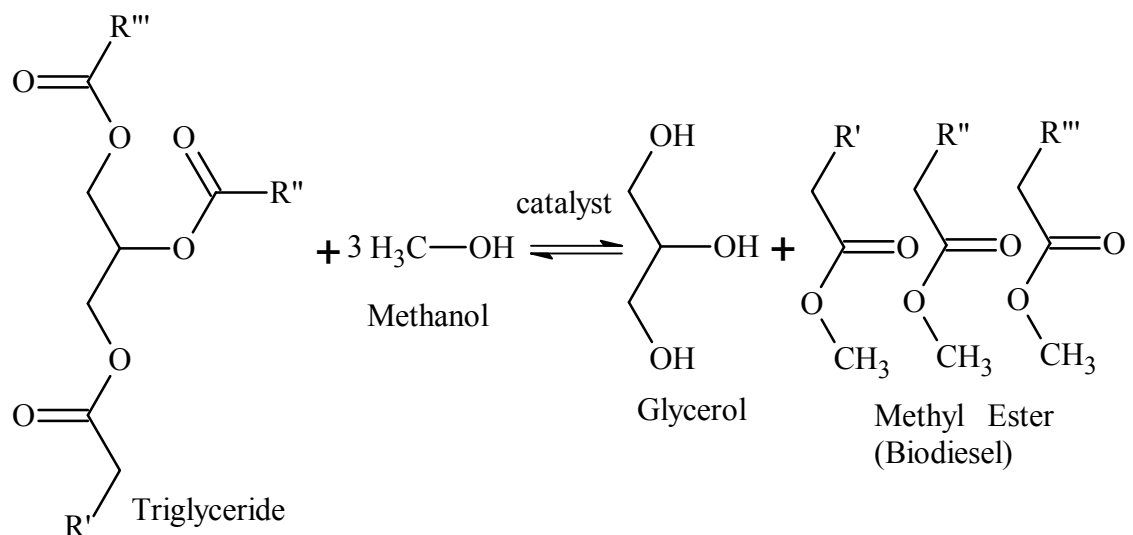
Figure 2.2   Transesterification reaction of triglyceride (Ma and Hanna, 1999).

As seen above, the transesterification is an equilibrium reaction in which excess alcohol is required to drive the reaction close to completion. Fortunately, the equilibrium constant favors the formation of methyl esters such that only a 5:1 molar ratio of methanol: triglycerides is sufficient for 95-98% yield of ester (Barnwal and Sharma, 2005). It might be anticipated that in such a system, glycerol would play a major role in achieving conversions close to 100% (Barnwal and Sharma, 2005).

A catalyst is usually used to improve the reaction rate and yield (Ma and Hanna, 1999). Several catalysts were tried for the purpose of transesterification by several researchers, e.g. magnesium, calcium oxides and carbonates of basic and acidic macro-reticular organic resin, alkaline alumina, phase transfer catalysts, sulfuric acids, p-toluene sulfonic acid, and dehydrating agents as co-catalysts (Nye and Southwell, 1983). The catalysts reported to be effective at room temperature were alkoxides and hydroxides (Agrawal, 1998). The purpose of the transesterification process is to lower the viscosity of the oil. The viscosity values of vegetable oils are between 27.2 and 53.6 mm^2s^{-1} whereas those of vegetable oil methyl esters are between 3.59 and 4.63 mm^2s^{-1} (Demirbas, 2005; Bala, 2005). Ideally, transesterification is potentially a less expensive way of transforming the large, branched molecular structure of the bio-oils into smaller, straight chain molecules of the type required in regular diesel combustion engines (Demirbas, 2007a).

Alcohols are primary and secondary monohydric aliphatic alcohols having 1-8 carbon atoms. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are use most frequently, especially methanol because of its low cost and its

physical and chemical advantages (polar and shortest chain alcohol) (Ma and Hanna, 1999). It can quickly react with triglycerides and NaOH is easily dissolved in it. To complete a transesterification stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is needed. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield. The reaction can be catalyzed by alkalis, acids, or enzymes. The alkalis include NaOH, KOH, carbonated and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Sulfuric acid, sulfonic acids and hydrochloric acid are usually used as acid catalysts. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and it most often used commercially (Ma and Hanna, 1999). If more free fatty acids are in the triglycerides, acid catalyzed transesterification can be used (Zhang and Jiang, 2008; Naik *et al.*, 2008; Jacobson *et al.*, 2008; Lou *et al.*, 2008).

During transesterification, two distinct phases are present as the solubility of the oil in methanol is low and the reaction mixture needs vigorous stirring. Optimum reaction conditions for the maximum yield of methyl esters have been reported to be 0.8% (based on weight of oil) potassium hydroxide catalyst and 100% excess methanol at room temperature for 2.5 h (Barnwal and Sharma, 2005). Glycerol phase separation does not occur when <67% of the theoretical amount of methanol is used. The excess methanol, however, is removed by distillation. Traces of methanol, KOH, free fatty acids (FFAs), chlorophyll, etc. go into the glycerin phase, which can be processed in two stages. Glycerin of 90-95% purity is obtained in the first stage and of 98% purity in the second stage. The basic process schematic of biodiesel production is given in Figure 2.3.
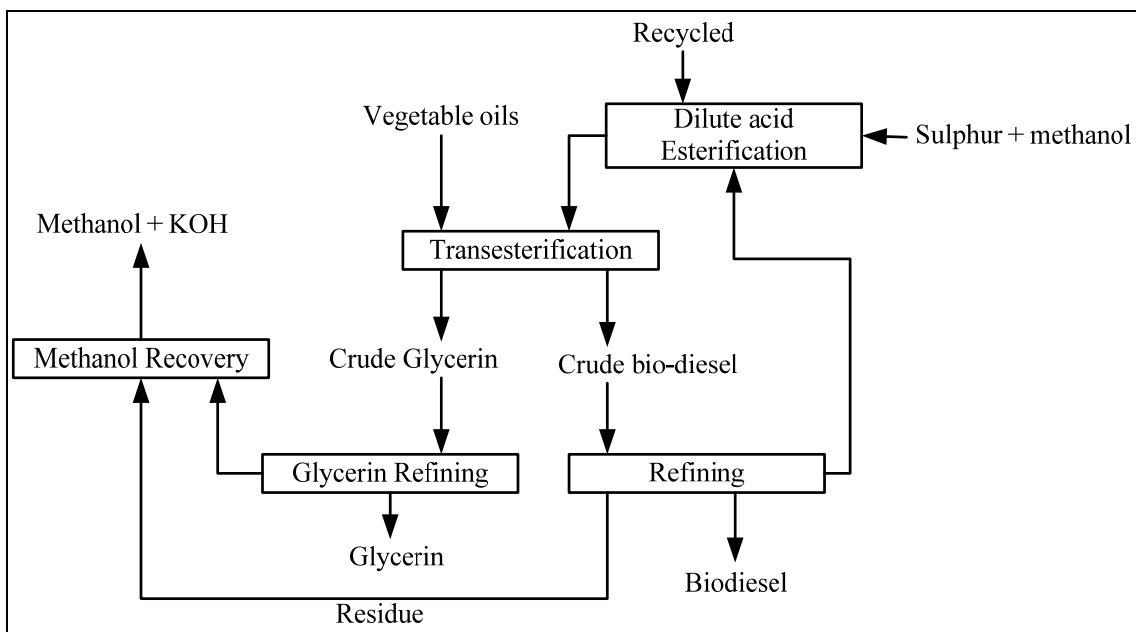
Figure 2.3   Transesterification process for biodiesel production (Barnwal and Sharma, 2005).

The process requires mixing of vegetable oil with a mixture prepared by dissolving KOH catalyst in methanol and heating at 70°C with stirring for 1 h. The mixture is allowed to settle under gravity. The glycerin, being heavier, settles down in the bottom layer and the upper layer constitutes the biodiesel (esters). The glycering is separated and the esters are washed with water for catalyst recovery. The biodiesel layer is finally dried using silica gel and it is now ready for blending with diesel in various proportions for engine operation. The blend, for convenience, is referred to as B_{xx}, where XX indicates the amount of biodiesel in percentage in the blend (i.e. B-20 blend is 20% biodiesel and 80% diesel) (Barnwal and Sharma, 2005).

The physical properties of the primary chemical products of transesterification are summarized in Table 2.3 and Table 2.4. The boiling points and melting points of the fatty acids, methyl esters, mono- (MG), di- (DG) and triglycerides (TG) increase as a the number of carbon atoms in the carbon chain

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increase, but decrease with increase in the number of double bonds. The melting points increase in the order of TG, DG and MG because of the polarity of the molecules and hydrogen bonding.

Table 2.3   Physical properties of chemicals related to transesterification (Zhang, 1994).

Name	Specific gravity, gmL^{-1} (°C)	Melting point (°C)	Boiling point (°C)	Solubility (>10%)
Methyl Myristate	0.875 (75)	18.8	-	-
Methyl Palmitate	0.875 (75)	30.6	196.0	Acid, benzene, EtOH, Et_2O
Methyl Stearate	0.850	38.0	215.0	Et_2O, chloroform
Methyl Oleate	0.875	-19.8	190.0	EtOH, Et_2O
Methanol	0.792	-97.0	64.7	H_2O, ether, EtOH
Ethanol	0.789	-112.0	78.4	H_2O (∞), ether (∞)
Glycerol	1.260	17.9	290.0	H_2O, EtOH

Table 2.4   Melting points of fatty acids, methyl esters and MG, DG, and TG (Formo, 1979).

Fatty acid		Melting point (°C)				
Name	Carbons	Acid	Methyl	1-MG	1.3-DG	TG
Myristic	14	54.4	18.8	70.5	66.8	57.0
Palmitic	16	62.9	30.6	77.0	76.3	63.5
Stearic	18	69.6	39.1	81.5	79.4	73.1
Oleic	18:1	16.3	-19.8	35.2	21.5	5.5
Linoleic	18:2	-6.5	-35.0	12.3	-2.6	-13.1

After transesterification of triglycerides, the products are a mixture of esters, glycerol, alcohol, catalyst and tri-, di- and monoglycerides. Obtaining pure esters was not easy, since there were impurities in the esters, such as di- and monoglycerides (Ma, 1998). The monoglycerides caused turbidity (crystals) in the mixture of esters. This problem was very obvious, especially for transesterification of animal fasts such as beef tallow (Ma *et al.*, 1999).

Currently, transesterification is the process used to make biodiesel fuel as it is defined in Europe and in the USA. It also is used to make methyl esters for detergents and cosmetics (Farris, 1979). Besides, there are numerous

transesterification citations in the scientific and patent literature (Bradshaw and Meuly, 1944; Allen *et al.*, 1945; Trent, 1945; Tanaka *et al.*, 1981; Freedman *et al.*, 1984; Freedman *et al.*, 1986; Schwab *et al.*, 1987; Wimmer, 1992; Shu *et al.*, 2007; Yuan *et al.*, 2008; Yan *et al.*, 2008; Trakarnpruk and Porntangjitlikit, 2008; Jeong *et al.*, 2009)

2.3 Comparison between Homogeneous and Heterogeneous Transesterification Process

For a homogeneous alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous (Schuchardt *et al.*, 1998) because water makes the reaction partially change to saponification, which produces soap . The soap lowers the yield of esters and renders the separation of ester and glycerol and the water washing is difficult. Low free fatty acid content in triglycerides is required for homogeneous alkali-catalyzed transesterification (Sinha *et al.*, 2008).

Commercially, methyl esters of fatty acids can be manufactured either by direct esterification of fatty acids or by transesterification of triglycerides. The esterification is carried out batch wise at $200 - 250^{o}C$ under pressure. In order to obtain a high yield, the water of reaction has to be removed continuously. Esterification can also be done continuously in a counter-current reaction column using superheated methanol (Kreutzer, 1984).

The predominant process for the manufacture of methyl esters is transesterification of triglycerides with methanol. The methanolysis of naturally occurring oils and fats with methanol take place quite readily at a temperature of about $50^{o}C - 70^{o}C$. Besides, methanolysis also take place at atmospheric pressure

with an excess of methanol and in the presence of an alkaline catalyst such as sodium hydroxide (Farris, 1979; Sonntage, 1982; Kreutzer, 1984; Freedman *et al.*, 1984; Sharma and Singh, 2008; Rashid *et al.*, 2008; Dias *et al.*, 2008). These mild reaction conditions, however, require an oil neutralized by means of alkali refining, steam distillation or pre-esterification of free fatty acids (Gervajio, 2008).

A process has been developed at Palm Oil Research Institute of Malaysia (PORIM) to convert crude palm oil, crude palm stearin and crude palm kernel oil with varying amounts of free fatty acids to methyl esters under mild conditions. This process which has been patented (Choo *et al.*, 1992) essentially consists of two steps: (a) esterification of the free fatty acids present in the oil into methyl esters followed directly by (b) transesterification of the neutral glyceride mixture directly into methyl esters without going through a washing stage. A schematic flow diagram of the process is shown in Figure 2.4.

In this process, the esterification process is carried out in the presence of a solid acid catalyst and excess of methanol in a fixed bed reactor. Several solid catalysts have been found effective for the esterification (Choo and Goh, 1987; Choo and Ong, 1989). The oil and methanol is pre-mixed in a 1:6 molar ratio before it is fed continuously into the reactor. The reaction temperature and pressure were maintained at about $80^{o}C$ and 3 $kgcm^{-1}$, respectively. The reaction is completed (>95%) within 30 minutes depending on the free fatty acids content. Excess methanol is recovered and recycled. The washing stage after esterification is obviated and this is an economic advantage (Choo and Ma, 1996).
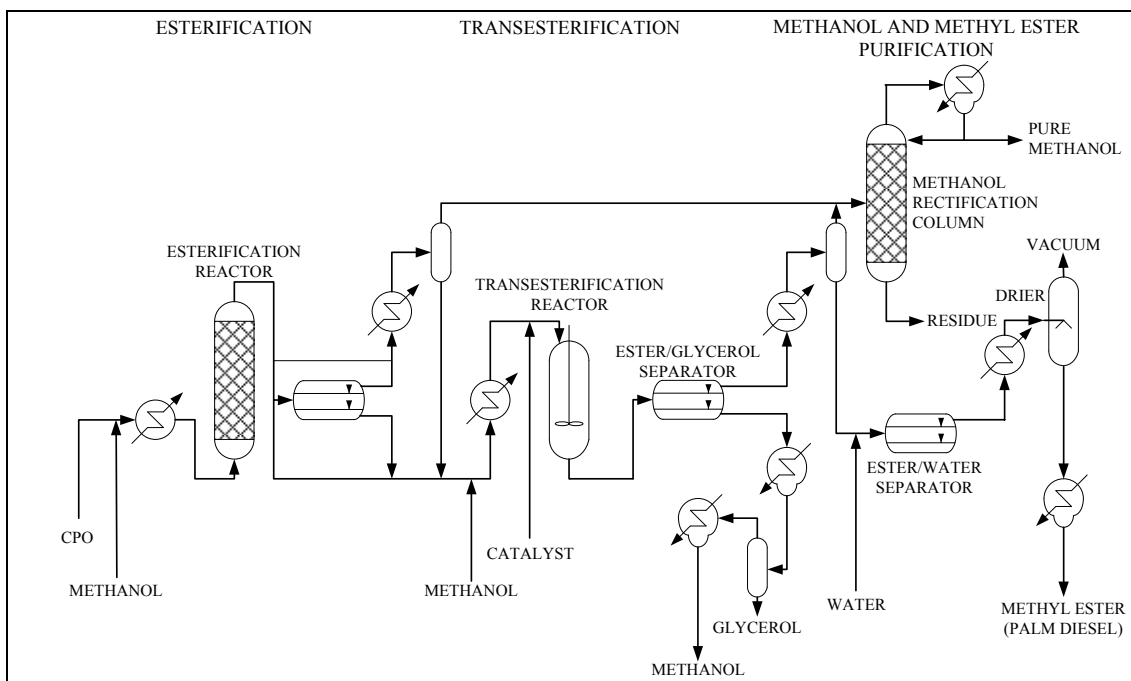
Figure 2.4   Schematic Flow Diagram of Palm Oil Methyl Esters Pilot Plant (Choo and Ma, 1996).

The esterification reaction products (methyl esters from free fatty acids and unreacted glycerides) are then transferred to the transesterification section, which consists of two stirred tank reactors in series. The transesterification reaction is carried out at a temperature of about $70^{o}C$ and at a pressure of 1 kgcm^{-2}. In the first reactor, a base catalyst, about 0.35 wt% of the feed is added. More than 80% conversion is obtainable within 30 minutes. The reaction co-product, i.e., glycerol, has to be removed continuously to enhance the reaction process. In the second reactor, an additional small amount of catalyst (7.2 wt% in methanol) is added to ensure the reaction goes into completion (> 98%). A small amount of glycerol is also formed which is removed in a similar manner. The excess methanol in the esters in flushed and recovered for reuse. The methyl esters are then washed with hot water and vacuum dried before they are sent for storage. A small amount of methanol is present in the crude glycerol thus produced. The methanol is recovered by passing