SYNTHESIS OF BIODIESEL FROM PALM OIL AND SEA MANGO OIL USING SULFATED ZIRCONIA CATALYST

by

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

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NOMENCLATURE AND ABBREVIATIONS

\[\alpha\]  Alpha (Axial distance from center point which makes the design rotatable
\(x_i\)  Variables studied
\(x_j\)  Variables studied
\(b_o\)  Offset term
\(b_j\)  Linear effect
\(b_{ij}\)  First order interaction effect
\(b_{jj}\)  Squared effect
\(k\)  Global reaction rate constant
ANOVA  Analysis of Variance
AOCS  American Oil Chemists’ Society
BET  Brunauer-Emmett-Teller
CCD  Central Composite Design
CPO  Crude Palm Oil
DF  Dilution factor
DG  Diglycerides
DOE  Design of Experiment
F-value  Fischer test value (Measurement of distance between individual distributions)
FAME  Fatty Acid Methyl Esters
FTIR  Fourier Transform Infra Red Spectroscopy
GC-FID  Gas Chromatography with Flame Ionization Detector
GC-MS  Gas Chromatography Mass Spectrometer
GL  Glycerol
H NMR  Hydrogen Nuclear Magnetic Resonance
HPLC  High Performance Liquid Chromatography
IS  Internal Standard (Methyl Heptadecanoate)
ME  Methyl Esters
MG  Monoglycerides
ML  Methyl Linoleate
MM  Methyl Myristate
MO  Methyl Oleate
MP  Methyl Palmitate
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<tr>
<td>MPOB</td>
<td>Malaysian Palm Oil Board</td>
</tr>
<tr>
<td>MS</td>
<td>Methyl Stearate</td>
</tr>
<tr>
<td>NIR</td>
<td>Near Infra Red</td>
</tr>
<tr>
<td>PLPO</td>
<td>Processed Liquid Palm Oil</td>
</tr>
<tr>
<td>PO</td>
<td>Palm oil</td>
</tr>
<tr>
<td>PD</td>
<td>Petroleum Diesel</td>
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<td>RSM</td>
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Penghasilan biodiesel daripada minyak kelapa sawit dan minyak mangga laut telah dikaji. Dua jenis mangkin heterogen telah digunakan dalam kajian ini; (a) mangkin zirconia tersulfat yang disintesis dalam makmal dan (b) mangkin komersial montmorillonite KSF. Bahagian awal dalam kajian ini adalah untuk mensintesis, mengoptimasi dan mencirikan mangkin zirconia tersulfat. Mangkin zirconia tersulfat yang dihasilkan ini kemudiannya digunakan dalam penghasilan biodiesel (proses transesterifikasi). Mangkin kedua, montmorillonite KSF (sebagai perbandingan) digunakan secara terus dalam proses transesterifikasi. Minyak kelapa sawit bertapis digunakan sebagai bahan pemula utama manakala minyak mangga laut digunakan sebagai bahan pemula sampingan. Minyak mangga laut ini diperolehi melalui pengekstrakan minyak daripada biji buah mangga laut. Pensintesisan mangkin zirconia tersulfat telah dijalankan menggunakan dan tanpa menggunakan penyokong. Aluminium oksida (Al₂O₃) digunakan sebagai penyokong. Mangkin zirconia tersulfat tersokong didapati mempunyai aktiviti pemangkinan yang tertinggi. Dengan menggunakan 6% berat mangkin zirconia tersulfat tersokong, sebanyak 82.8% hasilan metil ester asid lemak kelapa sawit (palm FAME) telah dihasilkan pada suhu tindakbalas 180 °C, masa tindakbalas 180 minit dan nisbah minyak kepada metanol pada 1:8. Menggunakan kuantiti mangkin yang sama, sebanyak 83.4% hasilan metil ester asid lemak mangga laut (sea mango FAME) telah dihasilkan pada keadaan
tindakbalas yang sama. Apabila mangkin komersial montmorillonite KSF digunakan, hasilan ester yang lebih rendah telah didapati. Hasilan ester kelapa sawit paling tinggi oleh mangkin montmorillonite KSF adalah sebanyak 79.6% (suhu tindakbalas 190 °C, masa tindakbalas 180 minit, nisbah minyak kepada metanol pada 1:8 dan amaun mangkin 3 wt%) manakala hasilan paling tinggi ester mangga laut oleh montmorillonite KSF adalah sebanyak 48.3% pada keadaan tindakbalas yang sama. Dalam kajian ini, minyak mangga laut didapati mempunyai potensi yang amat baik untuk digunakan sebagai bahan pemula dalam penghasilan biodiesel oleh kerana hasilan minyaknya yang tinggi sebanyak 54%. Pencirian mangkin zirconia tersulfat tersokong telah dijalankan menggunakan FTIR, XRD, BET, TGA dan SEM. Didapati bahawa mangkin zirconia tersulfat tersokong ini mempunyai sifat asid lampau serta luas permukaan dan keliang yang rendah. Pencirian ester (palm FAME) menunjukkan bahawa mangkin zirconia tersulfat dan montmorillonite KSF merupakan mangkin yang baik dalam penghasilan biodiesel yang menepati piawaian biodiesel antarabangsa dan Malaysia. Kinetik tindakbalas transesterifikasi menggunakan mangkin zirconia tersulfat turut dikaji dan kadar pembolehubahnya juga telah dipelajari. Tenaga pengaktifan sebanyak 50.05 kJ/mol dan faktor frekuensi 1.4 × 10⁵ min⁻¹ telah diperolehi bagi tindakbalas transesterifikasi ini.
SYNTHESIS OF BIODIESEL FROM PALM OIL AND SEA MANGO OIL
USING SULFATED ZIRCONIA CATALYST

ABSTRACT

The production of biodiesel from palm oil and sea mango oil (Cerbera odollam oil) using heterogeneous catalysts was studied. Two types of heterogeneous catalysts (a) sulfated zirconia which was synthesized in the laboratory and (b) a commercial montmorillonite KSF were used. The initial part of this research project was to synthesize, optimize and characterize sulfated zirconia catalyst. Then, the synthesized sulfated zirconia catalyst was used in the production of biodiesel (transesterification process). The second heterogeneous catalyst (for comparison purpose) a commercial montmorillonite KSF was used directly in the transesterification process. Refined palm oil was used as feedstock whereas sea mango oil was used as an alternative feedstock. Sea mango oil was extracted from the seeds of sea mango fruits. The synthesis of sulfated zirconia was carried out with and without a support. Aluminium oxide (Al₂O₃) was used as support. Supported sulfated zirconia gave the highest catalytic activity. With a catalyst loading of 6 wt%, palm fatty acid methyl esters (palm FAME) yield of 82.8% was obtained at the following reaction conditions; reaction temperature of 180 °C, reaction period of 180 minutes and ratio of oil to methanol at 1:8. Using the same catalyst loading, sea mango fatty acid methyl esters (sea mango FAME) with a yield of 83.4% were obtained at the same reaction conditions. On the other hand, when commercial montmorillonite KSF catalyst was used, a lower yield was obtained. The highest yield of palm FAME produced using montmorillonite KSF was 79.6% (reaction
temperature of 190 °C, reaction period of 180 minutes, ratio of oil to methanol at 1:8 and amount of catalyst 3%) and only 48.3% yield of sea mango FAME was produced at the same reaction condition. Nevertheless, sea mango oil was found to be a potential feedstock for biodiesel production due to its high oil content of 54%. The characterization of the supported sulfated zirconia was carried out using FTIR, XRD, BET, TGA and SEM. It was found that the supported sulfated zirconia has properties of solid superacid with low surface area and low porosity. The characterization of palm FAME indicated that the supported sulfated zirconia and montmorillonite KSF are reliable catalysts for the production of biodiesel that meets the international and Malaysian standard of biodiesel. The kinetic of the transesterification reaction using sulfated zirconia catalyst was also studied and the rate parameters were determined. An activation energy value of 50.05 kJ/mol and frequency factor of $1.4 \times 10^5$ min$^{-1}$ were obtained for the transesterification reaction.
CHAPTER 1

INTRODUCTION

Petroleum-based fuel plays an important role in the energy sector mainly as fuel for power plants, running vehicles and motor engines in the transportation sector. However, petroleum-based fuel is not sustainable and the prices are also not stable. Due to these factors, new alternative energy especially renewable energy has been widely studied to fulfill the world’s insatiable demand for energy. Examples of the new alternative energy are solar, wind, geothermal and biomass (Omer, 2008). Nevertheless, most of these alternative energy are only capable of generating thermal and electrical energy, whereas more than 40% of the world energy demand is in liquid form. Therefore, the use of biomass as a new source of alternative liquid fuel has attracted a lot of attention lately.

One of the options of utilizing biomass as liquid fuel is the use of vegetable oil in diesel engines. However, vegetable oils cannot be directly used in diesel engines due to its high viscosity. In order to utilize vegetable oils successfully in unmodified diesel engines, the viscosity of the vegetable oil must be lowered. Several methods have been developed to reduce the viscosity of the vegetable oil. These methods include blending with diesel, pyrolysis, microemulsification (co-solvent blending), and transesterification (Ma & Hanna, 1999).

Currently, blending and transesterification are the most common ways to lower the viscosity of vegetable oil. Blending is easier because it does not involve any chemical modification of the vegetable oil. However, blending is less attractive
because it requires purification of the vegetable oil prior to the blending process. Transesterification, on the other hand does not require purification of the vegetable oil. However, transesterification process involves chemical reactions to convert vegetable oil into biodiesel, which recently has become well known. Compared to blending, transesterification process is superior due to its ability to reduce effectively the viscosity of the vegetable oil and produces fuel which has similar properties with diesel. Figure 1.1 shows the schematic of a typical process flow diagram for biodiesel production.

![Figure 1.1 Typical process flow diagram for biodiesel production (Gerpen, 2005)](image)

There are two ways to carry out the transesterification process; catalytic and non-catalytic process. Under catalytic process, there are two methods namely homogenous and heterogeneous. Homogeneous transesterification method has been long regarded as the easiest method to produce biodiesel. Unfortunately,
homogeneous transesterification has many problems including complexity of the product separation and purification processes due to homogeneous nature of its mixture (reactants, catalyst and product). Homogenous transesterification process also tends to produce soap which leads to usage of a lot wash water and also formation of emulsion in the mixture. The formation of emulsion in the mixture could worsen the complexity of the separation and purification process. Furthermore, it could contribute to the loss of triglycerides. All these downsides eventually lead to a very high production cost. Due to these disadvantages, other alternatives have been considered; heterogeneous and non-catalytic transesterification process.

Non-catalytic transesterification process requires no catalyst. However, it is also less favorable due to its high energy demand as non-catalytic process usually operates at supercritical temperature and pressure of the alcohol (Fukuda et al., 2001; Ma & Hanna, 1999; Madras et al., 2004; Marchetti et al., 2007b). Furthermore, at supercritical conditions, non-catalytic transesterification process tends to become very difficult to handle. Due to these factors, other alternative method, which has a lower operational cost and simpler operational process, has to be considered. Thus, heterogeneous transesterification provides a better solution.

1.1 Heterogeneous Transesterification

The benefits of heterogeneous transesterification process include easier and simpler separation process (as the catalyst is in different phase from the product/reactants) and elimination of soap formation. Heterogeneous transesterification is a relatively cheaper alternative to the current homogenous transesterification for biodiesel production. Heterogeneous transesterification process
is also easier to perform due to moderate temperature and pressure required in the process compared to that of non-catalytic supercritical transesterification technology.

There are three types of heterogeneous transesterification process; basic (alkali), acidic and enzymatic. Up until today, there are many catalysts developed and used in the heterogeneous transesterification process. Examples of the heterogeneous catalysts are metal oxides (Liu et al., 2008; Zhu et al., 2006), zeolites (Suppes et al., 2004; Xie et al., 2007) and active metals loaded on supports (Albuquerque et al., 2008; Jitputti et al., 2006; Park et al., 2008). Each type of heterogeneous transesterification process has their own challenges. Enzymatic transesterification process for instance, requires activity of a living organism or cells (enzyme) to convert vegetable oil to biodiesel. This makes the enzymatic process very sensitive to disturbances. The enzyme could be easily inhibited when the conditions are unsuitable (Ranganathan et al., 2008). The enzymatic reactions are also very specific due to its specific active sites. Moreover, enzymes are costlier compared to basic and acidic solid catalysts. Due to these reasons, heterogeneous transesterification processes using basic and acidic solid catalysts seem to be more attractive. However, the heterogeneous transesterification itself has other challenges. The solid catalysts for the heterogeneous transesterification process must possess good catalytic properties to produce the desirable product. This actually has become the main hurdle in the development of heterogeneous catalysts that is to synthesize a very reactive catalyst that can catalyze the heterogeneous transesterification process.
1.2 Feedstock for Biodiesel Production

One of the starting materials required for the production of biodiesel via transesterification process is oil feedstock. Since vegetable oil is oil feedstock that is readily available in large quantities, it has been widely used for the conversion to biodiesel. Table 1.1 shows the common vegetable oil available in the world with its oil content, oil yield and major producing area. Majority of these vegetable oil have been utilized for the production of biodiesel via transesterification process such as soybean oil (Antunes et al., 2008; Ferreira et al., 2007; Liu et al., 2008; Yin et al., 2008), rapeseed oil (Li et al., 2006a; Morin et al., 2007; Saka & Kusdiana, 2001), canola oil (Dube et al., 2007; Kulkarni et al., 2007), palm oil (Crabbe et al., 2001; Jitputti et al., 2006; Joelianingsih et al., 2008; Sarin et al., 2007; Trakarnpruk & Porntangjitlikit, 2008) and sunflower oil (Granados et al., 2007; Stamenkovic et al., 2008).

In Malaysia, the most abundantly available vegetable oil is palm oil. Malaysia is currently the world second largest producer of palm oil after Indonesia. The production of palm oil in Malaysia from year 1964 to year 2006 is given in Figure 1.2. Based on Figure 1.2, it can be seen that the production of crude palm oil has been increasing from year 1964 to year 2006. This indicates that palm oil can be used as a stable supply of oil feedstock not only as food (edible oil), but also for the production of biodiesel (transesterification process). This therefore makes palm oil a viable feedstock for the production of palm biodiesel.
Table 1.1 Different types of vegetable oils: Oil content, oil yield and producing areas
(O’Brien, 2004)

<table>
<thead>
<tr>
<th>Oil</th>
<th>Oil content (%)</th>
<th>Oil yield (Pounds/Acre)</th>
<th>Major producing area</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oilseeds:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Canola</td>
<td>40 – 45</td>
<td>525 – 590</td>
<td>Canada, China, India, France, Austria, U.K., Germany, Poland, Denmark, Czechoslovakia, U.S.</td>
</tr>
<tr>
<td>Corn</td>
<td>3.1 – 5.7</td>
<td>215 -390</td>
<td>U.S., Mexico, Canada, Japan, China, Brazil, South Africa, Argentina, Russia, Commonwealth of Independent States (CIS), Belgium, France, Italy, Germany, Spain, U.K.</td>
</tr>
<tr>
<td>Cottonseed</td>
<td>18 – 20</td>
<td>185 – 210</td>
<td>China, Russia, U.S. India, Pakistan, CIS, Brazil, Egypt, Turkey, Australia</td>
</tr>
<tr>
<td>Peanut</td>
<td>45 – 50</td>
<td>1120 – 1245</td>
<td>China, India, Nigeria, U.S., Senegal, South Africa, Argentina</td>
</tr>
<tr>
<td>Safflower</td>
<td>30 – 35</td>
<td>545 – 635</td>
<td>China, U.S., Spain, Portugal</td>
</tr>
<tr>
<td>Soybean</td>
<td>18 – 20</td>
<td>400 – 590</td>
<td>U.S., Brazil, Argentina, China, India, Paraguay, Bolivia</td>
</tr>
<tr>
<td>Sunflower</td>
<td>35 – 45</td>
<td>460 – 590</td>
<td>Russia, Argentina, CIS, Austria, France, Italy, Germany, Spain, U.S., U.K.</td>
</tr>
<tr>
<td><strong>Tree fruits and kernels:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coconut</td>
<td>65 – 68</td>
<td>650 – 870</td>
<td>Philippines, Indonesia, India, Mexico, Sri Lanka, Thailand, Malaysia, Vietnam, Mozambique, New Guinea, Ivory Coast</td>
</tr>
<tr>
<td>Olive</td>
<td>15 – 35</td>
<td>90 – 260</td>
<td>Spain, Italy, Greece, Tunisia, Turkey, Morocco, Portugal, Syria, Algiers, Yugoslavia, Cyprus, Egypt, Israel, Libya, Jordan, Lebanon, Argentina, Chile, Mexico, Peru, U.S., Australia</td>
</tr>
<tr>
<td>Palm</td>
<td>45 – 50</td>
<td>2670 – 4450</td>
<td>Malaysia, Indonesia, China, Philippines, Pakistan, Mexico, Bangladesh, Colombia, Ecuador, Nigeria, Ivory Coast</td>
</tr>
<tr>
<td>Palm Kernel</td>
<td>44 – 53</td>
<td>267 – 445</td>
<td>Malaysia, Indonesia, China, Philippines, Pakistan, Mexico, Bangladesh, Colombia, Ecuador, Nigeria, Ivory Coast</td>
</tr>
</tbody>
</table>
Nevertheless, the conversion of edible oil to biodiesel gives another problem. Conversion of edible oil to fuel (biodiesel) led to controversies as famine and hunger still exist around the globe. Channeling edible oil into fuel industries makes biodiesel to actually compete limited land availability with the food industry for the same oil crop. Thus, instead of utilizing arable land to grow food, it is now being used to grow fuel. This subsequently raises the price of edible oil and therefore makes the biodiesel produced economically unfeasible compared to petroleum derived diesel. In order to overcome this issue, other alternative oil feedstock must be used to replace the edible oils in the biodiesel production. Few sources have been identified such as waste cooking oil and oil from non-edible producing plants such as jatropha oil (*Jatropha curcas* oil) (Berchmans & Hirata, 2008; Kumar Tiwari *et al.*, 2007; Shah & Gupta, 2007; Tamalampudi *et al.*, 2008), algae oil (Chisti, 2007, 2008), and

![Figure 1.2 Malaysia production of palm oil from year 1964 to 2006 (MPOB, 2008)](image-url)
waste oil (Issariyakul et al., 2007; Lapuerta et al., 2008a; Tsai et al., 2007; Yagiz et al., 2007).

As for non-edible sources in Malaysia, there are few choices; jatropha, rubber seeds and sea mango (Cerbera odollam). The former has a brighter commercial prospect, judged from the opening of new jatropha plantations around the country. Rubber seeds are readily available since there are already a lot of mature rubber plantations around the country. In contrast to the previous two, sea mango generally is unknown in the biodiesel production. Sea mango trees however are widely planted locally as ornamental plant by roadsides. Up until today, sea mango (Cerbera odollam) has never been used in the transesterification research.

1.3 Problem Statement

Biodiesel has been accepted worldwide as the immediate solution to the heavily reliance on petroleum-derived diesel oil. However, current commercial production technology of biodiesel via homogenous transesterification has a lot limitation, making the cost of biodiesel production economically unfeasible. On the other hand, heterogeneous transesterification process provides a cheaper, less problematic and easier operation compared to homogenous and non-catalytic transesterification processes. However, reactivity of the heterogeneous (solid) catalysts has always become a problem. Not many solid catalysts could produce high yield of fatty acid methyl esters (FAME) in the transesterification process. Hence, it becomes a challenge to create a practical, durable and highly reactive solid catalyst which can be used in the transesterification process.

The controversies of edible oils being converted to fuel bring new dimension to the transesterification process. Prolonged dependence and increasing demand on
edible oil as feedstock created a siphon which draws bigger portion of edible oils into the fuel industry. This consequently threatens the supply of edible oil to food industry. Due to these factors, it is crucial to find other alternative oil feedstock to substitute edible oil in the production of biodiesel (transesterification process).

Therefore, the main aim of this project is to synthesize a solid superacid catalyst (sulfated zirconia) that can be used as catalyst in the heterogeneous transesterification of palm oil to biodiesel. Subsequently, sea mango will be used as oil feedstock to study the feasibility of sea mango oil as a non-edible (alternative) oil for the production of biodiesel.

1.4 Project Objectives

This research project aims to achieve the following specific objectives.

(a) To synthesize, optimize and characterize sulfated zirconia as a solid superacid catalyst for the transesterification of palm oil under a number of catalyst preparation parameters/variables – calcination temperature, calcination period and ratio of catalyst to support

(b) To study and optimize the transesterification of palm oil using optimized sulfated zirconia catalyst under a wide range of operating parameters (reaction temperature, reaction period, ratio of oil/methanol and amount of catalyst) using design of experiment (DOE) and response surface methodology (RSM) and to compare its performance with montmorillonite KSF catalyst

(c) To study the feasibility of a non-edible oil (*Cerbera odollam* oil) as alternative feedstock in the transesterification process

(d) To characterize the product from the transesterification process (palm FAME)
(e) To study the kinetic of the transesterification process

1.5 Organization of Thesis

There are five chapters (including introduction) in this thesis and each chapter gives specific information about this research project.

Chapter 1 gives the introductory of this research project. This chapter starts with the current energy trend that leads to the development of alternative energy particularly biodiesel. This chapter also gives brief overview of the biodiesel production which leads to the development of heterogeneous transesterification process. The problem statement and objectives of this research project are also stated clearly in this chapter.

Chapter 2 gives literature review on this research project background. This chapter begins with information about biodiesel; definitions, common equations and basic principles. Further in this chapter are the reviews of the transesterification processes and methods and the latest research study in the heterogeneous transesterification process. Other topics covered in this chapter are the reviews of catalyst preparation methods for sulfated zirconia catalyst and its latest development in the literature.

Chapter 3 describes the materials and methodology used in this research project. The first part of this chapter gives the list of material and chemicals used in this research project. The subsequent topics describe clearly the methodology of this research project – synthesis, optimization and characterization of the sulfated zirconia catalyst, transesterification process using heterogeneous catalysts (sulfated
zirconia catalyst and montmorillonite KSF catalyst), extraction and transesterification process of sea mango oil, characterization of the product of this research project (FAME) and kinetic study.

Chapter 4 presents the results and discussions of this research project. The sequence of topics in this chapter follows the sequence of topics in Chapter 3. The first part of this chapter contains the results and discussion obtained from the synthesis, optimization and characterization of sulfated zirconia catalyst followed by the results and discussion obtained from the transesterification process studies. Subsequent topics on this chapter contain the results and discussion for the extraction and transesterification of sea mango oil and characterization of product (biodiesel). The final part of this chapter presents the kinetic study of the transesterification process.

Chapter 5 concludes the research project. Recommendations for future work related to this research project are also given.
CHAPTER 2

LITERATURE REVIEW

This chapter reviews background information on the subject of heterogeneous transesterification process that leads to this research project. It begins with the basic principles of biodiesel, advantages and disadvantages of biodiesel, methods, catalysts and feedstock in transesterification process and variables affecting the transesterification process. Further in this chapter are reviews on the development of heterogeneous catalysts that leads to the development of supported sulfated zirconia catalyst.

2.1 Biodiesel

2.1.1 Definition of Biodiesel

Biodiesel is defined as a domestic and renewable fuel for diesel engines, derived from vegetable oil which meets the specification of ASTM D6751 (Fukuda et al., 2001). Biodiesel consists of alkyl esters, which are produced from the transesterification reaction between triglycerides and alcohol. In experimental studies, the final product is termed as fatty acid alkyl esters or fatty acid methyl esters (FAME) instead of biodiesel unless it meets the specification of ASTM D6751 (Lois, 2007).
2.1.2 Advantages and Disadvantages of Biodiesel

Biodiesel is a sustainable energy (Ma & Hanna, 1999; Omer 2008) that is made from renewable sources such as vegetable oils and animal fats (Barnwal et al., 2005). These sources could always be re-planted or grown to ensure its sustainability. Other than that, biodiesel is a non-toxic and clean energy (Omer, 2008). The emissions from vehicles that are using biodiesel contains lower harmful gases such as carbon monoxide, sulfur dioxide (Demirbas, 2007b; Graham et al., 2008; Roskilly et al., 2008) and aromatic content (Ma & Hanna, 1999) compared to that of using petroleum derived diesel. Biodiesel could also reduce the emission of particulate matters (PM) (Lapuerta et al., 2008b; Ramadhas et al., 2005b).

Biodiesel also acts as a good lubricant to diesel engines (Shahid & Jamal, 2008). This could therefore prolong the self-life of the engines. Biodiesel also has higher flash point which makes it safer to handle compared to diesel (Shahid & Jamal, 2008). Other advantages of biodiesel as diesel fuel are liquid nature portability, readily available, renewability, higher combustion efficiency (Agarwal et al., 2008), higher cetane number (Knothe et al., 2003) and higher biodegradability (DeMello et al., 2007, Lapinskiene et al., 2006).

On the other hand, disadvantages of biodiesel include increased emission of NOx gas (Agarwal et al., 2006; Ban-Weiss et al., 2007; Lapuerta et al., 2008a), higher cloud and pour points (Ma & Hanna, 1999) and also costlier compared to diesel due to high price of vegetable oils especially those of edible type. However, the cost of biodiesel could vary depending on the source of feedstock (Demirbas, 2008). Biodiesel could also dissolve certain parts of the diesel engines, especially those made of elastomers (Flitney, 2007; Trakarnpruk & Porntangjikit, 2008). Nevertheless, the advantages of biodiesel superseded the disadvantages generally on
the environmental aspects, making it a very popular alternative to petroleum derived-diesel oil.

2.1.3 Transesterification Process

Biodiesel is mainly produced from a chemical process known as transesterification. Transesterification, also known as alcoholysis, is the displacement of alcohol group from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is employed instead of water (Fukuda et al., 2001). The transesterification process consists of three subsequent reversible reactions where the first reaction occurs between triglycerides and alcohol to produce diglycerides and an ester (Sharma et al., 2008). The second reaction continues with diglycerides (from the first reaction) reacting with alcohol to produce monoglycerides and an ester. The third reaction occurs between the monoglycerides (from the second reaction) and alcohol to produce glycerol and an ester. From these reactions, one molecule triglycerides requires three molecules alcohol to form three molecules fatty acid alkyl esters and one molecule glycerol. The general equation of the transesterification process is shown in Equation 2.1:

\[
\begin{align*}
\text{CH}_2\text{-OOC-R}_1 & \quad \text{R}_1\text{-OOC-}’ \quad \text{CH}_2\text{-OH} \\
\text{CH}_2\text{-OOC-R}_2 & + 3 \text{R’OH} \quad \leftrightarrow \quad \text{R}_2\text{-OOC-}’ + \quad \text{CH}_2\text{-OH} \\
\text{CH}_2\text{-OOC-R}_3 & \quad \text{R}_3\text{-OOC-}’ \quad \text{CH}_2\text{-OH}
\end{align*}
\]

Triglycerides  Alcohol  Fatty acid alkyl esters  Glycerol

The reaction is endothermic.
R₁, R₂, R₃ and R’ are different type of alkyl group. The elaborate equations of the transesterification process are presented in **Equations 2.2 (a-c)** (Fukuda et al., 2001; Ma & Hanna, 1999):

\[
\begin{align*}
\text{Triglycerides (TG) + } R'\text{OH} & \leftrightarrow \text{Diglycerides (DG) + } R'\text{COO}R_1 \quad (2.2a) \\
\text{Diglycerides (DG) + } R'\text{OH} & \leftrightarrow \text{Monoglycerides (MG) + } R'\text{COO}R_2 \quad (2.2b) \\
\text{Monoglycerides (MG) + } R'\text{OH} & \leftrightarrow \text{Glycerol (GL) + } R'\text{COO}R_3 \quad (2.2c)
\end{align*}
\]

Commonly in biodiesel production, side reaction can occur especially in the homogenous transesterification process when catalyst such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) is used. Instead of producing alkyl esters, soap is formed. This side reaction is called saponification. The saponification process is show in the **Equation 2.3** (Demirbas, 2003).

\[
\text{Vegetable oils or fats + NaOH } \rightarrow \text{RCOONa + Glycerin} \quad (2.3)
\]
2.1.4 Methods and Catalysts in Transesterification Process

Transesterification process can be performed with or without catalyst (Gerpen, 2005; Ma & Hanna, 1999; Marchetti, 2007b; Meher et al., 2006b). Transesterification process using catalyst is called catalytic transesterification process whereas transesterification process without catalyst is called non-catalytic transesterification process. However, conventional transesterification process has been using catalytic process to produce biodiesel due to its simpler operation and shorter reaction period to produce biodiesel (Ma & Hanna, 1999; Marchetti et al., 2007b). Non-catalytic transesterification process usually uses supercritical alcohol such as supercritical methanol (Demirbas, 2005, 2007a; Saka & Kusdiana, 2001; Song et al., 2008; Yin et al., 2008) and supercritical ethanol (Madras et al., 2004) to produce fatty acid alkyl esters (biodiesel).

Catalytic transesterification process is divided into two types; homogenous and heterogeneous process. Homogenous transesterification process usually uses catalysts such as sodium hydroxide (NaOH), potassium hydroxide (KOH) (Dias et al., 2008), sulfuric acid (H₂SO₄) (Marchetti & Errazu, 2008) and hydrochloric acid (HCl) (Al-Widyan & Al-Shyoukh, 2002) to catalyze the transesterification process. Heterogeneous transesterification process on the other hand uses solid catalyst such as metal oxides (Liu et al., 2007; Liu et al., 2008; Marchetti et al., 2007b, Mazzochia et al., 2004), active metals supported on various medium (Park et al., 2008; Xie & Lie, 2006), zeolites (Suppes et al., 2004), resins (Shibasaki-Kitakawa et al., 2007), membranes (Guerreiro et al., 2006) and enzymes (Ranganathan et al., 2008) to catalyze the transesterification process.

The division of methods in the transesterification process is best summarized in Figure 2.1:
2.1.5 Feedstock for Biodiesel Production

2.1.5 (a) Vegetable Oils and Animal fats

Generally all types of vegetable oil and animal fat could be used as feedstock in the transesterification process. Vegetable oils and animal fats contain triglycerides which are useful in the transesterification process (O’Brien, 2004; Sharma et al., 2008).

Vegetable oils and animal fats for the transesterification process is divided into two types; edible and non-edible type. Vegetable oil of edible type has long been used in the conventional transesterification process (production of biodiesel), largely due to the abundance availability of edible vegetable oil in the global market. Various vegetable oils and animal fats have been used in different countries as feedstock in the transesterification process owing to its availability (Sharma et al., 2008).

Examples of edible oil (vegetable oils and animal fats) that are being studied in the transesterification process are soybean oil (Antunes et al., 2008; Liu et al., 2008; Yin et al., 2008), rapeseed oil (Li et al., 2006a; Morin et al., 2007; Saka &
Kusdiana, 2001), sunflower oil (Arazamendi et al., 2008; Demirbas, 2007a; Granados et al., 2007), palm oil (Crabbe et al., 2001; Jitputti et al., 2006; Kalam & Masjuki, 2002; Song et al., 2008); Trakarnpruk & Porntangjilkit, 2008), coconut oil (Jitputti et al., 2006) and coffee oil (Oliveira et al., 2008). Examples of non-edible oil in the transesterification process are waste oil (Canakci, 2007; Felizardo et al., 2006; Issariyakul et al., 2007; Ozbay et al., 2008; Wang et al., 2007a; Yagiz et al., 2007; Zheng et al., 2006), jatropha oil (Berchmans & Hirata, 2008; Kumar Tiwari et al., 2007; Sarin et al., 2007; Shah & Gupta, 2007; Talampudi et al., 2008), cottonseed oil (Azcan & Danisman, 2007; Chen et al., 2006; Demirbas 2008b), rubber seed oil (Ramadhas et al., 2005a), algae oil (Christi, 2007, 2008) and tobacco oil (Veljkovic et al., 2006).

Table 2.1 shows the fatty acid composition of some selected vegetable oil samples.
Table 2.1 Fatty acid composition of vegetable oil samples (Demirbas, 2003)

<table>
<thead>
<tr>
<th>Sample</th>
<th>16:0</th>
<th>16:1</th>
<th>18:0</th>
<th>18:1</th>
<th>18:2</th>
<th>18:3</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cottonseed</td>
<td>28.7</td>
<td>0</td>
<td>0.9</td>
<td>13.0</td>
<td>57.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Poppyseed</td>
<td>12.6</td>
<td>0.1</td>
<td>4.0</td>
<td>22.3</td>
<td>60.2</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>3.5</td>
<td>0</td>
<td>0.9</td>
<td>64.1</td>
<td>22.3</td>
<td>8.2</td>
<td>0</td>
</tr>
<tr>
<td>Safflowerseed</td>
<td>7.3</td>
<td>0</td>
<td>1.9</td>
<td>13.6</td>
<td>77.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sunflowerseed</td>
<td>6.4</td>
<td>0.1</td>
<td>2.9</td>
<td>17.7</td>
<td>72.9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sesame seed</td>
<td>13.1</td>
<td>0</td>
<td>3.9</td>
<td>52.8</td>
<td>30.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Linseed</td>
<td>5.1</td>
<td>0.3</td>
<td>2.5</td>
<td>18.9</td>
<td>18.1</td>
<td>55.1</td>
<td>0</td>
</tr>
<tr>
<td>Wheat graina</td>
<td>20.6</td>
<td>1.0</td>
<td>1.1</td>
<td>16.6</td>
<td>56.0</td>
<td>2.9</td>
<td>1.8</td>
</tr>
<tr>
<td>Palm</td>
<td>42.6</td>
<td>0.3</td>
<td>4.4</td>
<td>40.5</td>
<td>10.1</td>
<td>0.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Corn marrow</td>
<td>11.8</td>
<td>0</td>
<td>2.0</td>
<td>24.8</td>
<td>61.3</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>Castorb</td>
<td>1.1</td>
<td>0</td>
<td>3.1</td>
<td>4.9</td>
<td>1.3</td>
<td>0</td>
<td>89.6</td>
</tr>
<tr>
<td>Tallow</td>
<td>23.3</td>
<td>0.1</td>
<td>19.3</td>
<td>42.4</td>
<td>2.9</td>
<td>0.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Soybean</td>
<td>13.9</td>
<td>0.3</td>
<td>2.1</td>
<td>23.2</td>
<td>56.2</td>
<td>4.3</td>
<td>0</td>
</tr>
<tr>
<td>Bay laurel leafc</td>
<td>25.9</td>
<td>0.3</td>
<td>3.1</td>
<td>10.8</td>
<td>11.3</td>
<td>17.6</td>
<td>31.0</td>
</tr>
<tr>
<td>Peanut kerneld</td>
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<td>0</td>
<td>2.4</td>
<td>48.3</td>
<td>32.0</td>
<td>0.9</td>
<td>4.0</td>
</tr>
<tr>
<td>Hazelnut kernel</td>
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<td>0.2</td>
<td>2.6</td>
<td>83.6</td>
<td>8.5</td>
<td>0.2</td>
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<tr>
<td>Walnut kernel</td>
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<td>0.2</td>
<td>1.9</td>
<td>18.5</td>
<td>56.0</td>
<td>16.2</td>
<td>0</td>
</tr>
<tr>
<td>Almond kernel</td>
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<td>0.5</td>
<td>1.4</td>
<td>70.7</td>
<td>20.0</td>
<td>0</td>
<td>0.9</td>
</tr>
<tr>
<td>Olive kernel</td>
<td>5.0</td>
<td>0.3</td>
<td>1.6</td>
<td>74.7</td>
<td>17.6</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td>Coconut</td>
<td>9.7</td>
<td>0.1</td>
<td>3.0</td>
<td>6.9</td>
<td>2.2</td>
<td>0</td>
<td>65.7</td>
</tr>
</tbody>
</table>

a Wheat grain oil contains 11.4% of 8:0 and 0.4% of 14:0 fatty acids.
b Castor oil contains 89.6% ricinoloic acid.
c Bay laurel oil contains 26.5% of 12:0 and 4.5% of 14:0 fatty acids.
d Peanut kernel oil contains about 2.7% of 22:0 and 1.3% of 24:0 fatty acids.

2.1.5 (b) Alcohol

Simpler alcohols (primary alcohol) such as methanol and ethanol are commonly used in the transesterification process due to its better reactivity compared to other higher order alcohols (Solomons & Fryhle, 2000). However, higher order alcohol such as propanol and butanol could also be used in the transesterification process depending on their suitability and compatibility in the transesterification process (Sharma et al., 2008). Recent studies in the literature showed that higher
order alcohols could be used in the transesterification process, not only as feedstock but also as solvent which could enhance the transesterification process (Royon et al., 2007).

2.1.6 Variables Affecting the Transesterification Process

There are number of factors which could affect the transesterification process. These factors include moisture content, free fatty acid contents, molar ratio of oil to alcohol, type and amount of catalyst, reaction time, reaction temperature, mixing intensity, and co-solvent (Demirbas, 2007c; Ma & Hanna, 1999; Meher et al., 2006b; Sharma et al., 2008). These factors or variables usually have different effect on the transesterification process depending on the method used for the transesterification process.

2.1.6 (a) Moisture and Free Fatty Acids Contents

Moisture and free fatty acids are two key parameters in determining the viability of the feedstock (vegetable oils) in the transesterification process. Generally, moisture and free fatty acids content of the feedstock must be reduced or lowered (<0.5% for homogenous process) to avoid its undesirable effect on the catalyst and the transesterification reaction (Ma & Hanna, 1999; Sharma et al., 2008). In homogenous transesterification process especially, moisture and free fatty acids in the feedstock could lead to a side saponification reaction, which produces soap and eventually emulsion (Gerpen, 2005; Ma & Hanna, 1999). The formation of soap and emulsion could further complicate the separation and purification process of the final product, which eventually leads to loss of triglyceride and product (biodiesel).
However in other transesterification process, moisture and free fatty acid contents in the feedstock could enhance the yield of fatty acid alkyl esters. For instance, in non-catalytic transesterification process using supercritical fluids for instance, it was found that the moisture and free fatty acid of the feedstock could increase the yield of fatty acid alkyl esters (Kusdiana & Saka, 2004). In enzymatic transesterification process, higher moisture content could enhance the enzymatic activity (Al-Zuhair et al., 2006); Kaieda et al., 2001). Recent development of the transesterification process showed feasible alternative methods for the transesterification process using vegetable oils with high moisture and free fatty acids content; homogenous acidic method using H$_2$SO$_4$ as catalyst (Berchmans & Hirata, 2008; Naik et al., 2008), heterogeneous method using resins as catalyst (Marchetti et al., 2007a) and two-step method using acid and base catalysts (Veljkovic et al., 2006).

2.1.6 (b) Molar Ratio of Alcohol to Oil and Type of Alcohol

Based on the stoichiometric of transesterification reaction, every mol of triglyceride requires three moles of alcohol to produce three moles of fatty acid alkyl esters and one mole of glycerol (Ma & Hanna, 1999). In the transesterification process however, alcohol is supplied in excess to induce higher yield of fatty acid alkyl esters. Molar ratio of oil to alcohol at 1:6 is considered as the standard ratio (Fukuda et al., 2001; Gerpen, 2005). However, other researches also shown that molar ratio of oil to alcohol from 1:5 (Alamu et al., 2008) up to 1:8 (Ramadhas et al., 2005a), 1:9 (Sahoo et al., 2007), 1:12 (Meher et al., 2006a), and higher could also be used as the optimum ratio for oil to methanol, depending on the quality of feedstock and method of the transesterification process. However, when the ratio of oil to
alcohol is too high, it could give adverse effect on the yield of fatty acid alkyl esters. Some researchers reported that addition of large quantity of methanol, i.e. at ratio of 1:70 and 1:84 could slow down the separation of esters and glycerol phases during the transesterification process, therefore affecting the final yield of fatty acid alkyl esters (Miao & Wu, 2006). It could also promote mass transfer problem between triglycerides, alcohol and catalyst, which eventually could reduce the yield of fatty acid alkyl esters.

Optimization of the ratio of oil to alcohol is usually carried out to determine the optimum ratio of oil to alcohol. Optimization process is usually carried out by varying the ratio of oil to methanol while maintaining the other variables at a certain fixed values and then subsequently comparing the yield or conversion of fatty acid alkyl esters.

2.1.6 (c) Type and Amount of Catalyst

The type and amount of catalyst required in the transesterification process usually depend on the quality of the feedstock and method applied for the transesterification process. For a purified feedstock, any type of catalyst could be used for the transesterification process. However, for feedstock with high moisture and free fatty acids contents, homogenous transesterification process is unsuitable due to high possibility of saponification process instead of transesterification process to occur (Gerpen, 2005).

The yield of fatty acid alkyl esters generally increases with increasing amount of catalyst (Demirbas, 2007b; Fukuda et al., 2001; Ma & Hanna, 1999). This is due to availability of more active sites by additions of larger amount of catalyst in the transesterification process. However, on economic perspective, larger amount of
catalyst may not be profitable due to cost of the catalyst itself. Therefore, similar to the ratio of oil to alcohol, optimization process is necessary to determine the optimum amount of catalyst required in the transesterification process.

2.1.6 (d) Reaction Time and Temperature

Current researches have shown that the reaction time for a non-catalytic transesterification process using supercritical alcohol is shorter compared to conventional catalytic transesterification process (Demirbas, 2003, 2005). For a heterogeneous transesterification process, the reaction period varies depending on the reactivity and type of the solid catalyst used.

For a practical and economic feasible transesterification process, it is necessary to limit the reaction time at a certain period. Longer reaction time could also permit reversible transesterification reaction to occur, which eventually could reduce the yield of fatty acid alkyl esters. Thus, optimization of reaction time is also necessary.

The operating temperature for transesterification process depends on the method used. Certain processes, such as homogenous transesterification process and enzymatic transesterification process, generally require moderate temperature to commence the transesterification reaction. However, non-catalytic transesterification process requires high temperature and pressure to yield the desired product (fatty acid alkyl esters). The operating temperature for heterogeneous transesterification process using solid catalyst (except enzymatic process) varies depending on the activation energy and conditions to produce high yield of fatty acid alkyl esters.
2.1.6 (e) Mixing Intensity

Transesterification process is usually associated with mass transfer problem due to opposite polarity of the two feedstock; triglycerides (oil) and alcohol. Triglycerides are hydrophobic whereas alcohol is hydrophilic. Mixing is very important in the transesterification process, as oils or fats are immiscible with alcohol (Meher et al., 2006b). Adequate mixing between these two types of feedstock is necessary to promote contact between these two feedstock, therefore enhance the transesterification reactions to occur. Mechanical mixing is commonly used in the transesterification process. The intensity of the mixing could be varied depending on its necessity in the transesterification process. In general, the mixing intensity must be increased to ensure good and uniform mixing of the feedstock. When vegetable oils with high kinematic viscosity are used as the feedstock, intensive mechanical mixing is required to overcome the negative effect of viscosity to the mass transfer between oil, alcohol and catalyst.

2.1.6 (f) Co-solvent

In the transesterification process, co-solvent is used to enhance the mixing between triglycerides and alcohol. Co-solvent could also function as a reaction medium (Li et al., 2006a), stabilizer (Li et al., 2008) and binder between triglycerides and alcohol to allow contact between the two polar feedstocks. Selection of suitable co-solvent is crucial to enhance the yield of fatty acid alkyl esters. Some co-solvents could also act as an agent to reduce the operating temperature and pressure required for the transesterification process particularly for supercritical transesterification process (Han et al., 2005). Examples of co-solvent include tert-butanol (Royon et al., 2007; Wang et al., 2006), tert-pentanol, isoctane