

**REACTIVE EXTRACTION FOR THE SYNTHESIS OF FAME/FAEE FROM
JATROPHA CURCAS L. SEEDS**

by

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
AR4	The Fourth Assessment Report
ASTM	American Society for Testing and Materials
B5	5% of petro-diesel with palm-biodiesel
CJCO	Crude <i>Jatropha curcas</i> oil
CI	Confidence interval
CCD	Central composite design
DDGS	Distiller dried grains with soluble
DEM	Diethoxymethane
DOE	Design of experiment
f	Function
FAME	Fatty acid methyl esters
FAEE	Fatty acid ethyl esters
FFA	Free fatty acids
FID	Flamed ionized detector
F-value	Fisher test value
GC	Gas chromatography
IPCC	Intergovernmental Panel on Climate Change
IS	Internal standard
LD	Lethal dose
MBM	Meat and bone meal
NGO	Non-governmental organization
PM _{2.5}	Fine particulate matter
Prob	Probability
RSM	Response surface methodology

LIST OF SYMBOLS

α	Rotatability of CCD
ε	Error
A	Coded term of reaction time
$\beta_{0,1,2,..,k}$	Regression coefficients for Equation (2.1)
B	Coded term of reaction temperature
C	Coded term of methanol/ethanol to seed ratio
C_{IS}	Concentration of IS (g/L)
D	Coded term of catalyst loading
DF	Dilution factor
k	Design factor
R_f	Ratio of peak area of individual ethyl ester to peak area of IS in standard reference
R_s	Ratio of peak area of individual ethyl ester to peak area of internal standard (IS) in the sample
V	Volume of oil (mL)
$x_{0,1,2,..,k}$	Independent variables for regression equation in Equation (2.1)
Y	Dependent variables for regression equation in Equation (2.1)

**PENYARIAN BERTINDAK BALAS DALAM SINTESIS FAME/FAEE
DARIPADA BIJI *JATROPHA CURCAS* L.**

ABSTRAK

Oleh sebab sifat minyak yang tidak boleh dimakan dan kesesuaian untuk ditanam di iklim tropika Malaysia, minyak daripada biji *Jatropha curcas* L. dipercayai berpotensi untuk menjadi sumber minyak dalam penghasilan biodiesel selepas minyak kelapa sawit. Biodiesel daripada biji *Jatropha curcas* L. adalah secara konvensional dihasilkan melalui dua langkah; pengekstrakan minyak diikuti dengan pengesteran/ transesterifikasi untuk menjadi ester metil asid lemak iaitu biodiesel. Sebaliknya, dalam kerja penyelidikan ini, biodiesel yang dihasilkan daripada biji *Jatropha curcas* L. dalam satu langkah in situ pengekstrakan, pengesteran dan transesterifikasi (secara kolektif dikenali sebagai penyarian bertindak balas) telah dikaji. Biji *Jatropha* yang digunakan dalam penyelidikan ini didapati mengandungi kandungan lembapan dan minyak sebanyak 5.39% dan 54.4% masing-masing. Sementara itu, minyak *Jatropha* yang diekstrak didapati mengandungi asid lemak bebas (FFA) yang tinggi. Kerja penyelidikan ini bermula dengan menguji kesan pelbagai saiz dan kandungan lembapan biji *Jatropha* terhadap proses penyarian bertindak balas. Selepas itu, kajian proses bagi penyarian bertindak balas dengan menggunakan metanol dan ethanol dijalankan dengan proses parameter berikut: masa tindak balas, 1-24 jam; suhu tindak balas, 30-60 °C, (50–70°C bagi ethanol); nisbah metanol kepada biji *Jatropha*, 5-20 ml/g (5-15 ml/g bagi ethanol) dan pemuatan pemangkin 5-30 % jisim. Mangkin yang digunakan dalam penyelidikan ini ialah asid sulfurik, H₂SO₄. Untuk memastikan kajian proses dijalankan dengan sistematik,

rekabentuk ujikaji gabungan pusat (CCD) dan metodologi permukaan sambutan (RSM) telah digunakan untuk mengkaji hubungkait di antara hasil biodiesel dengan parameter proses yang dikaji. Maklumat ini seterusnya digunakan bagi tujuan pengoptimuman. Bagi penyarian bertindak balas dengan menggunakan metanol sebagai pelarut, hasil biodiesel optimum sebanyak 98.1 % jisim adalah didapati pada suhu 60°C, dengan nisbah metanol kepada biji *Jatropha* 10.5 ml/g, pemuatan pemangkin 21.8 % jisim dan masa tindak balas selama 10 jam. Apabila menggunakan etanol sebagai pelarut, hasil biodiesel optimum adalah hanya 80.9 % jisim diperolehi pada suhu 65°C, dengan nisbah etanol kepada biji *Jatropha* 8.5 ml/g, pemuatan pemangkin 23.75 % jisim dan masa tindak balas selama 18 jam. Perbezaan di antara kedua-dua hasil optimum ini adalah disebabkan oleh kadar tindak balas yang lebih lambat bagi etanol berbanding dengan metanol. Pemulihan minyak yang hampir sifar daripada biji *Jatropha* yang telah melalui penyarian bertindak balas menunjukkan bahawa hampir semua minyak dalam biji *Jatropha* telah diekstrak keluar untuk pengesteran/transesterifikasi dan ini juga menunjukkan keupayaan penyarian bertindak balas untuk mencapai kecekapan pengestrakan yang tinggi. Pencirian biodiesel yang diperolehi daripada penyarian bertindak balas daripada biji *Jatropha* dengan menggunakan metanol dan etanol menunjukkan bahawa teknologi ini berupaya untuk menghasilkan biodiesel yang boleh menepati piawaian biodiesel antarabangsa.

REACTIVE EXTRACTION FOR THE SYNTHESIS OF FAME/FAEE FROM *JATROPHA CURCAS* L. SEEDS

ABSTRACT

Owing to the non-edible nature and suitability for cultivation in local tropical climate in Malaysia, *Jatropha* oil (*Jatropha curcas*) is believed to be a potential oil source for biodiesel production after palm oil. Biodiesel from *Jatropha curcas* L. seed is conventionally produced via two steps method; extraction of oil and subsequent esterification/transesterification to fatty acid methyl esters (FAME) or commonly known as biodiesel. Contrary, in this research work, a single step in-situ extraction, esterification and transesterification (or collectively known as reactive extraction) of *Jatropha curcas* L. seed to biodiesel was studied. The *Jatropha* seed used in this study was found to have a moisture and oil content of 5.39% and 54.4% respectively, while the extracted oil was found to have high free fatty acid (FFA) content. In the preliminary study, this research work began by studying the effect of different *Jatropha* seed size and moisture content on the reactive extraction process. Subsequently, process study for reactive extraction of *Jatropha* seeds using methanol and ethanol was carried out by varying the following process parameters: reaction time, 1 – 24 hours; reaction temperature, 30 – 60°C; (50 – 70°C for ethanol) methanol to seed ratio, 5 – 20 ml/g (5 – 15 ml/g for ethanol) and catalyst loading, 5 – 30 wt%. Catalyst used in this study was sulphuric acid, H₂SO₄. In order to have a systematic process study, design of experiment (DOE) coupled with Response Surface Methodology (RSM) and Central Composite Design (CCD) was used to investigate the relationship between the yield of biodiesel with the process

parameters studied, which was then used for optimization purposes. For reactive extraction using methanol as solvent, an optimum *Jatropha* biodiesel yield of 98.1 wt% was obtained at reaction temperature of 60°C with methanol to seed ratio of 10.5 ml/g and 21.8 wt% of catalyst in 10 hours reaction time. When using ethanol, the optimum yield was only 80.9 wt% obtained at reaction temperature of 65°C with ethanol to seed ratio of 8.5 ml/g and 23.75 wt% of catalyst in 18 hours reaction time. The difference in optimum yield of biodiesel and optimum reaction conditions was due to the slow reaction rate of ethanol as compared to methanol. Negligible, oil recovery from spent *Jatropha* seeds indicated that almost all oil has been successfully extracted out from seeds for transesterification/esterification during reaction and thus indicating that reactive extraction can achieve high extraction efficiency. Characterization of biodiesel produced from reactive extraction of *Jatropha* seeds using both methanol and ethanol showed that this technology is feasible to produce biodiesel that can meet international biodiesel standards.

CHAPTER ONE:

INTRODUCTION

This chapter provides detail introduction of this research project. Brief definition, current market supply and demand of biodiesel are included at the beginning of this chapter. In addition, information about transesterification process is also included. This chapter concludes with problem statement, objectives and thesis organization of this research project.

1.1 Why Biodiesel?

Fossil fuels such as petroleum, coal and natural gas have been hailed as major energy resources in the world since its discovery. However, environmental problems caused by using these fossil fuels and the depletion petroleum reserve have driven the world to find alternative energy source to replace fossil fuels. In this regard, biodiesel becomes an attractive and promising alternative to replace conventional petroleum-derived fuels.

The energy demand in Malaysia has been rapidly increasing for the last 30 years as shown in **Figure 1.1**. The energy demand is forecasted to reach almost 100 Mtoe (million tonne of oil equivalent) by year 2030 (APEC energy demand and supply outlook, 2006).

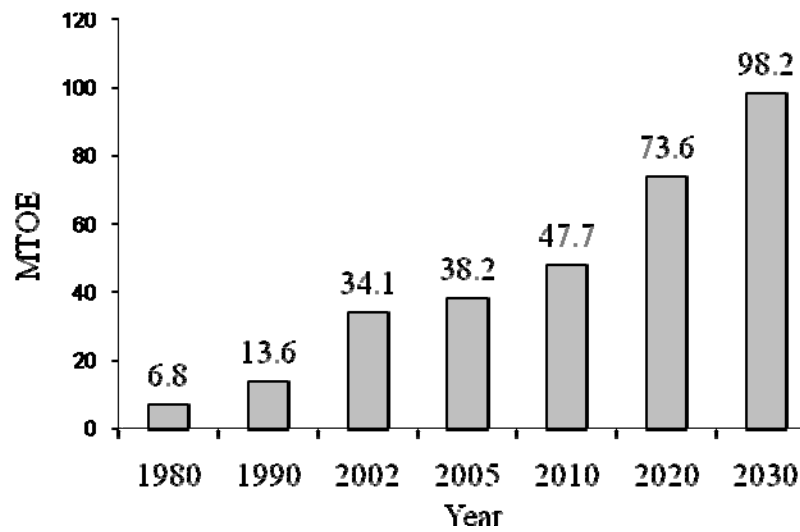


Figure 1.1: Energy demand in Malaysia (APEC energy demand and supply outlook, 2006).

Based on 2005 data as shown in **Table 1.1**, 93% of Malaysia energy consumption is still dependent heavily on fossil fuels which includes natural gas, coal, diesel and oil, while only 0.5% of energy came from renewable sources such as biomass (excluding hydropower) (Malaysian-German Chamber of Commerce, 2008). If this trend was to continue, Malaysia would suffer from lack of energy security as Malaysia fossil fuel reserves is predicted to last only up to the year 2100, if no new oil is discovered (Choo *et al.*, 2005). Beyond that, Malaysia will become the net importer of fossil fuel, mainly oil and gas. Therefore, it is inevitable that Malaysian government has to start looking for reliable source of renewable energy especially renewable energy that can be used as vehicles fuel such as biodiesel. The need for an urgent source of renewable vehicles fuel is further supported by the current increasing price of fossil fuel mainly petroleum. With price of crude oil at USD \$ 121.91 per barrel in July 2008, Malaysian government needs to spend a lot on subsidy to keep the cost of energy, mainly transportation fuel low (Oil-Price Net,

2008). In 2007 alone, Malaysia's fuel subsidies cost the country about RM40 billion (The Brunei Times, 2008).

Table 1.1: Malaysia's energy mix in 2005 (Malaysian-German Chamber of Commerce, 2008).

Source	Percentage, %
Gas	72.5
Coal	16.5
Hydropower	6.2
Diesel	3.2
Oil	0.8
Biomass	0.5
Others	0.3

Furthermore **Figure 1.2** indicates that transportation sector itself has contributed 30% of Malaysia total carbon dioxide emission in the year 2007 which is the second highest carbon dioxide emission sector after industry (PTM, 2007). Thus, in order to reduce emission of greenhouse gases, substitution of petroleum-derived vehicles fuel with renewable fuel such as biodiesel should be part of the climate change solution. In fact, the Government of Malaysia has embarked on this ideology by drafting the National Biofuel Policy that states the use of environmentally friendly, sustainable and viable sources of energy to reduce the dependency of depleting fossil fuels. Besides, The National Biofuel Policy also envisions that biofuel including biodiesel will be one of the five energy sources for Malaysia, enhancing the nation's prosperity and well being (Ministry of Plantation Industries and Commodities Malaysia, 2006).

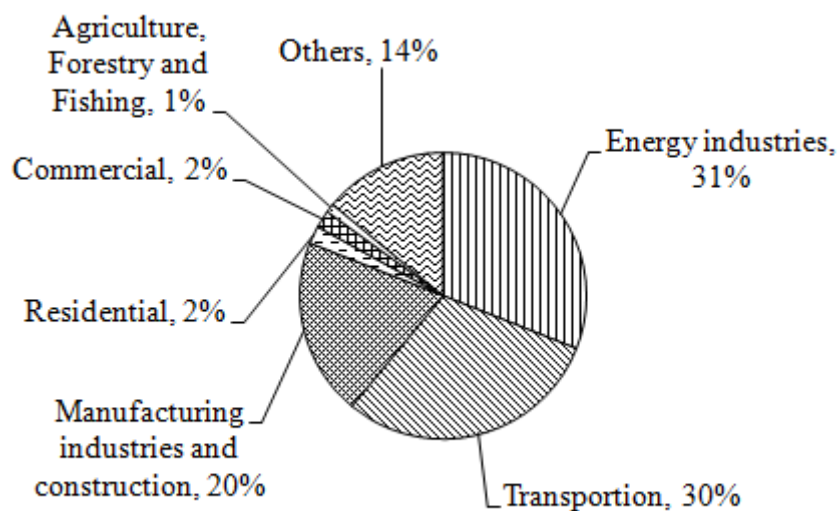


Figure 1.2: CO₂ emissions from various energy sectors in Malaysia (PTM, 2007).

1.1.1 Current Biodiesel Scenario

Biodiesel is also known as monoalkyl esters of long chain fatty acids which is derived from renewable feedstock such as edible oil, non-edible oil and even waste cooking oil (Apostolakou *et al.*, 2009). The physical and chemical properties of biodiesel are similar to petroleum-derived diesel which makes biodiesel a potential substitute fuel for petroleum-derived diesel. Apart from that, biodiesel is superior to petroleum-derived diesel since it is biodegradable, renewable, clean, non-toxic, has low emission profile and therefore is environmental friendly (Ma and Hanna, 1999).

Currently, edible oil is the most common feedstock for biodiesel production which accounts more than 95% of the world total biodiesel production owing to its easy availability. Rapeseed oil contributed 84% of the world biodiesel production, meanwhile sunflower oil contributed 13% and the remaining 3% is from palm oil (1%), soybean oil and others (2%) (Gui *et al.*, 2008). The practice of using edible oil

as feedstock for biodiesel production has raised objections from various organizations especially non-governmental organization (NGO), claiming that biodiesel is competing resources with the food industry causing the depletion of vegetable oil supply and subsequently increase in vegetable oil prices. In another words, to produce biodiesel, food resources are actually being converted into automobile fuels and it is believed that large scale production of biodiesel from edible oil may eventually bring global imbalance in the food demand and supply market (Monbiot, 2004). Therefore, a possible solution to overcome the food versus fuel issue is to produce biodiesel from non-edible oil. Various types of non-edible oil sources such as *Jatropha* oil (Om Tapanes *et al.*, 2008), beef tallow (Nelson *et al.*, 2006), waste cooking oil (Chhetri *et al.*, 2008) and *Cerbera odollam* (sea mango) (Kansedo *et al.*, 2009) have been introduced as potential feedstock for biodiesel production in order to ensure that biodiesel is being produced in a more sustainable manner.

1.2 Biodiesel in Malaysia

1.2.1 Biodiesel Production and Consumption in Malaysia

According to European Biodiesel Board, currently Europe and US are the biggest biodiesel market in the world especially Europe which accounts over 90% of all biodiesel consumed and produced (Thurmond, 2007). Malaysia's first commercial scale biodiesel plant started operating in August 2006. In 2006, a total capacity of 150 thousand tonnes of biodiesel was produced in Malaysia and the production capacity increased to 600 thousand tonnes in 2007. However, the production capacity in 2008 decreased since many biodiesel producers had to suspend operations due to the dramatic increase in the price of CPO towards the end of 2007. Therefore, in

2008 only 134 thousand tonnes of biodiesel was produced. If the high feedstock price issue can be overcome, the total production capacity of biodiesel in 2009 is estimated to be 2680 thousand tonnes (Lopez and Laan, 2008).

There is no official data to show the actual consumption rate of biodiesel in Malaysia since most of the biodiesel produced in Malaysia is exported to US, the EU, Singapore and Australia (Lopez and Laan, 2008). The only indication of biodiesel consumption in Malaysia is the government's intention to replace 5% of petro-diesel with palm-biodiesel, B5 (Hor, 2009). By assuming the national consumption of diesel at 10 million tonnes per year, therefore 500,000 tonnes of palm biodiesel is needed to blend with the petro-diesel if the biodiesel policy is fully implemented in Malaysia (Ministry of Plantation Industries and Commodities Malaysia, 2006).

1.2.2 Oil Source for Biodiesel Production in Malaysia

Palm oil is the one and only oil source used as biodiesel feedstock in Malaysia due to its large availability. However, biodiesel produced using edible oil has pushed up the prices of food crops (Raswant, 2008). For example, the price of palm oil had tripled since early 2005 due to rising demand as it is not only used as food source but also as feedstock to produce biodiesel in Malaysia (Butler, 2008). Therefore, in order to avoid the food versus fuel issue, Malaysia has to find an alternative source for producing biodiesel particularly using non-edible oil. Among the non-edible oil feedstocks that have been mentioned in **section 1.1.1**, *Jatropha curcas* L. seed has the potential to replace palm oil as feedstock for biodiesel production in Malaysia since it is a multipurpose species with many attributes and considerable applications. With oil properties such as good oxidation stability

compared to soybean oil, low viscosity compared to castor oil and better cold properties compared to palm oil (Om Tapanes *et al.*, 2008), *Jatropha curcas* L. seeds oil is indeed a better feedstock for biodiesel production. Therefore, Malaysia currently is diversifying its biodiesel feedstock towards *Jatropha*. *Jatropha* plantation area in Malaysia, at the end of 2008 was estimated at 750,000 acres and is expected to increase to 1.5 million acres in 2009 and 2.5 million acres in 2010 (Energy Current, 2009).

1.3 Transesterification Reaction

Transesterification, also called alcoholysis, is a reaction between fat/oil (triglycerides) and alcohol to form esters as main product and glycerol as by-product. Transesterification is a reversible reaction in which excess alcohol is used to shift the equilibrium towards the product side (Helwani *et al.*, 2009). Alcohols used in the transesterification are primary and secondary monohydric aliphatic alcohol with 1 to 8 carbon atoms. Methanol, ethanol, propanol, butanol and amyl alcohol are the common alcohols used in the transesterification reaction but methanol and ethanol are most frequently used, especially methanol due to its low cost and physical as well as chemical advantages (polar and shortest chain alcohol) (Ma and Hanna, 1999). **Figure 1.3** shows the overall reaction scheme for transesterification of triglyceride (Kim *et al.*, 2004).

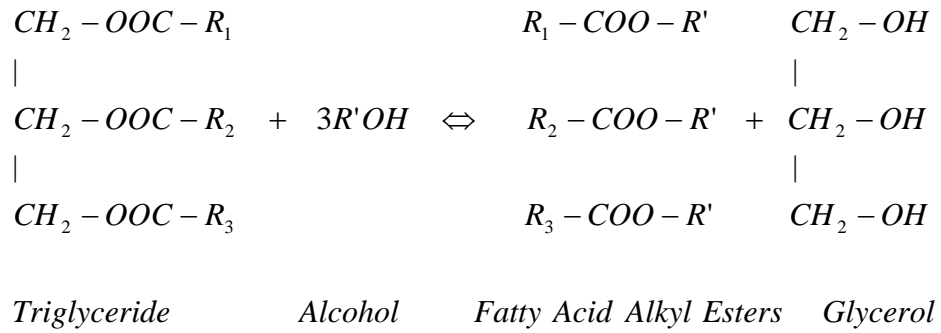


Figure 1.3: Transesterification of triglycerides with alcohol (Kim *et al.*, 2004).

Transesterification can be classified into 3 sub-categories; catalytic transesterification (Ma and Hanna, 1999), supercritical transesterification (Gui *et al.*, 2008) and in situ transesterification (Georgogiannia *et al.*, 2008). Transesterification reaction is a relatively slow if it is carried out in normal room temperature due to the two-phase nature of alcohol-oil mixture that has contrast polarity. Therefore, catalyst is needed to overcome this limitation and thus improve the reaction rate and products yield. There are generally 3 groups of catalysts that have been commonly used in catalytic transesterification reaction either homogeneously or heterogeneously (Marchetti *et al.*, 2007). The 3 groups of catalyst are as the following:

i. Alkali catalyst

Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the most common alkali catalysts used in the commercial production of biodiesel. The limitation of alkali-catalyzed transesterification is the requirement of high purity reactant (oil with lower content of free fatty acid and water concentration). High content of free fatty acid and water in the reactant will cause saponification to take place and soap will be produced instead of desired product, biodiesel (Marchetti *et al.*, 2007).

ii. Acid catalyst

Acid-catalyzed transesterification is the second most popular conventional way of producing biodiesel. Sulphuric acid and sulfonic acid are the two most common used acid catalysts. This type of catalyst gives very high ester yield but the reaction is very slow, requiring more than one day for complete reaction (Marchetti *et al.*, 2007). However, acid catalyst is suitable to be used in transesterification that involves oils with higher free fatty acid content.

iii. Enzyme

Enzyme used in the transesterification reaction is also known as bio-catalyst. The type of enzyme that is used in transesterification is normally lipase. Lipases are enzyme used to catalyze reaction such as hydrolysis of glycerol, alcoholysis and acidolysis, but it has been lately discovered that they can

also be used as catalyst in transesterification/esterification reactions as well. However, biocatalyst such as enzyme is more expensive than chemical catalyst (alkali or acid catalyst) and it has short operational life that caused by the negative effects of excessive short-chained alcohol and by product glycerol (Marchetti *et al.*, 2007; Su *et al.*, 2007).

It was reported that biodiesel can also be produced without the presence of catalyst by heating up alcohol to its supercritical stage and reacting it with oil. This technology is known as supercritical alcohol technology (Gui *et al.*, 2009). Transesterification in supercritical alcohol can be achieved by maintaining the reaction temperature and pressure above the critical point of alcohol. Supercritical alcohol technology usually involves high temperature and pressure, for example in supercritical methanol technology, temperature and pressure have to be maintained at 239 °C and 8.0 MPa respectively (Demirbas, 2003).

In situ transesterification or reactive extraction is another possible technology for biodiesel production. Reactive extraction involves direct reaction of oil-bearing materials instead of purified oil with alcohol. Reactive extraction needs the help of catalyst in order to speed up the reaction to produce high yield of biodiesel. Catalysts involve in this method includes alkali catalyst, acid catalyst and enzyme (Zeng *et al.*, 2009).

1.4 Problem Statement

There are a lot of limitations and disadvantages in the production of biodiesel using conventional method. Conventional method for the production of biodiesel involves various stages; oil extraction, solvent recovery, oil purification (degumming, deacidification, dewaxing, dephosphorization, dehydration, etc.) and subsequently esterification/transesterification. The requirement of these multiple processing stages constitute over 75% of the total production cost of biodiesel if refined oil is used as feedstock (Pruszko, 2007). Therefore, development of in-situ extraction, esterification and transesterification or simply term as reactive extraction has the potential to cut down the processing cost. Reactive extraction differs from the conventional biodiesel production process in which the oil-bearing material contacts with alcohol directly instead of reacting with pre-extracted oil. In another words, extraction and transesterification proceed in one single step, with alcohol acting both, as an extraction solvent and a transesterification reagent. In addition, more chemical reagents and substances are required in the conventional method, for instance, hexane needs to be used as solvent to extract oil from seeds and methanol is then used as reactant (Georgogiannia *et al.*, 2008). However, in the reactive extraction method, only methanol is needed for extraction and production of biodiesel.

Reactive extraction is usually carried out using homogeneous catalyst such as homogeneous base catalyst, homogeneous acid catalyst or even enzyme catalyst (Zeng *et al.*, 2009; Mondala *et al.*, 2009; Su *et al.*, 2007). Alkali-catalyzed transesterification undeniably is a much faster process than acid-catalyzed transesterification and is most often used commercially (You *et al.*, 2008), however

free fatty acid (FFA) are strong poison to this alkali catalyst and lead to the problem such as soap formation and difficulty in product separation. The FFA content in the oil is considered low if it is lower than 1wt% (usually in refined oil) (Ni and Meunier, 2007). Therefore, it is recommended that acid-catalyzed transesterification to be used for lipid feedstock with high FFA content (Veljkovic *et al.*, 2006). Since crude *Jatropha curcas* L. seed oil contains high free fatty acid, which is about 15%, therefore concentrated sulphuric acid will be used as the transesterification catalyst (Berchmans and Hirata, 2008).

Due to the dramatic increase in biodiesel demand, edible oil sources such as soybean oil, palm oil, corn oil and rapeseed oil might not be sustainable sources to support the demand as these oil sources also play a vital role in the food industry. Therefore, diversifying the oil feedstock into non-edible oil could be the better solution to fulfil the increasing demand of biodiesel while avoiding the food versus fuel issue. In this aspect, *Jatropha* oil could be used as oil feedstock to produce biodiesel.

After summarizing all the problems encountered by the biodiesel industry, production of biodiesel from *Jatropha* seed using acid-catalyzed reactive extraction technology is chosen as the theme in this study. Reactive extraction technology provides a more promising solution than conventional transesterification process; meanwhile, the use of *Jatropha* oil provides an alternative oil source instead of palm oil for biodiesel production.

1.5 Objectives

- i. To study the effect of process parameters such as reaction temperature, reaction time, alcohol to *Jatropha* seeds ratio and catalyst loading on the yield of the reactive extraction process using methanol and ethanol as alcohol source.
- ii. To optimize the yield of biodiesel produced from methanol and ethanol using response surface methodology (RSM) couple with central composite design (CCD).
- iii. To characterize the biodiesel produced.

1.6 Scope of Study

The first step in this study was to investigate the important physical and chemical properties of *Jatropha* seed and its oil which include the oil and moisture content of the seed and fatty acid composition of the oil. This data is crucial as basic information required prior to conduct the experimental works.

Secondly, reaction process study was carried out to study the yield of biodiesel produced from *Jatropha curcas* seed via reactive extraction in a wide range of operating conditions; reaction temperature, reaction period, methanol to seed ratio and catalyst loading. The effect of these process parameters on the yield of biodiesel was also studied and then optimized. The process parameters optimization was performed using design of experiment occupying Response Surface Methodology

(RSM) coupled with Central Composite Design (CCD) with the assistant of computer software, Design Expert 6.0.6.

Then, the research work was followed by production of biodiesel using ethanol as reaction solvent instead of methanol via reactive extraction and under the same process conditions except reaction temperature since the boiling point of ethanol is different from methanol. The process conditions for optimum yield of biodiesel from reactive extraction of *Jatropha* seed with ethanol as solvent were then obtained using the same procedure used for methanol. Moreover, the results obtained from both solvents were compared and investigated.

Lastly, characterization of biodiesel produced from *Jatropha* seeds using both methanol and ethanol as reaction solvent was made in order to investigate the ability of the obtained biodiesel to comply with the standards set by ASTM and EN standards. However, due to the limitation of products, the characterization works were only done for important properties such as viscosity, density, methanol content, flash point, water content, sulphur content, sulphated ash, acid value, and iodine value.

1.7 Organization of the Thesis

This thesis consists of five chapters. Chapter one provides an outline of the overall research project including introduction on biodiesel, oil sources for biodiesel production in Malaysia, production and consumption of biodiesel in Malaysia and various technologies for biodiesel production. Problem statement was written after reviewing the current scenario for biodiesel market in Malaysia. The problem statement reveals the problems faced by the biodiesel industry and the importance of this research project. The objectives of this research project were then carefully formulated with the intention to address the problems encountered by the biodiesel industry. Lastly, organization of the thesis highlights the content of each chapter.

Chapter two gives an overall review of various research works reported in the literature in this area of study which includes production of biodiesel from *Jatropha* oil, reactive extraction technology for the production of biodiesel, biodiesel standards and specifications, and design of experiment. Feasibility and advantages of using reactive extraction technology for biodiesel production is also reported.

Experimental materials and methodology were discussed in chapter three. This chapter describes detail information on the overall flow of this research work and some experimental methods in conducting this research project. In addition, material, chemicals and equipments used in this study were also reported. This chapter also includes the information that is required for the calculation of yield and data analysis.

Chapter four is the heart of the thesis since it includes detail discussion on the results obtained in the present research work. This chapter consists of six sections which have been divided according to the stages of this research work. First section of this chapter presents the characterization of raw materials (determination of moisture and oil content of *Jatropha* seeds) that had been done before further experimental works were carried out. Section two reports the preliminary studies on the effect of different seed size and seed moisture content on reactive extraction. Process studies on the reactive extraction of *Jatropha* seed using methanol and ethanol as reaction solvent are discussed in detail in section three and four respectively and these two sections are the most crucial sections in this chapter. Section five presents the process optimization for maximum yield of biodiesel using both methanol and ethanol. At the end of this chapter, characterization of biodiesel produced under optimum conditions was reported.

Chapter five, the last chapter of this thesis, provides a summary on the results obtained in this research project. This chapter concludes the overall research project and gives some recommendations for future studies related to this research work.

CHAPTER TWO:

LITERATURE REVIEW

This chapter reviews studies reported in the literature related to this research project. Initially, suitability of *Jatropha* seed as oil source and reactive extraction as the biodiesel production technology were reviewed and reported in this chapter. In addition, the concept of reactive extraction and the advantages of this technology as compared with conventional transesterification are also discussed in detail. Furthermore, review on statistical design of experiment was reported at the end of this chapter.

1.8 Biodiesel Feedstock Consideration

2.1.1 Edible Oil vs. Non-edible Oil

Edible oils especially refined edible oils are the most common feedstock in biodiesel production. However since about 75% of the total production cost is accounted by the cost of feedstock, the high price of refined oils has resulted to high biodiesel cost (Pruszko, 2007). This is because refined oil needs to be further processed as compared to crude oil such as neutralization of oil to remove free fatty acid (FFA) by adding caustic soda, bleaching process to remove the oil colour and finally deodorization to remove the smell of oil (Edible Oil Refinery: Cooking Oil Refinery: Vegetable Oil Refinery, 2009). Therefore, there is a big difference between the price of crude oil and refined oil. For example, the price of refined palm oil is 13% higher than crude palm oil (Kuala Lumpur Kepong Berhad, 2008). Thus, using

crude oil for biodiesel production becomes an attractive alternative to reduce the production cost of biodiesel.

Even though biodiesel production cost can be reduced by using crude oil instead of refined oil, this practise still faces one major challenge; the food versus fuel issue which is often debated around the world now. Food crop prices have shot up since edible oil is not only used as edible source for human consumption, but also as feedstock for fuel production (biodiesel and bioethanol) (Raswant, 2008). For instant, the increasing demand for bioethanol in America has raised the price of corn, and is inducing farmers to plant more acreage at the expense of other commodities such as soybean and wheat. In return, the decreased production of soybean and wheat commodities will raise the global price for these crops (Muller *et al.*, 2007). Besides, the same trend can also be applied to palm oil in which its price had tripled since early 2005 due to the increasing demand for commercial/domestic consumption and biodiesel production (Butler, 2008). Many of the urban poor people in developing countries suffer from the increasing price of food crops since people in these countries spend 50% of their income on food. Therefore, any price increase for food will result to hunger and malnutrition (Institute for Agriculture and Trade Policy, 2007). In view of this problem, non-edible oils posed a better alternative as biofuel feedstock. *Jatropha curcas* L. seed seems to be a very attractive feedstock for biodiesel production as compared to other non-edible oils since it can be cultivated in dry and marginal lands (Prueksakorn and Gheewala, 2008) and thus it does not compete arable land that would have otherwise being planted with food crops. In addition, its oil yield as shown in **Table 2.1** is comparable to palm oil but much

higher as compared to other edible oil crops such as rapeseed, sunflower and soybean (REUTERS, 2009; Lam *et al.*, 2009).

Table 2.1 Oil yield of *Jatropha curcas* L. seed and other major oil crops.

Oil crop	Oil yield (ton/ha/year)
<i>Jatropha curcas</i> L. seed	2.70 (REUTERS, 2009)
Oil palm (mesocarp)	3.62 (Lam <i>et al.</i> , 2009)
Rapeseed	0.68 (Lam <i>et al.</i> , 2009)
Sunflower	0.46 (Lam <i>et al.</i> , 2009)
Soybean	0.40 (Lam <i>et al.</i> , 2009)

2.1.2 *Jatropha* Seed and Its Oil

Jatropha curcas belongs to the family *Euphorbiaceae* and is thus closely related to other important cultivated plants like rubber tree, casster and etc. The genus name, *Jatropha* was derived from the Greek word *jatros* (doctor) and *trophe* (food), which implies medicine uses. *Jatropha* tree is believed to be a native of Mexico, Central America, Brazil, Bolivia, Peru, Argentina and Paraguay (Achten *et al.*, 2008) but is now widely distributed in Africa, India and South East Asia (Kumar and Sharma, 2008).

Jatropha plant is also known as physic nut plant which is found in the tropical and sub-tropical area (Amoah, 2006). *Jatropha* can adapt well to arid and semi-arid soil conditions and therefore it can grow almost anywhere even on gravelly, sandy and saline soils except waterlogged lands. It can also grow vigorously even on the poorest stony soil and crevices of rocks (Kumar and Sharma, 2008). The trees are deciduous and shed leaves during dry season. Flowering occurs during the wet season and two flowering peaks are often observed. In permanently humid regions, flowering occurs throughout the year (Achten *et al.*, 2008). With good rainfall conditions, nursery plant may bear fruits after the first rainy season (Kumar and Sharma, 2008). Therefore, the climate in Malaysia is found to be very suitable to plant and cultivate *Jatropha*.

The seed is similar to castor seed in shape (ovoid shape) but is smaller in size, 2.5 cm long and dark brown colour (Makkar *et al.*, 1997; Singh *et al.*, 2008). The seeds mature in about 3 to 4 months after flowering and the seed yield is up to 5 tons per hectare (Kumar and Sharma, 2008; Makkar *et al.*, 1997). Weight of the seeds is about 0.64 g (Makkar, *et al.*, 1997). Dry *Jatropha* fruit contains about 62.5% seed and the remaining 37.5% shell. The seed on the other hand contains about 42% hull/husk and 58% kernel (Singh *et al.*, 2008).

Jatropha seed contains 40 to 60% oil, depending of the variety. The oil contains approximately 20.8% saturated fatty acid (palmitic acid and stearic acid) and 78.6% of unsaturated fatty acids (oleic acid and linoleic acid). **Table 2.2** exhibits the typical physical and chemical properties, including fatty acid composition of *Jatropha* oil (De Oliveira *et al.*, 2008; Kumar and Sharma, 2008).

Table 2.2: Typical physical and chemical properties of *Jatropha* oil (De Oliveira *et al.*, 2008; Kumar and Sharma, 2008)

Properties	Value
Specific gravity, 15 °C	0.8874
Calorific value (MJ/kg)	40.31
Kinematic viscosity, 40 °C (cSt)	30.686
Pour point (°C)	-2
Fatty acid composition (%)	
Palmitic acid	14.1
Stearic acid	6.7
Oleic acid	47.0
Linoleic acid	37.6

1.9 Reported Technology on Production of Biodiesel from *Jatropha* Oil

Berchamans and Hirata (2008) reported that when crude *Jatropha curcas* oil (CJCO) was subjected to one step alkaline transesterification (using sodium hydroxide (NaOH) as catalyst), the maximum reported FAME yield was only 55% because crude *Jatropha curcas* L. oil contains high free fatty acid (FFA) at about 15%. According to Berchamans and Hirata (2008), FFA in the oil will deactivate the catalyst (NaOH), forming fatty acid salt which is simply known as soap. In addition, the use of excess amount of NaOH will cause the formation of emulsion which will increase the solution viscosity, leading to the formation of gels and the problem associated with glycerol separation and eventually loss in ester yield. Therefore, *Jatropha curcas* oil that contains high FFA is not suitable for conventional transesterification using homogeneous alkaline catalyst. Generally, there are four types of transesterification methods that have been proposed by other researchers for effective conversion of *Jatropha* oil into biodiesel, which are; homogeneous two

steps esterification followed by transesterification reaction (Berchamans and Hirata, 2008), heterogeneous base/acid transesterification (Zhu *et al.*, 2006; Patil *et al.*, 2009), supercritical alcohol technology and reactive extraction technology (Hawash *et al.*, 2008; Gui *et al.*, 2009).

Homogeneous two steps esterification followed by transesterification reaction was proposed as one of the solutions to overcome the problems faced by homogeneous alkaline transesterification of oil with high FFA content. In the research work done by Berchamans and Hirata (2008), *Jatropha* oil was first subjected to acid esterification and pretreatment for removing FFA in the oil. The acid esterification of *Jatropha* oil was carried out at temperature 50 °C for one hour. The process was intended to convert FFA to esters using acid catalyst (H₂SO₄, 1% w/w) and subsequently reduce the FFA concentration of *Jatropha* oil to below 2%. The second step was alkaline base catalyzed transesterification in which the reaction was carried out at 65 °C for two hours, using NaOH as catalyst. The reported FAME yield for this two steps transesterification was about 90% which is much higher than the one step alkaline base transesterification. Although this process can achieve high FAME yield, but it involves more processing steps and chemicals. After acid esterification, the reaction mixture must be left to settle for two hours and then the methanol-water fraction at the top layer was removed before alkaline base transesterification. Besides, more NaOH was needed in this two steps process since it does not only serve as catalyst but also to neutralize H₂SO₄ in the acid esterification.

Heterogeneous base-catalytic transesterification was another possible method to produce biodiesel from raw oil that contain high FFA. In a research work done by Zhu *et al.* (2006), transesterification of *Jatropha* oil was performed with methanol and catalyzed by specially treated CaO as solid base catalyst. CaO used in the transesterification was treated with an ammonium carbonate solution and calcinated at high temperature. This treated CaO was reported as a solid super base catalyst and can achieve FAME yield of 93% which is similar to the conventional homogeneous transesterification. Alumina loaded with potassium nitrate ($\text{KNO}_3/\text{Al}_2\text{O}_3$) was reported by Vyas *et al.* (2009) as another suitable solid base catalyst that can be used to transesterified *Jatropha* oil into biodiesel. The catalyst was prepared via impregnation of alumina with an aqueous solution of potassium nitrate and the maximum FAME yield that can be obtained was 84%. This catalyst was reported to be able to be recycled and reused for at least three times.

For *Jatropha* oil, many research works have only reported the use of heterogeneous acid catalyst to pre-treat (esterification) the oil to reduce FFA content and the resulting pre-treated oil will eventually be subjected to homogeneous alkaline transesterification. Patil *et al.* (2009) used ferric sulfate catalyst, $\text{Fe}_2(\text{SO}_4)_3$ to pre-treat *Jatropha* oil at 100°C for one hour, then the esterified *Jatropha* oil was transesterified using potassium hydroxide, KOH at 100°C for one hour. This $\text{Fe}_2(\text{SO}_4)_3$ catalyst had very low solubility in oil, therefore it can be used as heterogeneous catalyst and the reported FAME yield was 90%. Besides, in the research work done by Lu *et al.* (2009), solid acid catalyst, $\text{SO}_4^{2-}/\text{TiO}_2$ prepared by calcining metatitanic acid at 300°C was used in the pre-esterification of *Jatropha* oil. The pre-esterification process was carried out at 90°C for two hours and then

transesterification using KOH as catalyst was performed at 64°C with 1.3 wt% catalyst for one hour. The maximum FAME yield for this heterogeneous pre-esterification followed by homogeneous alkaline transesterification was about 95%. Although heterogeneous catalysis has the advantage of easy catalyst separation as compared to homogeneous catalysis (Zhu *et al.*, 2006), but it still has its own limitations. More energy is needed to synthesis heterogeneous catalysts since most of heterogeneous catalysts need to be calcined at high temperature which is usually more than 200°C and some can go up to 500°C (Lu *et al.*, 2009 and Albuquerque *et al.*, 2008). Moreover, recycling and reusability of catalyst are the major problem faced by heterogeneous catalysis. Garcia *et al.*, 2008 reported that FAME yield dropped significantly when sulfated zirconia (S-ZrO₂) was reused and recycled due to sulfate leaching. In the second cycle, FAME yield dropped to 59% and further reduced to 14% in the fourth cycle. Komintarachat and Chuepeng (2009) also reported that WO_x/Al₂O₃ catalyst was reusable for only three times, significant losses in activity were observed at the fourth cycle and onward.

Another possible method to produce biodiesel from *Jatropha* oil is using supercritical alcohol technology. Hawash *et al.* (2008) reported that biodiesel can be produced from transesterification of *Jatropha* oil with methanol via supercritical technology. In their study, supercritical transesterification of *Jatropha* oil with methanol was carried out under different reaction conditions; temperature from 240 to 340°C, reaction pressure from 5.7 to 8.6 MPa and methanol to oil ratio from 10 to 43. Hawash *et al.* (2008) found that at reaction temperature 320°C, pressure of 8.4 MPa and molar ratio of methanol to oil of 43:1, *Jatropha* oil was completely converted to biodiesel in 4 minutes of reaction time. Besides, the feasibility of