SUPERCRITICAL ETHANOL TECHNOLOGY FOR THE PRODUCTION OF BIODIESEL FROM PALM OIL AND JATROPHA OIL

by

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
CI	Confidence interval
CCD	Central composite design
DG	Diglycerides
DOE	Design of experiment
EE	Ethyl esters
FAAE	Fatty acid alkyl esters
FAEE	Fatty acid ethyl esters
FFA	Free fatty acids
FID	Flamed ionized detector
FT-IR	Fourier Transformed Infrared Spectroscopy
F-value	Fisher test value
GC	Gas chromatography
GL	Glyceride
MG	Monoglycerides
ME	Methyl esters
N/A	Not available
Prob	Probability
RSM	Response surface methodology
TG	Triglycerides
TGA	Thermogravimetric analysis
uME	Unmethyl esterified compounds

LIST OF SYMBOLS

α	Rotatability of CCD
a_o, a_1, a_2, a_3	Polynomial coefficients in Equation (4.13 and 4.14)
A	Coded term of reaction time
A	Pre-exponential factor
$\beta_{0,1,2..,k}$	Regression coefficients for Equation (2.1 and 2.2)
B	Coded term of reaction temperature
C	Coded term of molar ratio of ethanol to oil
C_{FAEE}	Concentration of FAEE (mol/dm^3)
C_{IS}	Concentration of IS (g/L)
$C_{TG,0}$	Initial concentration of palm oil (mol/dm^3)
C_{TG}	Final concentration of triglyceride (mol/dm^3)
$C_{TG,T}$	Final concentration of triglycerides at different temperature (mol/dm^3)
DF	Dilution factor
E	Activation energy (J/mol)
k	Reaction rate constant (min^{-1})
k	Design factor
n	Reaction rate order
N_{FAEE}	Mol of FAEE produced (mol)
$N_{TG,0}$	Initial mol of TG used (mol)
N_{TG}	Mol of unreacted TG (mol)
$N_{TG,\ reacted}$	Mol of TG reacted (mol)
r_{FAEE}	Production rate of FAEE (mol/dm^3 ·min)
r_{TG}	Consumption rate of triglycerides (mol/dm^3 ·min)
R	Gas constant, (8.314 J/mol ·K)
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
t	Reaction time, min
T	Reaction temperature (K)
V	Volume of oil (mL)
$x_{0,1,2..,k}$	Independent variables for regression equation in Equation (2.1 and 2.2)
X	Conversion
y	Dependent variables for regression equation in Equation (2.1 and 2.2)

PENGHASILAN BIODIESEL DARIPADA MINYAK KELAPA SAWIT DAN MINYAK BUAH JARAK MENGGUNAKAN TEKNOLOGI ETANOL GENTING LAMPAU

ABSTRAK

Minyak kelapa sawit; yang terdapat di seluruh Malaysia, merupakan sumber minyak yang berpotensi untuk penghasilan biodiesel di kawasan ini. Sementara itu, minyak jarak, juga dipercayai adalah sumber minyak yang berpotensi disebabkan kesesuaiannya untuk keadaan cuaca di Malaysia. Oleh itu, penghasilan biodiesel daripada minyak kelapa sawit and minyak jarak telah dikaji dalam projek ini dengan menggunakan teknologi genting lampau etanol tanpa penggunaan mangkin. Pada mulanya, pencirian minyak kelapa sawit dan minyak jarak telah dikaji untuk ciri-ciri fizikal, kimia dan therma. Seterusnya, biodiesel disintesis daripada kedua-dua minyak ini dalam reaktor jenis berkelompok. Proses transesterifikasi telah dijalankan dengan mengubah kondisi-kondisi proses seperti yang berikut: masa tindakbalas, 2 – 30 min, suhu tindakbalas, 300 – 400^{o}C, and nisbah etanol kepada minyak, 5 – 50. Rekabentuk ujikaji gabungan pusat (CCD) dan metodologi permukaan sambutan (RSM) telah digunakan untuk mengkaji hubungan antara hasilan biodiesel dengan kesan-kesan perubahan parameter tindakbalas. Hasilan optima biodiesel daripada minyak kelapa sawit yang sebanyak 79 wt% telah diperolehi daripada tindakbalas pasa suhu 350^{o}C, dengan nisbah etanol kepada minyak 33 dalam tindakbalas selama 29 min. Sementara itu, hasilan optima biodiesel daripada minyak jarak yang sebayak 74 wt% diperolehi daripada transesterifikasi pada takt suhu tindakbalas yang lebih rendah, iaitu 300^{o}C, tetapi dengan nisbah etanol kepada minyak (nisbah 28) dan masa tindakbalas (30 min) yang lebih kurang sama dengan transesterifikasi minyak kelapa sawit. Perbezaan hasilan optima biodiesel dan optima kondisi tindakbalas antara dua jenis minyak ini adalah disebabkan kandungan asid lemak bebas (FFA) dan komposisi asid lemak yang berbeza. Selain itu, transesterifikasi tanpa mangkin dengan menggunakan teknologi genting lampau etanol didapati lebih effektif daripada tindakbalas pemangkinan transesterifikasi biasa dari segi toleransi ke atas kandungan air dan FFA. Kandungan air dan FFA didapati tidak memberi kesan yang signifikasi ke atas proses ini. Pencirian biodiesel yang diperolehi daripada minyak kelapa sawit dan minyak jarak menunjukkan bahawa teknologi ini berupaya untuk menghasilkan biodiesel yang boleh menepati piawaian biodiesel antarabangsa. Kinetic tindakbalas transesterifikasi minyak kelapa sawit turut dikaji. Tenaga pengaktifan yang sebanyak 8.23 KJ/mol telah diperolehi untuk proses ini dan didapati adalah lebih rendah daripada proses transesterifikasi biasa.

SUPERCRITICAL ETHANOL TECHNOLOGY FOR THE PRODUCTION OF BIODIESEL FROM PALM OIL AND JATROPHA OIL

ABSTRACT

Palm oil; which is available throughout Malaysia is a potential oil feedstock for the production of biodiesel in this region. Jatropha (Jatropha *curcas*) oil, on the other hand, is believed to be another potential oil source for biodiesel production due to its non-edible nature and high suitability to tropical climate in Malaysia. Therefore, production of biodiesel from palm oil and jatropha oil was studied in the present research work via non-catalytic transesterification in supercritical ethanol technology. Initially, palm oil and jatropha oil were characterized for their physical, chemical and thermal properties. Subsequently, both oils were transesterified to biodiesel using a batch type reactor system. The transesterification process was carried out by varying the following process parameters: reaction time, 2 – 30 min; reaction temperature, 300 – 400 ^{o}C; and molar ratio of ethanol to oil, 5 – 50. Design of experiment (DOE) coupled with Response Surface Methodology (RSM) and Central Composite Design (CCD) was used to investigate the relationship between yield of biodiesel with the process parameters studied, which was then used for optimization studies. The optimum palm biodiesel yield of 79 wt % was obtained at reaction temperature 350^{o}C with molar ratio of ethanol to oil of 33 and 29 min reaction time. On the other hand, the optimum yield of biodiesel from jatropha oil (74 wt %) was obtained at lower reaction temperature (300^{o}C) but with similar molar ratio of ethanol to oil (ratio of 28) and reaction time (30 min). The difference in optimum yield of biodiesel and optimum reaction conditions was due to different free fatty acid (FFA) content and composition of both oils. Nevertheless, it was found that non-catalytic transesterification reaction using supercritical ethanol technology was superior than conventional catalytic reaction with higher tolerance to water and FFA contents. Water content in ethanol and FFA content in oil was found to have no significant effect on the yield of biodiesel. Characterization of both palm and jatropha biodiesel shows that this technology is feasible to produce biodiesel that can meet international biodiesel standards. The kinetics of transesterification of palm oil using supercritical ethanol technology was also studied and the activation energy of 8.23 KJ/mol was obtained; which was lower than conventional transesterification process.

CHAPTER ONE:

INTRODUCTION

This chapter gives detail introduction on the entire research project. Brief definition and current market supply and demand for biodiesel is outline at the beginning of this chapter. Besides, information on palm oil and jatropha oil used in this study and as well as transesterification reaction are also given. This chapter concludes with the problem statement, project objectives and thesis organization of this research project.

1.1 Biodiesel

In the past few decades, fossil fuels mainly petroleum, natural gas and coal have been playing an important role as the major energy resources worldwide. However, these energy resources are non-renewable and are projected to be exhausted in the near future. The situation has worsened with the escalating energy consumption worldwide due to rapid population growth and economic development. Therefore, there is an urgent need to find a new energy resources that are renewable, clean, reliable and yet economically feasible as a substitution to the current fossil fuels. In this context, recently, biodiesel derived from vegetable oil has been shown to be a potential alternative replacing petroleum-derived diesel oil for diesel engine.

Biodiesel is fatty acid alkyl esters (FAAE) derived from any type of vegetable oils and animal fats which has fatty acid contents such as edible oil, non-edible oil, and waste cooking oil. The similarity in physical and chemical properties of biodiesel and petroleum-derived diesel has made biodiesel a potential substitute fuel for petroleum-derived diesel. On top of that, biodiesel is superior to petroleum-derived diesel in terms of renewability and environmental friendly behavior (Ma and Hanna, 1999). The combustion of biodiesel in diesel engine gives less emission while remain the engine performance nearly identical to those of petroleum-derived diesel. The physical and chemical properties of biodiesel are ruled by biodiesel standards to ensure the compatibility of the biodiesel with petroleum derived diesel. Table 1.1 below shows some of the important biodiesel properties according to the biodiesel standards given by European and United States, as compared to petroleum-derived diesel.

Table 1.1: Biodiesel standards given by European and United States (Biofuel system, 2009)

		Biodiesel		Petroleum-derived Diesel
		Europe	United States	
Specification		EN 41214: 2003	ASTM D 6751-07b	EN 590:1999
Applies to		FAME	FAAE	Diesel
Density 15°C	g/cm^3	0.86-0.90	-	0.82-0.845
Viscosity 40°C	$mm^2.s$	3.5-5.0	1.9-6.0	2.0-4.5
Distillation	% @ °C	-	90%, 360°C	85%, 350°C – 95%, 360°C
Flash point	°C	120 min	93 min	55 min
Sulphur	mg/kg	10 max	15 max	350 max
CCR 100%	%mass	-	0.05 max	-
Carbon residue (10% dist. residue)	%mass	0.3 max	-	0.3 max
Water	mg/kg	500 max	500 max	200 max
Oxidation stability	hrs; 110°C	6 hours min	3 hours min	-
Cetane number		51 min	47 min	51 min

1.1.1 The Biodiesel Debate

Currently, biodiesel is produced from edible oil due to its abundant and easy availability. About 84 % of the world biodiesel production is met by rapeseed oil; meanwhile the remaining portions are from sunflower oil (13 %), palm oil (1 %), and soybean oil and others (2 %) (Thoenes, 2007). Since more than 95 % of the biodiesel is produced from edible oil, there are many claims that a lot of problems may arise, such as depletion of vegetable oil supply and increase in vegetable oil prices. By converting edible oils into biodiesel, food resources are actually being converted into automotive fuels. It is believed that large-scale production of biodiesel from edible oils may bring global imbalance to the food supply and demand market (Monbiot, 2007). Lately, there has been significant expansion in the production of edible oil for biodiesel in the past few years in order to fulfill the continuous increasing demand of biodiesel. **Figure 1.1** shows the trend in global vegetable oil ending stocks due to the production of biodiesel in the years 1991 – 2005 (Fox Investments, 2007). Although there is continuous increase in the production of vegetable oil; however, the ending stocks of vegetable oils are continuously decreasing due to increase production of biodiesel. Eventually, with the implementation of biodiesel as a substitute fuel for petroleum-derived diesel oil, this may lead to the depletion of edible oil supply worldwide.

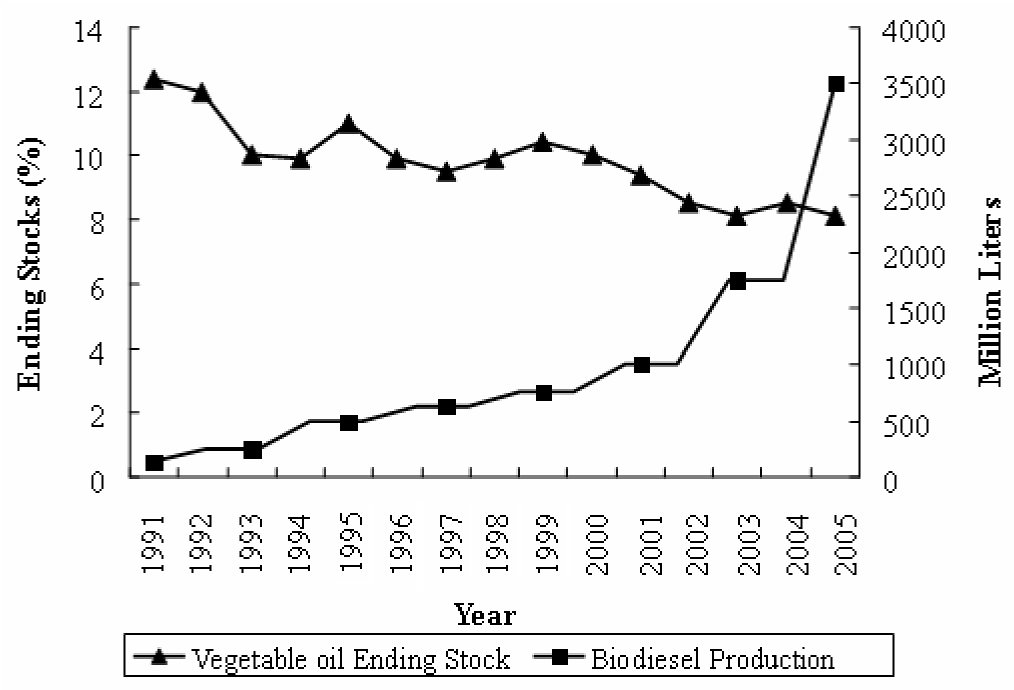


Figure 1.1: Global vegetable oil ending stock and biodiesel production (Fox Investments, 2007).

1.2 Oil Sources for Biodiesel Production in Malaysia

There are various vegetable oil sources available for the production of biodiesel. Almost all types of vegetable oils are suitable for biodiesel production. Therefore, the oil feedstock for biodiesel production in every country is different, depending on the availability of the oil resources in the respective country.

1.2.1 Palm Oil

1.2.1 (i) Availability of Palm Oil

Palm oil has become a popular oil feedstock for production of biodiesel in tropical countries such as Malaysia, Indonesia and Thailand because of its abundance availability in these countries. Besides that, being an oil crop with the highest oil yield per hectare and production rate among other oil crops, palm oil has eventually become a potential sustainable oil source for production of biodiesel worldwide. The oil yield per hectare for oil palm is approximately 5 MT/hectare (MPOB, 2007). This value is much higher than the oil yield for other oil seeds such as rapeseed or soybean which only has oil yield about 0.4 -1 MT/hectare (USDA, 2007; Canola Council of Canada, 2007).

Since Malaysia is one of the leading countries in palm oil production, therefore palm oil has become the most suitable oil source for biodiesel feedstock in Malaysia. Palm oil industry in Malaysia has expanded largely within the last few decades with nearly 900 % increment since the year 1975 till year 2007 (MPOC, 2009). **Figure 1.2** shows oil palm plantation area throughout Malaysia in the past few decades. As it can be seen from **Figure 1.2**, plantation area for oil palm has increased from about 0.5 million hectare in the year 1975 to about 4.5 million hectare for the year 2007. Large plantation area with high production of palm oil has secured the availability and supply of palm oil for biodiesel production in this region. Although rapeseed and soy oil has been claimed to be the quality oil sources for biodiesel production due to better cold flow properties than palm oil; however, these oils are not suitable to be used as biodiesel feedstock in Malaysia because of its low availability and very limited supply. Furthermore, it is not economically feasible to produce biodiesel from imported vegetable oil sources such as rapeseed or soy oil.

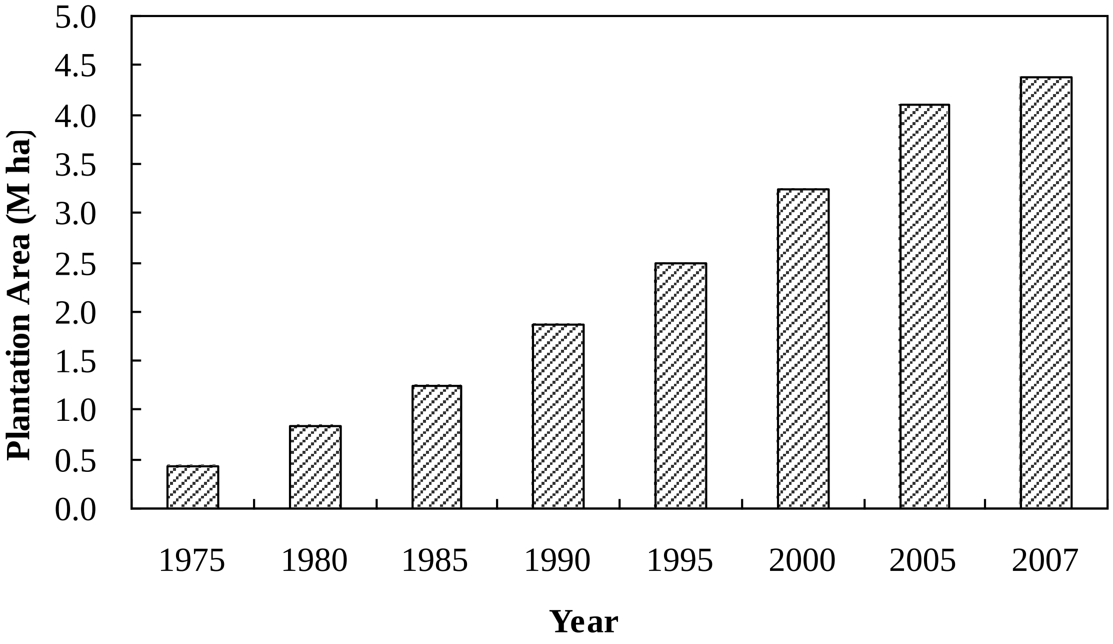


Figure 1.2: Oil palm plantation area throughout Malaysia in 1975-2007 (MPOC, 2009) (M ha = million hectare).

1.2.1 (ii) Physical and Chemical Properties of Palm Oil

Generally, palm oil has a balance ratio of unsaturated and saturated fatty acids. It contains almost 40 % oleic acid and 10 % linoleic acid which are unsaturated fatty acid and; 45 % palmitic acid and 5 % stearic acid which are saturated fatty acid (MPOC, 2007). The physical and chemical properties of palm oil include fatty acid compositions, are as shown in **Table 1.2** (O’Brien, 2004).

Table 1.2: Physical and chemical properties of palm oil (O'Brien, 2004).

Properties	Value
Iodine value	53
Saponification number	196
Melting point (^{o}C)	37.5
Fatty acid composition (%):	
- Lauric acid (C12:0)	0.2
- Myristic acid (C14:0)	1.1
- Palmitic acid (C16:0)	44.0
- Palmitoleic acid (C16:1)	0.1
- Stearic acid (C18:0)	4.5
- Oleic acid (C18:1)	39.2
- Linoleic acid (C18:2)	10.1
- Linolenic acid (C18:3)	0.4
- Arachidic acid (C20:0)	0.4

1.2.2 Jatropha Oil

1.2.2(i) Availability of Jatropha Oil

In order to overcome the food versus fuel debate for biodiesel production, researchers and biodiesel producer are shifting their focus on non-edible oils as alternative or greener oil sources to produce biodiesel in a more sustainable scale. Various types of non-edible oil sources such as sea mango, castor, Pongamia *pinnata*, rubber seed and jatropha have been introduced as feedstock for biodiesel production. Among all the non-edible oil sources, jatropha oil offers a better future prospect since it has a wider natural habitat distribution area in the world. Jatropha is reported to grow naturally worldwide covering south America, Africa and many regions of Asia (Jongschaap et al., 2008). In Asia region, jatropha plant is easily found in semi-wild condition in the vicinity area of India. Jatropha is grown in India not only as oil crops but also for other purposes such as ornamental, as fence in agricultural field, for enrichment of soil and many more (Openshaw, 2000).

Jatropha oil is currently a potential oil source for biodiesel production not only because of the similarity in fatty acid components with that of palm oil but also the benefits it brings economically. Jatropha was first introduced in Malaysia in year 2005 as a biofuel crop due to the escalating price of crude palm oil (Jatro LGM, 2009). Currently, the plantation of jatropha in Malaysia are mainly still on experimental scale.

1.2.2(ii) Physical and Chemical Properties of Jatropha Oil

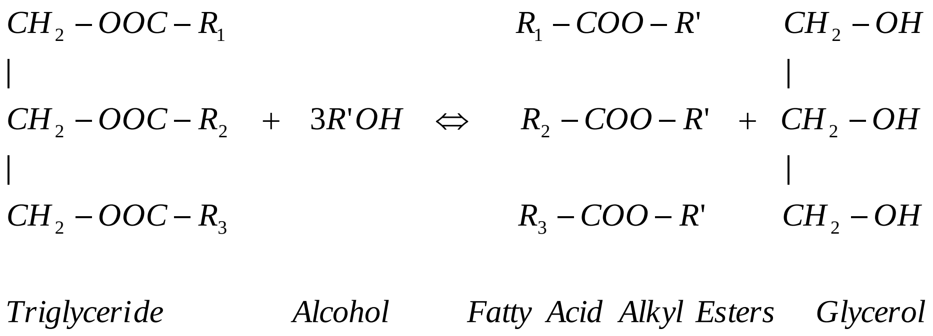
Jatropha oil is extracted from the seed of jatropha plant with oil content ranging from 35 % to 40 % depending on the oil extraction method. Jatropha oil contains approximately 21 % saturated fatty acids and 79 % unsaturated fatty acids and varies according to many factors such as cultivation area and species (Berchmans and Hirata, 2008). However, jatropha oil composition is generally similar with the composition of palm oil, which contains mainly palmitic acid, stearic acid, oleic acid and linoleic acid. **Table 1.3** exhibits the physical and chemical properties, including fatty acid composition of jatropha oil (De Oliveira et al., 2008).

Table 1.3: Physical and chemical properties of jatropha oil (De Oliveira et al., 2008).

Properties	**Value**
Specific gravity, 15^{o}C	0.8874
Calorific value (MJ/kg)	40.31
Acid value (mg KOH/g)	8.45
Kinematic viscosity, 40^{o}C (cSt)	30.686
Pour point (^{o}C)	-2
Fatty acid composition (%)	
- Lauric acid (C12:0)	5.9
- Myristic acid (C14:0)	2.7
- Palmitic acid (C16:0)	13.5
- Stearic acid (C18:0)	6.1
- Oleic acid (C18:1)	21.8
- Linoleic acid (C18:2)	47.4

1.3 Transesterification Reaction

The reaction to convert triglycerides in vegetable oil and short chain alcohol into FAAE is known as transesterification reaction. **Equation 1.1** below shows the reaction equation of the transesterification reaction (Marchetti, 2007).



$$\begin{array}{lcccccl}
CH_2-OOC-R_1 & & & & R_1-COO-R' & & CH_2-OH \\
| & & & & & & | \\
CH_2-OOC-R_2 & + & 3R'OH & \Leftrightarrow & R_2-COO-R' & + & CH_2-OH \\
| & & & & & & | \\
CH_2-OOC-R_3 & & & & R_3-COO-R' & & CH_2-OH \\
 & & & & & & \\
Triglyceride & & Alcohol & & Fatty\ Acid\ Alkyl\ Esters & & Glycerol
\end{array} \qquad (1.1)$$

During transesterification reaction, alkoxy groups in triglyceride are exchanged with alkyl group from alcohol, resulting in the formation of FAAE as product and glycerol as by-product. Transesterification reaction in normal room conditions is relatively slow (almost nil) due to the two-phase nature of alcohol-oil mixture that has contrast polarity, in which alcohol is a polar solvent but oil is non-polar substance. A catalyst is usually used to overcome this limitation and thus improve the reaction rate and product yield. There are generally three categories of catalysts that have been used to improve the transesterification reaction either homogeneously or heterogeneously (Marchetti, 2007). These are:

i. Alkali catalyst

Currently, most of the commercial production of biodiesel uses alkali catalyst. Among various alkali catalysts, the most commonly used are sodium hydroxide (NaOH), sodium methoxide, and potassium hydroxide (KOH). In this process, alcoxy is produced during the alcoxy reaction before the reaction to produce alcohol ester (Marchetti, 2007).

ii. Acid catalyst

Acid catalyst is the second most common type of catalyst used for biodiesel production, such as sulfonic acid and sulfuric acid. This type of catalyst can give a very high yield in esters but the reaction is extremely slow, requiring almost always more than one day for complete reaction (Marchetti, 2007). Acid catalyst is usually used for transesterification reaction which involves oils with high free fatty acid content.

iii. Enzyme

The enzyme used to catalyze transesterification reaction is normally lipase. Lipases are enzymes used to catalyze reactions such as hydrolysis of glycerol, alcoholysis and acidolysis, but it has been discovered that they can be used as catalyst for transesterification and esterification reaction as well (Marchetti, 2007).

Recent researches have proved that the solubility of vegetable oil in alcohol can be improved by using supercritical alcohol technology. Supercritical alcohol is alcohol at temperature and pressure above its thermodynamic critical point. At supercritical stage, alcohol has the unique ability of both gas and liquid. Apart from that, the density can change significantly with small changes in temperature or pressure. The supercritical point of each substance is different according to the thermodynamic properties. Ethanol, which is an ethyl-alcohol, is believed to have the unique thermodynamic properties at supercritical stage similar with methanol. **Figure 1.3** presents the two dimensional phase diagram of ethanol. The supercritical point for ethanol is at temperature of 243^{o}C and 6.14 MPa (approximately 600 bar) (Warabi et al., 2004). Transesterification in supercritical ethanol can be achieved by maintaining the reaction temperature and pressure above the critical point of ethanol.

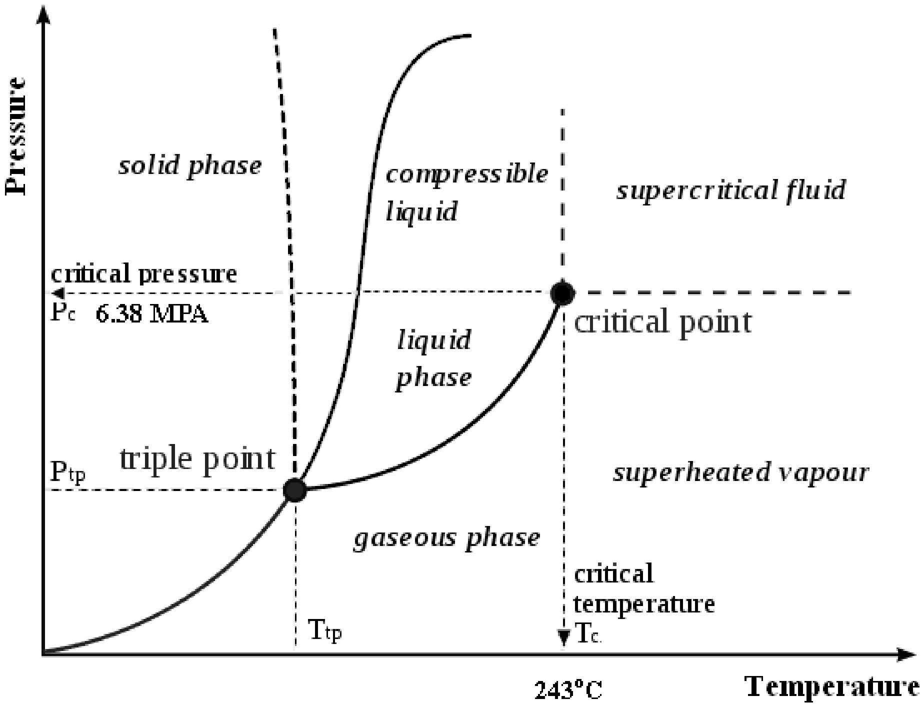


Figure 1.3: Two dimensional phase diagram of ethanol (Wikipedia, 2009).

1.4 Problem Statement

Currently, the most commonly applied process for commercial production of biodiesel is by methanol transesterification reaction in the presence of acidic or alkali catalyst to improve the reaction rate and yield of the product. The commonly used acidic and alkali catalysts are H_2SO_4 and NaOH, respectively. The main disadvantage of this catalytic transesterification process is the requirement of product purification process. The purification process includes several complicated, expensive, and time-consuming separation steps for the removal of catalyst, un-reacted substances and by-products in order to obtain biodiesel with high purity. Consequently, in order to overcome these problems and to make the production process more convenient, there is an urgent need to study the production of biodiesel using non-catalytic transesterification reaction in supercritical alcohol state. Without the use of catalyst, it is expected that supercritical alcohol technology will only require much simpler biodiesel purification methods which will also reduce the cost for biodiesel production.

In biofuel industry, biodiesel is currently produced from transesterification of vegetable oil and methanol. Since methanol is derived from petroleum and natural gas (finite sources), this has made the overall biodiesel production process not really renewable. On the other hand, extensive development has allowed the production of ethanol from renewable sources, which is well known as bioethanol and is widely used as substitute fuel for petrol. Therefore, in this study, biodiesel is produced by using ethanol instead of methanol. This is mainly due to the better sustainability prospect of ethanol as compared to methanol. Ultimately this will make the overall biodiesel production process independent of petroleum and natural gas resources and attractive.

The feasibility of using non-edible oil instead of edible oil will also be studied in this research. Due to the exponential increase in biodiesel demand, edible oil sources such as palm oil, soybean oil and rapeseed oil might not be a sustainable source to fulfill the demand as these oil sources also play important roles in the food industry, which must not be neglected. Therefore, a diversified oil feedstock is important to fulfill the high demand of biodiesel. In this aspect, non-edible oil such as jatropha oil could be used to reduce the dependency on edible oil for biodiesel production.

After summarizing all the problems faced by the biodiesel industry, production of biodiesel from palm oil and jatropha oil using non-catalytic transesterification in supercritical ethanol technology was chosen in this study. Transesterification in supercritical ethanol 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 yield of biodiesel using supercritical ethanol technology under a wide range of operating conditions (reaction temperature, reaction time and ethanol ratio).

ii. To study the feasibility of using non-edible oil (jatropha oil) as biodiesel feedstock.

iii. To optimize the yield of biodiesel obtained from palm oil and jatropha oil.

iv. To characterize the biodiesel produced from palm oil and jatropha oil.

v. To develop suitable kinetic model for the non-catalytic transesterification reaction of palm oil.

1.6 Scope of study

In the first step of this work, important physical, chemical and thermal characteristics of palm oil and jatropha oil were investigated. Important physical and chemical properties of these oils, such as fatty acid composition, acid value, moisture content and others were analyzed. This information is vital as basic information required prior to conduct the experimental works.

Next, reaction process study was carried out to study the yield and conversion of palm oil in various process parameters that are reaction temperature, reaction time, and molar ratio of ethanol to oil. The effect of these process parameters on the yield of biodiesel was also studied. The optimum process conditions for optimum yield of biodiesel was obtained 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.

The research work was then followed by production of biodiesel from jatropha oil using the same process conditions used for transesterification of palm oil. The process conditions for optimum yield of biodiesel from transesterification of jatropha oil were obtained using the same procedure used for transesterification of palm oil. In addition, the results obtained from transesterification of palm oil and jatropha oil were compared and investigated.

Characterization of biodiesel converted from palm oil and jatropha oil are important to investigate the ability of the biodiesel obtained to comply with the standards ruled by ASTM and EN standards. In this work, due to the limitation of reactor scale, the characterization works were only done for important properties such as viscosity and density.

Lastly, at the final stage of the research work, a simple kinetic study was done for transesterification reaction of palm oil. Kinetic model to represent non-catalytic transesterification of palm oil in supercritical ethanol was obtained and was verified with series of experimental works done.

1.7 Organization of the Thesis

This thesis consists of five chapters. Chapter one gives an outline of the overall research project covering introduction on biodiesel, oil sources for biodiesel production in Malaysia and transesterification reaction. Problem statement was then written after reviewing the scenario for biodiesel market in Malaysia. The problem statement reveals problems faced currently in the biodiesel industry and the need of this research project. The objectives of this research project were then carefully devised with the aim to solve the problems faced by the biodiesel industry. Finally, the 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 research. The various research works includes production of biodiesel from palm oil and jatropha oil, supercritical ethanol technology for production of biodiesel, design of experiment and lastly, reaction kinetic modeling. The review reports on the feasibility and advantages of using supercritical ethanol technology for production of biodiesel. Meanwhile the review on design of experiment and reaction kinetic modeling was made to identify the suitable types of statistical method and model for this research project.

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

Chapter four is the most important chapter in the thesis. It encompasses detail discussion on the results obtained in the present research work. This chapter consists of eight sections which have been divided according to the stages of this research work. First section of this chapter presents characterization of raw materials that was done before any further experimental works were carried out. This was then followed by preliminary studies on temperature and pressure profiles of the reactor system. Section three and four reports the process study and process optimization on the transesterification of palm oil and jatropha oil, respectively and are the most important section in this chapter. This was then followed by studies on the effect of water content on transesterification reaction using supercritical ethanol technology. In the next section, the characterization of biodiesel sample obtained in this project was reported. At the end of this chapter, reaction kinetic studies and the kinetic model developed for transesterification of palm oil was also presented.

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

CHAPTER TWO:

LITERATURE REVIEW

This chapter reports the literature review related to this research project. Suitability of palm oil and jatropha oil as raw materials for production of biodiesel was reviewed and reported in this chapter. Besides, the concept of supercritical alcohol technology for production of biodiesel including the advantages of this technology as compared with conventional transesterification technology is also discussed in detail. Review on statistical design of experiment and kinetic study is reported at the end of this chapter.

2.1 Technology Reported on Production of Biodiesel from Palm Oil

In recent years, palm oil has become one of the popular oil feedstock for production of biodiesel due to its abundance availability in Malaysia and Indonesia. Transesterification of palm oil especially with methanol using various processes is widely reported. This sub-section summarizes the technologies for synthesizing biodiesel via transesterification of palm oil.

Jitputti et al. (2006) investigated various solid catalysts suitable for transesterification of crude palm oil to biodiesel. In their series of experimental works that uses several types of acidic and alkaline catalysts such as ZnO_2, ZnO, SO_4^{2-}/SnO_2, SO_4^{2-}/ZrO_2, KNO_3/KL zeolite and KNO_3/ZrO_2, it was reported that only two solid catalysts, namely ZnO and SO_4^{2-}/ZrO_2 are suitable for the transesterification of crude palm oil to biodiesel. This preliminary study shows that only specified solid catalyst is suitable for different types of oils, owing to the different chemical compositions of different oils.

The transesterification of palm kernel oil with methanol can be actively catalyzed over modified dolomite catalysts at low temperature (of around only 60°C) (Ngamcharussrivichai et al., 2007). The preparation of modified dolomite catalysts is simple, using conventional precipitation method with nitrate salt solution of these metals. This study reported that calcium was the most active and suitable catalyst for transesterification of palm kernel oil which gives the highest yield of biodiesel of about 99.9 %. The effect of catalyst calcination temperature and comparison of the catalyst activity among different metal oxides were the main focus of this study.

Ngamcharussrivichai et al. (2008) further improved their research work with detail studies on transesterification of palm kernel oil using calcium and zinc catalysts. Transesterification of palm kernel oil with methanol was carried out over mixed oxides of Ca and Zn in a batch reactor system at 60°C and 1 atm. CaOZnO catalysts were prepared via conventional co-precipitation of the corresponding mixed metal nitrate solution. In their experimental work, high yield of biodiesel (of more than 94 %) was obtained under suitable transesterification conditions at 60°C (catalyst amount = 10 wt%, methanol/oil molar ratio = 30, reaction time = 1 h) with the Ca/Zn ratio of 0.25. According to the trend of results obtained, they eventually summarized that alkaline heterogeneous-catalyzed transesterification reaction is strongly dependent on the amount of alkaline sites.

Advance study on optimizing the transesterification process of palm oil was reported by Kansedo et al. (2008) and Hameed et al. (2008) with the use of design of experiment. Kansedo et al. (2008) reported on transesterification process optimization using montmorillonite KSF as a heterogeneous catalyst instead of other solid catalysts. On the other hand, Hameed et al. (2009) reported on the optimization of alkaline-catalyzed transesterification of palm oil using KF/ZnO. Both research works utilized design of experiment to simulate optimum process condition and a mathematical model to represent the heterogeneous catalytic transesterification involving similar process parameters that are reaction temperature, reaction time, methanol to oil molar ratio, and catalyst loading. Two types of mathematical models were proposed to represent the reaction process by these two research groups, indicating that different reaction conditions for the reactions catalyzed by different type of catalysts (Kansedo et al., 2008; Hameed et al., 2009).

Other than methanol, it was also proven that biodiesel can be produced from transesterification of palm oil using ethanol as alcohol source. This research work was done by Alamu and his research group (Alamu et al., 2008). In their study, biodiesel was produced from ethanol and palm kernel oil using alkali-catalyzed transesterification reaction.

Non-catalytic transesterification of palm oil using supercritical methanol technology was introduced by Song et al. (2007). At supercritical methanol condition, the conversion of palm oil into biodiesel was extremely fast and almost complete conversion can be achieved in short reaction time (approximately 5 min) as compared to catalytic-transesterification process. Joelianingsih et al. (2008) proposed non-catalytic transesterification of palm oil at sub-critical methanol. The transesterification reaction was carried out with superheated methanol at atmospheric pressure. The semi-batch reactor system successfully achieved high yield of biodiesel with a reaction time of 5 hr. Despite the long reaction time required, this study has shown the feasibility of producing biodiesel with high yield without the use of catalyst.

Table 2.1 compares the transesterification of palm oil using supercritical alcohol technology with catalytic process and transesterification conducted in sub critical methanol. Referring to **Table 2.1**, transesterification using supercritical methanol was found to give the highest yield of biodiesel within the shortest reaction period. The yield of biodiesel can achieve higher than 95 % within a short reaction period of 5 min. As compared to other processes that require few hours to achieve high yield of biodiesel, transesterification in supercritical methanol technology was shown to be faster and more convenient for production of biodiesel from palm oil.

Table 2.1: Various methods for transesterification of palm oil with methanol/ethanol.

		Reaction conditions					
Type of alcohol	**Catalyst used**	**Reaction temperature (^oC)**	**Reaction time**	**Molar ratio of alcohol to oil**	**Catalyst loading (wt%)**	**Biodiesel yield (%)**	**Reference**
Catalytic transesterification process:							
Methanol	SO_4^{2-}/ZrO and ZnO	200	4.0 hr	6 : 1	3.0	78 -86	Jitputti et al. (2006)
Methanol	Montmorillonite KSF	150	2.5 hr	10 : 1	4.0	79	Kansedo et al. (2008)
Methanol	KF/ZnO	65	9.7 hr	11 : 1	5.5	89	Hameed et al. (2009)
Methanol	$CaO \cdot ZnO$	60	1.0 hr	30 : 1	10.0	>94	Ngamcharussrivichai et al. (2008)
Ethanol	KOH	60	2.0 hr	0.2 : 1	1.0	96	Alamu et al. (2008)
Transesterification using subcritical alcohol technology:							
Methanol	N/A	250	5.0 hr	N/A	N/A	95	Joelianingsih et al. (2008)
Transesterification using supercritical alcohol technology:							
Methanol	N/A	350	5 min	45 : 1	N/A	> 90	Song et al. (2007)

2.2 Technology Reported on Production of Biodiesel from Jatropha Oil

Jatropha oil is a popular biofuel resource for tropical regions such as India, Africa and Indonesia due to its abundance availability in these regions. Jatropha oil which has high content of FFA up to 14 % is not suitable for conventional transesterification reaction using homogeneous alkaline catalysts due to soap formation and catalyst deactivation. Generally, four types of transesterification methods have been proposed by many researchers for effective transesterification of jatropha oil into biodiesel, which are; acid-catalyzed reaction, solid alkaline-catalyzed reaction, two-step esterification followed by transesterification reaction and supercritical alcohol technology.

Heterogeneous alkali-catalytic transesterification method was proposed as solution to overcome the shortcomings of homogeneous alkaline-catalyzed reaction for transesterification of oil with high FFA content. In a research work done by Zhu et al. (2006), transesterification of jatropha oil was performed with methanol and catalyzed by CaO as solid alkaline catalyst. CaO was reported as a potential solid super base catalyst which is relatively cheap, easily prepared, and can give biodiesel yield as high as conventional transesterification reaction. Vyas et al. (2009) reported the use of alumina loaded with potassium nitrate (KNO_3/Al_2O_3) as solid alkaline catalyst for transesterification of jatropha oil with methanol. Compared with CaO super base catalyst reported by Zhu et al. (2006), KNO_3/Al_2O_3 catalyst is superior in terms of its reusability; in which KNO_3/Al_2O_3 catalyst was reported can be recycled and reused for at least three times.

Acid-catalyzed transesterification reaction seems to be the most suitable method for production of biodiesel from jatropha oil with high FFA content. Problems such as soap formation and catalyst deactivation can be fully eliminated using acid catalyst instead of alkaline catalyst. However, acid-catalyzed reaction is relatively slow as compared to other catalytic-reaction process. Therefore, in recent years, two-step reaction process has been introduced by many researchers for production of jatropha biodiesel as an improvement to conventional transesterification. In the two-step reaction, jatropha oil with high FFA content was initially pretreated with acid to reduce the FFA content and followed by transesterification using alkaline-catalyst. The first reaction step involves esterification of FFA with alcohol catalyzed by acid catalyst such as H_2SO_4. Next, the FFA-free jatropha oil was transesterified with alcohol using conventional alkaline catalytic reaction, catalyzed by alkaline catalyst such as sodium hydroxide or potassium hydroxide (De Oliveira et al, 2008; Berchmans et al., 2008; Lu et al., 2008; Kumar Tiwari et al.; 2007). Kumar Tiwari et al. (2007) conducted process optimization studies on this method and reported a maximum biodiesel yield of 99% can be obtained at the optimum reaction conditions of: 1.43 %v/v H_2SO_4, 0.28 v/v methanol/oil ratio, 88 min reaction time at 60^oC for the first step reaction, and the optimum reaction conditions for second step reaction are: 0.55 %w/v KOH, 0.16v/v methanol/oil ratio, 24 min reaction time at 60^oC.