BIODIESEL PRODUCTION FROM *JATROPHA CURCAS* L. OIL USING SUPERCRITICAL METHYL ACETATE AND METHANOL PROCESS

by

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TABLE OF CONTENTS

Page

CHAPTER FOUR – RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATE

LIST OF ABBREVEATIONS

ANOVA	Analysis of Variance
ASTM	American Society Testing and Materials standard
AV	Acid value
CCD	Central Composite Design
CH_2CH_3	Ethanol
CH_3	Methanol
CH_3ONa	Sodium methoxide
C_{IS}	Concentration of internal standard
CO	Carbon Monoxide
DF	Dilution factor
DG	Diglyceride
DOE	Design of Experiment
EN	European Union
FAAE	Fatty acid alkyl esters
FAME	Fatty Acid Methyl Esters
FFA	Free fatty acids
FID	Flame ionized detector
GC	Gas chromatography
GL	Glycerol
H_2O	Water
H_2SO_4	Sulphuric Acid
H_3PO_4	Phosphoric Acid
IS	Internal standard
IV	Iodine Value
KOH	Potassium hydroxide
M	Molecular weight
MA	Methyl Acetate
MeOH	Methanol
MG	Monoglyceride
MPOB	Malaysian Palm Oil Board
NaOH	Sodium hydroxide
R_f	Ratio of reference
R_s	Ratio of sample
RSM	Response Surface Methodology
R-squared	Regression squared
SCM	Supercritical Methanol
SCMA	Supercritical Methyl Acetate
SV	Saponification value
TG	Triglyceride
V	Volume
VL	Vapour-liquid
VLL	Vapour-liquid-liquid

LIST OF SYMBOLS

°	Degree
α	Distance of axial point from center
n	Number of independence variables
x	Independence variables
β	Regression coefficient
ε	Random error
T_c	Critical temperature
T_b	Boiling point
P_c	Critical pressure
d	Density
δ	Polarizability parameter
Y	Yield/response
e	Experimental error
f	function

PENGHASILAN BIODIESEL DARI MINYAK JARAK MENGGUNAKAN PROSES METIL ASETAT DAN METANOL GENTING LAMPAU

ABSTRAK

Biodiesel yang disintesis dari minyak tidak boleh makan iaitu minyak *Jatropha curcas* L. (*Jatropha*) menawarkan beberapa beberapa faedah berbanding minyak boleh makan seperti tidak bersaing dengan sumber makanan. Namun, minyak *Jatropha* mengandungi kandungan asid lemak bebas yang tinggi, maka penghasilan biodiesel melalui mangkin alkali konvesional boleh menyebabkan masalah saponifikasi. Selain itu, penggunaan methanol dalam proses transesterifikasi mungkin akan menimbulkan penghasilan gliserol yang berlebihan sebagai produk sampingan. Oleh itu, dalam kajian ini, kaedah genting lampau tanpa pemangkinan menggunakan metil asetat sebagai pelarut telah digunakan dalam transesterifikasi minyak *Jatropha* untuk menghasilkan biodiesel. Namun demikian, kaedah metanol genting lampau (SCM) juga telah diselidiki untuk tujuan perbandingan. Pengaruh jangka masa, suhu tindakbalas dan nisbah molar pelarut terhadap minyak *Jatropha* telah dikaji dan dioptimumkan menggunakan "Design of Experiment". Tekanan bagi tindakbalas dijalankan secara konsisten pada tekanan kritikal metal asetat dan methanol iaitu 40 dan 80 bar. Keputusan kajian menunjukkan bahawa untuk proses genting lampau menggunakan metil asetat (SCMA), keadaan optimum untuk menghasilkan biodiesel, berada pada waktu tindakbalas 32 minit, suhu tindakbalas 399 °C dan nisbah molar metil asetat terhadap minyak pada 50. Keputusan hasil optimum biodiesel adalah 71.8 wt%. Sementara itu, untuk proses SCM, hasil optimum FAME yang sebenar diperolehi adalah lebih tinggi iaitu 89.4 wt% dan

boleh dicapai pada keadaan optimum seperti berikut: masa tindakbalas 27 minit, suhu tindakbalas 358 °C dan nisbah molar metanol terhadap minyak pada 44. Didapati bahawa metil asetat mempunyai kelarutan yang tinggi dalam trigeliserida, menyebabkan kereaktifan yang lebih rendah dalam tindakbalas SCMA, sehingga hasil biodiesel yang diperolehi lebih rendah daripada yang diperolehi dalam proses SCM. Namun demikian, reaksi SCMA telah menunjukkan bahawa triasetin dapat dihasilkan dalam tindakbalas dan bukan gliserol. Semua pembolehubah individu dipelajari dalam proses SCMA dan SCM menunjukkan kesan positif terhadap hasil FAME. Sementara hanya beberapa interaksi pembolehubah mempengaruhi hasil FAME. Selain itu, dalam kajian kestabilan terma, metil linoleat dan triasetin didapati menjadi tidak stabil dalam tindakbalas SCMA apabila bertindakbalas pada suhu yang tinggi kerana fenomena penguraian. Kedua-dua kaedah didapati mempunyai kesan yang boleh diabaikan terhadap kewujudan air dan kandungan asid lemak bebas dalam tindakbalas. Pengaruh penambahan asid asetik dalam proses SCMA menunjukkan kesan positif terhadap hasil FAME kerana ia menyediakan kesan pemangkin dalam tindakbalas. Pencirian biodiesel *Jatropha* menunjukkan bahawa biodiesel *Jatropha* dapat memenuhi spesifikasi ASTM D6751.

BIODIESEL PRODUCTION FROM *JATROPHA CURCAS* L. OIL USING SUPERCRITICAL METHYL ACETATE AND METHANOL PROCESS

ABSTRACT

Biodiesel synthesized from non-edible oil of *Jatropha curcas* L. (*Jatropha*) oil offers several advantages compared with edible oil such as it does not compete with food resources. However, *Jatropha* oil consists of high free fatty acids content, hence, the production of biodiesel through conventional alkaline catalyst may lead to problems with saponification. Furthermore, the application of methanol in transesterification process may result to oversupply of glycerol production as by-product. Therefore, in this study non-catalytic supercritical method using methyl acetate as the solvent was employed in transesterification of *Jatropha* oil to produce biodiesel. Nevertheless supercritical methanol (SCM) method was also been investigated for comparison purposes. The effects of reaction time, reaction temperature and molar ratio of solvent to oil were studied and optimized using Design of Experiment. The reaction pressure was consistently operated at critical pressure of methyl acetate and methanol which were 40 and 80 bar, respectively. The results revealed that for supercritical methyl acetate (SCMA) process the optimum conditions to produce biodiesel, were at reaction time of 32 minutes, reaction temperature of 399 °C and molar ratio of methyl acetate to oil at 50. The actual optimum yield of BDF was 71.8 wt%. Meanwhile, for SCM process, the actual optimum yield of FAME obtained was higher which was 89.4 wt% and can be achieved at the following optimum conditions: reaction time of 27 minutes, reaction temperature of 358 °C and molar ratio of methanol to oil at 44. It was found that

methyl acetate has high solubility in triglyceride, leading to lower reactivity in the SCMA reaction, thus the yield of biodiesel obtained was lower than the one obtained in SCM process. Nevertheless, the SCMA reaction has shown that triacetin can be produced from the reaction instead of glycerol. All individual variables studied in SCMA and SCM process shows positive influence towards the yield of FAME, while only some interaction between variables affects the yield of FAME. Apart from that, in thermal stability study, methyl linoleate and triacetin were found to be not stable in SCMA reaction when reacting at high temperature due to decomposition phenomenon. Both methods were found to have negligible effect on presence of water and free fatty acids content in the reaction. The effect of acetic acid addition in SCMA process showed a positive influence on the yield of FAME as it provides catalytic effect in the reaction. The characterization of *Jatropha* biodiesel indicated that *Jatropha* biodiesel met the specification for biodiesel according to ASTM D6751.

CHAPTER ONE

INTRODUCTION

1.0   Biodiesel from Vegetable Oil

The current energy scenario is undergoing a period of transition as many energy consumers have realized and understand the problems resulted from fossil fuels. Declining oil reserves and the enormous impact of transportation's demand for oil on the economy and global climate change suggest that the most critical need for a sustainable energy future is a new way to fuel our vehicles. Examples of alternative fuel options that can be utilized to replace fossil fuels are mainly biogas, producer gas, biomethanol, bioethanol and vegetable oils (Dorado, 2008). However, biogas and producer gas have low energy contents per unit mass and can substitute for diesel only up to 80%. Meanwhile, methanol and ethanol can only substitute up to 20-40% apart from having very poor calorific value and a low cetane number, which is unsuitable for high-compression diesel engines. Therefore, the use of vegetable oils as a new source for alternative fuel has attracted a lot of attention lately.

Processing of vegetable oils and animal fats as biodiesel can reduce exhaust emissions from compression ignition engines such as nitrogen and carbon monoxide (Nag, 2008). However, vegetable oil or animal fats cannot be used directly in diesel engine due to many problems. These include carbon deposits, oil ring sticking, lubricating problems, and thickening and gelling of the lubricating oil as a result of contamination by vegetable oils (Ma & Hanna, 1999). Other disadvantages to the direct use of vegetable oils are the high viscosity (about 11 to 17 times higher than

1

petroleum based diesel fuel), lower volatilities content which causes the formation of deposits in engines due to incomplete combustion and inappropriate vaporization characteristics. Thus, many recent developments have been studied to reduce the viscosity associated with vegetable oil. One of them is transesterification which seems to be the best choice since it is possible to produce fatty acid alkyl esters (biodiesel) with physical properties very close to petroleum-derived diesel (Demirbas, 2006). Figure 1.1 shows the conventional biodiesel production and purification steps.
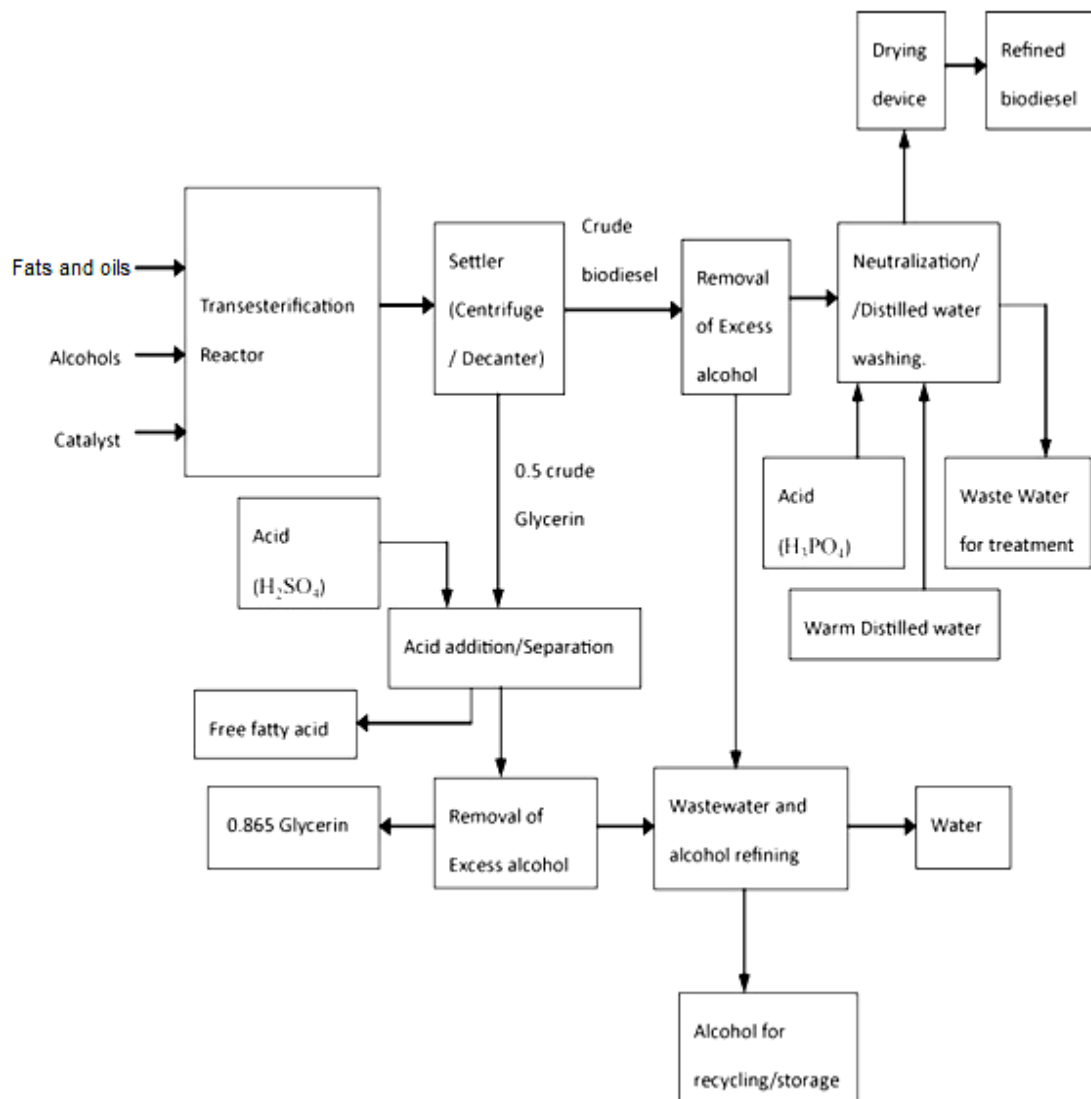
Figure 1.1: Conventional biodiesel production and purification steps (Atadashi et al., 2010)

Transesterification is an equilibrium reaction which will convert triglyceride to FAME and by-products. Generally, the reaction will result to high yield of biodiesel, however, low yield of biodiesel could be obtained due to low conversion of the feedstocks (unreacted feedstock) in the reaction. This unreacted feedstock will result in the presence of impurities such as glycerol, monoglyceride and diglyceride, which are unfavourable for engine performance. The most common methods to produce biodiesel are through conventional catalytic and supercritical non-catalytic transesterification. In conventional catalytic transesterification, either homogenous or heterogeneous base or acid catalyst can be applied. Even though there is a great interest in both of these processes, there are some drawbacks that need to be considered. The problem with homogenous transesterification is that it is very sensitive to fatty acids and water concentration which could lead to saponification. The soap formed prevents glycerol separation and will damage the engine in the long run; hence, a further purification step is needed to separate it from biodiesel. Apart from that, there is also the problem of immiscible phases of the lipid and alcohol, which requires vigorous stirring to enable good contact of reactants for the reactions to occur (Kusdiana & Saka, 2001). Even though heterogeneous transesterification offers a series of advantages such as recovery of catalyst, however, refined feedstock is still specifically required for the base catalyst and they tend to lose their catalytic activity after several reuses (Di Serio et al., 2007; Di Serio et al., 2008; Marchetti et al., 2007a; Ngamcharussrivichai et al., 2007). Furthermore, the disadvantages of heterogeneous solid acid catalyst include corrosive, longer reaction time and weak catalytic activity (Juan et al., 2011). Due to these disadvantages, another alternative has been considered; supercritical non-catalytic transesterification process.

1.1 Supercritical Non-catalytic Method for Biodiesel Production

One of the advantages of biodiesel production by supercritical method is it does not require any catalysts or auxiliary chemical and does not generate significant wastes (Demirbas, 2002; Kusdiana & Saka, 2001; Pinnarat & Savage, 2008; Saka & Kusdiana, 2001). Figure 1.2 shows a schematic diagram for biodiesel production by supercritical methanol (SCM). This figure shows that biodiesel production by SCM requires a minimum number of processing steps because the feedstock pre-treatment to remove moisture and free fatty acids, as well as some of the product post-treatment steps, such as neutralization, washing and drying are not necessary (Sawangkeaw et al., 2010). As a consequence, this method has a low overall production time.
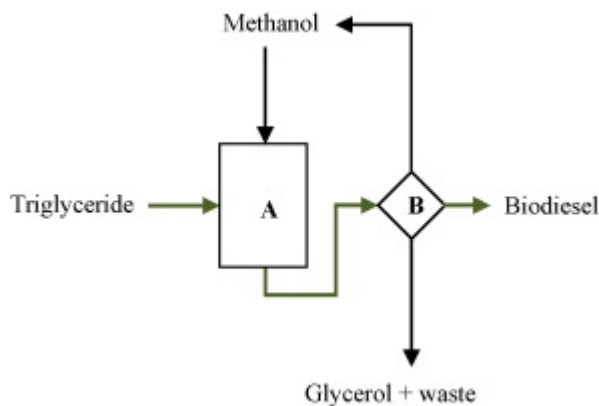
Figure 1.2: Biodiesel production with SCM: (A) reactor and (B) product separation and methanol recovery unit (Sawangkeaw et al., 2010)

Currently, most of researches on biodiesel production have been conducted on supercritical alcohol. Methanol (Demirbas, 2009a) and ethanol (Vieitz et al., 2008) are the most common type of alcohols used to make biodiesel. Biodiesel production with SCM still has several challenges in its research and development. For example, to achieve the highest oil and methanol to FAME conversion rates and

yields, high pressures (19-45 MPa), high temperatures (320-350 °C) and high methanol to oil ratios (40:1-42:1) have been reported in several studies (Demirbas, 2002; Kusdiana & Saka, 2001; Saka & Kusdiana, 2001). Hence, there are some researches that have been conducted which focused upon reducing the high operating pressure, temperature and methanol to oil molar ratio by several techniques such as the addition of co-solvents or catalysts by using a modified supercritical process (Cao et al., 2005; Han et al., 2005; Tan et al., 2010a; Yin et al., 2008).

Even though the application of co-solvents to reduce the high operating pressures, temperatures and molar ratio of methanol to oil ratio make this process attractive, however, the over-produced glycerol becomes another hurdle in the supercritical methanol process. Consequently, the non-catalytic supercritical method has turned to a new solvent application such as methyl acetate to produce glycerol-free biodiesel. Supercritical methyl acetate (SCMA) produces triacetin at the end of reaction other than FAME. Triacetin has no adverse effects on the main fuel characteristics and the addition of triacetin to methyl oleate improved the pour point of biodiesel (Saka & Isayama, 2009). Hence, supercritical methyl acetate technology is a promising method to produce a clean renewable fuel.

1.2   Feedstock for Biodiesel Production

Vegetable oil has commonly been used as oil feedstock for biodiesel production since it is readily available in large quantities. Figure 1.3 shows the global vegetable oil production (Carter et al., 2007). In year 2008, palm oil is the largest supply of edible oil in the world with Malaysia being the largest producer (Sumathi

et al., 2008). Palm oil has dominated the world's vegetable oil demand because of its versatile applications ranging from food to consumer products, and currently being utilized as biodiesel. Furthermore, palm oil has high oil yield, requires smaller area of land to produce oil and has the lowest production cost relative to other energy crops (Janaun & Ellis, 2010). However, in terms of the properties of biodiesel derived from palm oil, even though it meets the requirement of EN 14214 and ASTM D6751 standards, palm oil biodiesel is typically associated with high cloud point and pour point, limiting its usage in warmer climates (Janaun & Ellis, 2010). In addition, utilization of palm oil like other edible oils (soybean, canola, sunflower, and rapeseed) is expected to create a short supply of food for human consumption (Emil et al., 2010).
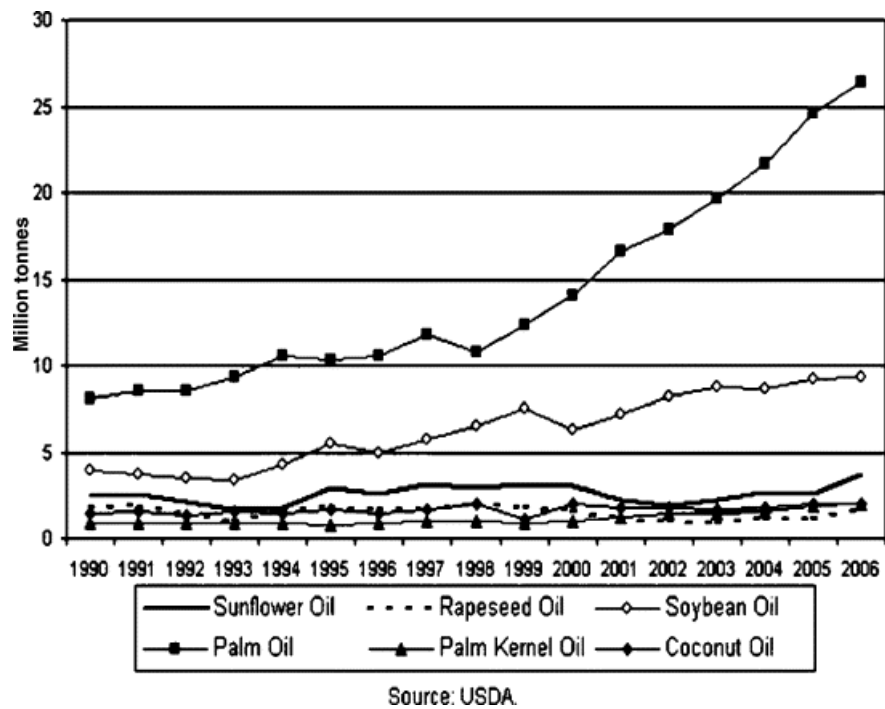
Figure 1.3: Global vegetable oil production (Carter et al., 2007)

The utilisation of non-edible oil as biodiesel feedstock is expected to minimize the problems associated with edible oil. Table 1.1 shows the examples of non-edible oil source and its oil yield. Among the oils, *Jatropha* is receiving considerable attention in many parts of the world due to the advantages such as higher yield than other vegetable oils, easy to cultivate and possible reclamation of waste land for cultivation (Openshaw, 2000). In addition, conversion of *Jatropha* oil into biodiesel is comparable in the process and quality to other type of edible oils (Pinzi et al., 2009).

Table 1.1: Oil yield for major non-edible oil resources (Gui et al., 2008)

Oil source	Oil yield (kg oil/ha)	Oil yield (wt %)
Jatropha	1590	Seed (35-40); Kernel (50-60)
Rubber seed	80-120	40-50
Castor	1188	53
Pongamia pinnata	225-2250	30-40
Sea mango	N/A	54

1.3   Problem Statement

Fatty acid methyl esters, also called biodiesel have been accepted widely and have become the leading biofuel for diesel engines since they have very similar fuel properties to fossil fuel and can be used without any changes to the engine. However, current production technology of biodiesel through conventional homogenous transesterification is time consuming and may require complicated purification steps. On the other hand, non-catalytic supercritical methanol method offers less

problematic and easier operation compared with homogenous reaction. However, supercritical method using methanol as the solvent produces glycerol as side product which may also complicate the separation process. Hence, a new solvent for glycerol free biodiesel production could create simpler reaction and solve the problems with overproduced glycerol.

The exploitation of edible oils for biodiesel production may lead to controversial issues of food versus fuel. This is because the supply and demand of oil for fat and food industries may be jeopardize if edible oils are being utilized for fuel as well. Due to this factor, it is crucial to search for other alternative oil feedstock for biodiesel production to substitute edible oils.

Therefore, the aim of this work is to study the feasibility of methyl acetate as a solvent for non-catalytic supercritical method in the production of biodiesel. *Jatropha curcas* oil will be used as oil feedstock to investigate its feasibility as non-edible oil for biodiesel production via glycerol – free production method.

1.4   Research Objective

This research project aims to achieve the following objectives:

i)   To study, optimize and compare the transesterification of *Jatropha curcas* oil using SCMA and SCM with varying process variables; reaction time, reaction temperature and molar ratio of methyl acetate (MA)/methanol (MeOH) to oil.

ii)   To investigate the thermal stability of FAME and triacetin in supercritical methyl acetate

iii) To study the effects of water, free fatty acids and acid acetic concentration on FAME yield in supercritical treatment.

iv)   To characterize the extracted *Jatropha* oil and the *Jatropha* biodiesel produced from SCMA reaction according to the required standard.

1.5   Scope

This study consists of oil extraction, transesterification process study using supercritical methyl acetate and methanol, thermal stability study of fatty acid methyl esters (FAME) and triacetin in supercritical methyl acetate, and effect of water, free fatty acid and acetic acid concentration on FAME yield. The purpose of oil extraction is to obtain the oil required throughout this study and also to determine the oil content of *Jatropha curcas*. The extracted oil was also characterized based on Malaysian Palm Oil Board (MPOB) standard method (MPOB P2.3, P2.5, P3.1, P3.2) to determine its basic properties such as acid value, iodine and fatty acid value as well as peroxide value.

For transesterification process study, biodiesel was synthesized using methyl acetate as solvent by non-catalytic supercritical method. The range of temperature studied was from 340 °C to 420 °C, reaction time of 10 to 110 minutes and molar ratio of methyl acetate to oil from 20 mole/mole to 60 mole/mole. All these process variables were then optimized. Subsequently, the feasibility of methyl acetate as a solvent in transesterification of FAME was compared with supercritical methanol. The range of temperature studied for supercritical methanol is 276 °C to 394 °C,

reaction time from 5 to 35 minutes and molar ratio of methanol to oil from 5 mole/mole to 61 mole/mole. The ranges of variables chosen in this study are also comparable with reported studies for biodiesel production using supercritical method.

Finally, thermal stability study of FAME and triacetin, and the effects of water, free fatty acid and acetic acid concentration on biodiesel yield by supercritical methyl acetate was investigated further. This study was investigated based on the optimum conditions obtained in transesterification process studied using supercritical methyl acetate. The subsequent results obtained from effects of water and free fatty acids studies were compared with supercritical methanol based on experimental runs. The FAME sample obtained was also characterized and compared with the American Society Testing and Materials (ASTM D6751) and European standard (EN 14214) standard.

1.6   Organization of Thesis

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

Chapter 1 gives the introductory of the research project. This chapter starts with current energy scenario that leads to development of alternative energy particularly biodiesel. This chapter also gives brief information about biodiesel production particularly supercritical method and also example of feedstock to produce biodiesel.

The problem statement, scope and objective 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 definition of biodiesel, advantages and disadvantages of biodiesel, and transesterification process. Further in this chapter gives the reviews on feedstock and solvents available for synthesis of biodiesel. Other topics covered in this chapter include description on variables affecting transesterification process, thermal stability, biodiesel quality and design of experiment.

Chapter 3 describes the materials and methodology used in this project. The first part explains about the list of materials and chemical used in this research project. The subsequent topics describe the methodology of extraction and characterization of *Jatropha curcas* oil, transesterification process study, analysis and characterization of FAME.

Chapter 4 presents the results and discussions of this project. The first part of the chapter contains the results and discussion of *Jatropha* oil properties. This is followed by transesterification study using supercritical methyl acetate. The results and discussion include design of experiment, development of regression model equation, results on statistical analysis, effects of process variables and optimization study. Similar topics are also discussed for transesterification study using supercritical methanol. Then, thermal stability study in supercritical methyl acetate, as well as the effects of water, free fatty acids and acetic acid concentration on FAME are discussed. Subsequent topic on this chapter contains the discussion on

difference between the performance of supercritical methyl acetate and methanol. The final part of this chapter presents the results and discussion of biodiesel characterization.

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

CHAPTER TWO

LITERATURE REVIEW

This chapter reviews background information of the study. It begins with brief information on biodiesel, advantages and disadvantages of biodiesel, methods and feedstock to produce biodiesel, introduction on solvents, *Jatropha curcas* oil, and variables affecting transesterification reaction. The description on biodiesel quality is presented in the subsequent topic. Finally the design of experiments (DOE) using response surface methodology (RSM) combined with central composite design (CCD) is presented at the end of chapter.

2.1   Biodiesel

2.1.1   Definition of Biodiesel

Biodiesel is defined as an alternative diesel fuel comprised of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fat. This fuel is obtained by a transesterification reaction with an alcohol; with or without the presence of a catalyst to produce glycerol as co-product (Janaun & Ellis, 2010). In experimental studies, the final product is termed as fatty acid alkyl esters (FAAE) or fatty acid methyl esters (FAME) instead of biodiesel unless it meets the specification of ASTM D6751 (Knothe, 2010).

2.1.2 Advantages and Disadvantages of Biodiesel

The application of biodiesel in diesel engines is advantageous for its environmental friendliness over petrol-diesel. The main advantage of using biodiesel is that it helps to reduce carbon dioxide and other pollutants emitted from vehicle engines (Juan et al., 2011). The use of millions of vehicles across the globe contribute a lot in generating green house gases such as carbon dioxide, carbon monoxide, nitrogen oxide and sulphur which cause climatic distraction such as global warming (Atadashi et al., 2010). It has been reported that commercial biodiesel fuel can significantly reduced exhaust emissions by 75-83% compared to petro-diesel based fuel (Demirbas, 2009b). Furthermore, Helwani et. al (2009) have reported that combustion of neat biodiesel decreases carbon monoxide (CO) emission by 46.7%, particulate matter emission by 66.7% and unburned hydrocarbons by 45.2%.

Biodiesel also provides significant lubricity improvement over petro-diesel fuel (Demirbas, 2009b; Quesada-Medina & Olivares-Carrillo, 2011). This lubrication property helps in improving the fuel injectors and fuel pumps lubrication capacity. This could therefore prolong the self-life of the engines. Biodiesel also has better properties compared to petro-diesel in terms of biodegradability, free sulphur content, viscosity, density and flash point (Andrade et al., 2011; Prafulla & Shuguang, 2009). Other advantages of biodiesel are it is synthesized from renewable sources (Juan et al., 2011), portability, lower aromatic content and high combustion characteristics (Atadashi et al., 2010).

Although the environmental considerations for biodiesel are particularly favourable in terms of overall reduced emissions, however, the disadvantages of biodiesel include increase emission of nitrogen oxides (Szybist et al., 2005) and higher fuel cost compared to petroleum due to higher cost of lipid feedstock (Knothe, 2010). However, the cost of biodiesel could vary depending on local conditions such as distance from plantation to production site and availability of local feedstock (Soetaert & Vandamme, 2009). Another disadvantage associated with the use of biodiesel is poor low-temperature flow properties, due to relatively high cloud and pour point (Knothe et al., 2005; Mittelbach & Remschmidt, 2004). This problem could clog fuel lines and filters and causing major operability problems. Despite of these several drawbacks of biodiesel, the advantages of biodiesel nevertheless superseded generally on the environmental aspects, thus making it a very popular alternative fuel to replace petroleum derived diesel oil.

2.1.3 Transesterification Process

Several methods have been developed to convert vegetable oil such soy and rapeseed oil into biodiesel. These methods include direct use of vegetable oil, micro-emulsion, thermal cracking and transesterification (Juan et al., 2011). Direct use of vegetable oil is not applicable to most of diesel engines as the high viscosity would damage the engine by causing coking and trumpet formation (Agarwal & Agarwal, 2007). Meanwhile, biodiesel obtained from micro-emulsion and thermal cracking methods would likely lead to incomplete combustion due to a low cetane number and energy content (Leung et al., 2010). Cetane number is a measure of ignition quality. Hence, when cetane number is low, it shows an increased emission due to incomplete

combustion in the engine. Consequently, transesterification seems to be the best choice since the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel and the process is relatively simple (Demirbas, 2005).

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. As shown in Equation 2.1, transesterification is a reversible reaction and the transformation occurs essentially by mixing reactants. The source of vegetable oil (triglycerides) can be from edible or non-edible oil. The oil can be obtained from waste cooking oil or obtain directly from the oil-bearing seeds. The alkyl esters produced depend on the alcohol used where methanol ($R = CH_3$) and ethanol ($R = CH_2CH_3$) are the most common. The reaction can be catalyzed by homogenous, heterogeneous or enzymatic catalyst. Excess alcohol with adequate catalyst generally forces the reaction equilibrium toward the products of biodiesel esters and glycerol (Meher et al., 2006). The stoichiometric relationship requires 3 mol of alcohol per mole of triglyceride (3:1).

$$
\begin{array}{llll}
CH_2\text{-}OOC\text{-}R_1 & R_1\text{-}OOC\text{-}R' & CH_2\text{-}OH & \\
| & & | & \\
CH_2\text{-}OOC\text{-}R_2 \ + 3\,R'OH \quad \leftrightarrow \quad R_2\text{-}OOC\text{-}R' \ + & CH_2\text{-}OH & (2.1) \\
| & & | & \\
CH_2\text{-}OOC\text{-}R_3 & R_3\text{-}OOC\text{-}R' & CH_2\text{-}OH & \\
\end{array}
$$

Triglycerides   Alcohol   Fatty acid alkyl esters   Glycerol
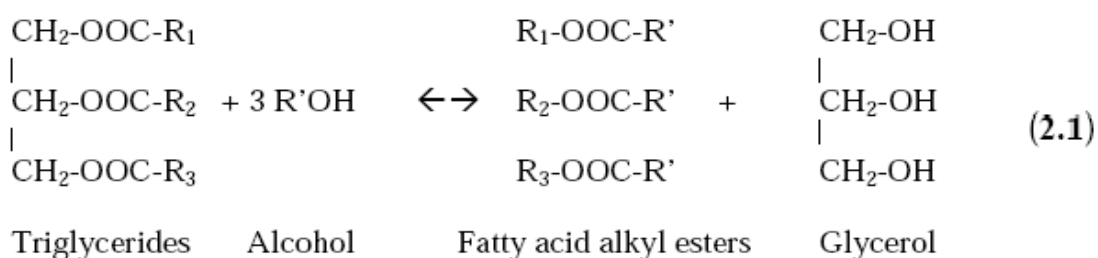
The overall process to produce alkyl esters is reversible in which it consists of three consecutive steps as can be seen in Equation 2.2a, 2.2b and 2.2c (Ma & Hanna, 1999). In the first step, reaction between triglyceride and alcohol produces

diglyceride and ester. Then in the second reaction, diglyceride from the first reaction step reacts with alcohol to produce monoglyceride and esters. Finally, the reaction between monoglyceride from the second reaction with alcohol produces esters and glycerol.

$$\text{Triglycerides (TG)} + \text{R'OH} \leftrightarrow \text{Diglycerides (DG)} + \text{R'COOR}_1 \qquad (2.2a)$$

$$\text{Diglycerides (DG)} + \text{R'OH} \leftrightarrow \text{Monoglycerides (MG)} + \text{R'COOR}_2 \qquad (2.2b)$$

$$\text{Monoglycerides (MG)} + \text{R'OH} \leftrightarrow \text{Glycerol (GL)} + \text{R'COOR}_3 \qquad (2.2c)$$
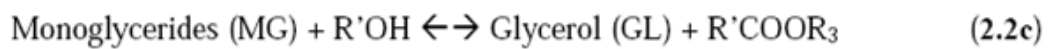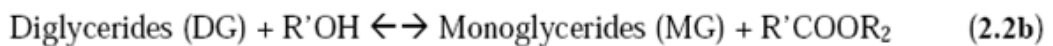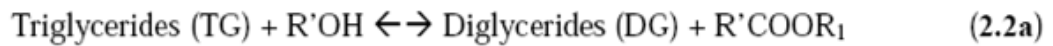
Other than alcohol, biodiesel can also be produced using other type of solvent. For instance, methyl acetate has been utilized to produce biodiesel. The reaction is presented in Equation 2.3 where the reaction between triglyceride and methyl acetate produces FAME and triacetin.

$$
\begin{array}{llll}
CH_2 - OCOR^1 & & R_1COOCH_3 & CH_2 - OCOCH_3 \\
| & & & | \\
CH - OCOR^2 & + 3\ CH_3COOCH_3 \leftrightarrow & R_2COOCH_3 \quad + & CH - OCOCH_3 \\
| & & & | \\
CH_2 - OCOR^3 & & R_3COOCH_3 & CH_2 - OCOCH_3 \\
\\
\text{Triglycerides} & \text{Methyl Acetate} & \text{FAME} & \text{Triacetin}
\end{array}
\qquad (2.3)
$$
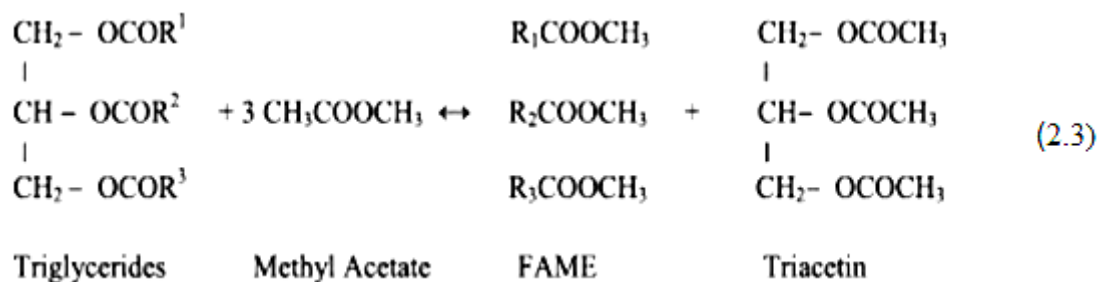
Similar to the reaction between triglyceride with alcohol, the reaction between triglycerides and methyl acetate is reversible and produces one molecule at a time to generate one molecule each of monoacetylglyceride and FAME. In the same manner, diacetylglyceride and FAME are generated from monoacetylglyceride and methyl acetate, and finally triacetin and FAME are generated from

diacetylglyceride and methyl acetate (Saka & Isayama, 20009). When methyl acetate is utilized, triacetin generated is also considered as the product since it can act as biodiesel additive.

2.1.4   Methods and Catalysts for Biodiesel Production

Generally, there are two methods of transesterification which are catalytic and non-catalytic transesterification. In catalytic reaction, various catalysts are employed such as homogenous base and acid catalyst, heterogeneous and enzymatic catalyst. Meanwhile, non-catalytic reaction includes supercritical and subcritical processes, and co-solvent system.

2.1.4 (a) Catalytic Method

In general, a catalyst is used to initiate the esterification reaction for making biodiesel. The catalyst enhances the solubility of alcohol and thus increase the reaction rate (Karmakar et al., 2010). The type of catalyst used for producing biodiesel is very much dependent on free fatty acids (FFA) content of vegetable oil (Juan et al., 2011). The most commonly used base catalysts are sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium methoxide (CH_3ONa) (Vicente et al., 2004). Normally, homogenous base catalytic method is used when FFA content of the feedstock is less than 1%. The base-catalyzed process proceeds faster than acid-catalyzed reaction and a successful transesterification reaction by this catalyst produces two liquid phases which are ester and crude glycerol (Demirbas, 2008).

However, base-catalyzed reaction is affected by water content and free fatty acids of oils or fat. Free fatty acids can react with base catalysts to form soaps and water, thus decreasing the yield of biodiesel and make the separation of biodiesel and glycerol difficult.

On the other hand, homogenous acid catalyst is used when there is a high amount FFA content of more than 1%. The examples of acid catalysts used are sulphuric acid (H_2SO_4) and phosphoric acid (H_3PO_4). Acid catalysts can simultaneously catalyze both esterification and transesterification reactions. The advantage of using acid catalyst is that they can directly produce biodiesel from low-cost lipid feedstock, generally associated with high FFA concentrations (Lotero et al., 2005). However, reaction with acid catalysts has slow reaction rate and requires high ratio of alcohol to triglyceride (Karmakar et al., 2010).

Heterogeneous catalyst is a type of solid catalyst which allows the catalyst to be easily separated from the biodiesel by simple filtration. The heterogeneous catalyzed process used solid catalyst such as metal oxides (Marchetti et al., 2007b), zeolites, resins, membranes and enzyme to catalyze the transesterification process. Application of heterogeneous catalyst could eliminate those post-reaction purification steps such as neutralization and washing as needed in homogenous catalyst process (Atadashi et al., 2011). In addition, it could potentially lead to cheaper production costs because the catalyst can be reused since it can be separated easily (Lopez et al., 2005). However, generally heterogeneous catalyst system faces difficulties in term of leaching of active sites from solid catalyst (Lopez et al., 2005).

Enzymatic transesterification using lipase is another method of biodiesel production. This method has advantages in terms of easy product separation, minimal wastewater treatment needs, easy glycerol recovery and absence of side reactions (Raman et al., 2008). However, the largest obstacle of this method is the high cost for applying enzymes to industrial systems where the goal is to make a product in high volume and at lower cost (Modi et al., 2007).

2.1.4 (b) Non-catalytic Method

Supercritical and subcritical alcohol transesterification are the examples of reaction without the need of catalyst. This method could omit costly and time-consuming steps of removing catalyst as well as special equipment required for handling highly corrosive catalyst. In addition, transesterification reaction in supercritical conditions can be completed within minutes, while conventional catalytic transesterification normally takes several hours (Huayang et al., 2007). Another positive effect of using supercritical conditions is that the alcohol does not only act as reactant but also as an acid catalyst (Kusdiana & Saka, 2004).

Above the critical temperature, a gas cannot be liquefied. Thus, supercritical fluid poses liquid as well as gaseous properties that have a lot of application including to carry out chemical reactions (Mittelbach, 2009). Table 2.1 shows the critical states for alcohol ranging from methanol to 1-octanol as reported by Warabi et. al (2004a). In their study, the reaction conditions for esterification and transesterification of different alcohols were determined where percent conversion to fatty acids esters were shown at 10 minutes and 30 minutes reaction times of 300

20

°C. In general, the more unsaturated the fatty acid is, the faster the rates of esterification. Meanwhile, transesterification of rapeseed oil triglycerides exhibited slower rates of conversion than esterification reactions. However, the duration required for complete conversion was close to the alkali-catalyzed transesterification. Referring to Table 2.1, it shows that methanol is the best solvent for transesterification since the yield of FAME obtained is much higher than other types of alcohols used. In methanolysis, the methoxide ion formed could break down the triglyceride easily to form FAME and glycerol. Hence, this could be one of the reasons why reaction with methanol produces higher yield.

Table 2.1: Critical states and yield of fatty acids esters for different alcohols (Warabi et al., 2004a)

Alcohol	Critical temperature (°C)	Critical pressure (MPa)	Reaction pressure at 300 °C (MPa)	Esterification yield (10 min) %	Transesterification yield (30 min) %
Methanol	239	8.09	20	98	98
Ethanol	243	6.38	15	79	88
1-propanol	264	5.06	10	81	85
1-butanol	287	4.90	9	80	75
1-octanol	385	2.86	6	-	-

In another study on supercritical alcohol reported by Kusdiana and Saka (2001), the reaction kinetics for subcritical and supercritical transesterification of rapeseed oil was investigated. They reported that supercritical methanol performed much better than subcritical conditions with an optimum reaction temperature of 350 °C and optimum pressure of 19 MPa. In addition, high molar ratio of methanol to oil of 42:1 significantly increases conversion rates. The conversion of biodiesel reported

at this optimum condition were nearly 95 wt% compared to 60 wt% for a 6:1 ratio at 350 °C when reaction duration was fixed at 4 minutes.

2.1.5 Side Reactions: Saponification and Hydrolysis

Normally, transesterification reaction can be accompanied with side reactions such as saponification and hydrolysis. These reactions depend on the quality of feedstock. High FFA content present in vegetable oil will be neutralized with excess base, thus potentially resulting in two undesirable products (Lotero et al., 2005).

As shown in Equation 2.4, saponification creates soap and water from excess free fatty acids in the mixture. Meanwhile Equation 2.5 shows a second type of side reaction, hydrolysis reaction, which causes conversion of biodiesel esters, via base catalysis to free fatty acids. The free fatty acids can subsequently react with base-catalyst and will result in the formation of more soap and water until the catalyst is finally consumed and deactivated.

$$RCOOH \quad + \quad NaOH \quad \longleftrightarrow \quad R'COONa^+ \quad + \quad H_2O \qquad (2.4)$$

FFA   Base catalyst   Soap   Water

$$RCOOR' \quad + \quad H_2O \quad \longleftrightarrow \quad RCOOH \quad + \quad R'OH \qquad (2.5)$$

Alkyl ester   Base catalyst   FFA   Alcohol
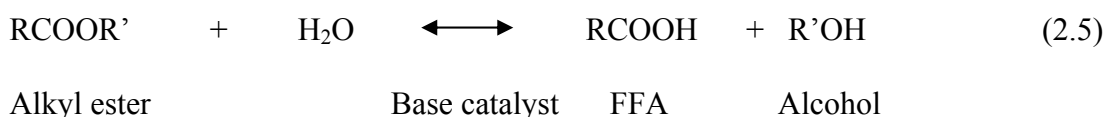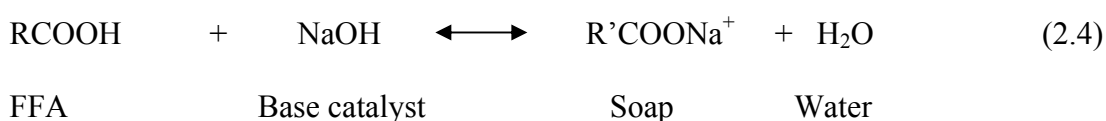
2.1.6   Glycerol Production

The production of biodiesel is accompanied by the formation of glycerol as the by-product when reacting triglycerides with alcohol. Glycerol is commonly used for personal care products such as soaps, cosmetics, hair care, toothpaste, in pharmaceutical, and also used as sweetener in candies and cake (Behr et al., 2008; Jakobson et al., 1989; Morrison, 1994).

The increase of biodiesel production in recent years has led to the oversupply of glycerol. Glycerol obtained from transesterification reaction does not require any further processing except purification (Knothe, 2010). However, in alkaline catalyzed method, glycerol phase was recovered along with a mixture of methanol, water, and alkaline catalyst. Thus, in order to produce pure glycerol, crude glycerol must be neutralized by acid such as sulphuric acid and this process forms a large quantity of salt. Therefore, purification of crude glycerol is complicated and cost consuming. The sales value of this crude glycerol is extremely low at approximately USD 0.1/kg, compared with the purified glycerol at approximately USD 1.3-2.0/kg. When the cost of transportation is considered, the market price becomes uneconomical (Johnson & Taconi, 2007). Therefore, effective production of biodiesel without glycerol formation is worth to be established.

There are a few processes proposed to overcome this problem. For instance, Fabbri et al. (2007) have proposed a study in which soybean oil was reacted with dimethyl carbonate, in the presence of sodium methoxide as homogenous catalyst to produce FAME and glycerol carbonate (GC) simultaneously. In this process, dimethyl carbonate is utilized as methylating agent instead of methanol and GC is

obtained as side product rather than the lower-valued glycerol. Even though the properties of biodiesel produced were comparable with those produced from conventional method-based reaction, however this method suffers from long reaction time (5 hours) and it still requires alkaline catalyst in the reaction which is difficult to be adapted for some vegetable oil especially those with high content of free fatty acids such as *Jatropha curcas* oil. Furthermore, the presence of catalyst necessitates tedious separation and purification procedures.

2.1.7   Feedstock to Produce Biodiesel

Generally, all types of vegetable oils and animal fats can be utilized as feedstock for biodiesel production. Most of these oils and fats have a similar chemical composition which consists of triglyceride with different amounts of individual fatty acids. The major difference between methyl esters from different feedstock is the amount of unsaturated fatty acids. The best combustion characteristics as well as oxidation stability of biodiesel can be obtained when it is derived from saturated fatty acids. However, cold temperature behaviour is unfavorable due to high melting points of these fatty acids. On the other hand, high unsaturated fatty acids leads to optimum cold temperature properties, but the oxidation and storage stability is not so good (Mittelbach, 2009).

Table 2.2 shows the oil and fatty acid composition of some selected vegetable oil sample.