SYNTHESIS OF FATTY ACID METHYL ESTERS (FAME) FROM PALM OIL VIA NON-CATALYTIC SUPERCRITICAL FLUID REACTION

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by

TAN KOK TAT

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First of all, I would like to dedicate this thesis to my late father who was my inspiration and strength during the difficult moments. His words of wisdom and invaluable advices were my main driving forces during the completion of this thesis. Not to forget my beloved family members who have always supported me during good and bad periods.

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LIST OF SYMBOLS

A	Reaction temperature code (°C)
A_i	Pre-exponential Factor, i = 1,2,3,4,5 and 6 (dm^3/mol.s)
ANOVA	Analysis of variance
B	Solvent to oil molar ratio code (mol/mol)
C	Reaction time code (minute)
Ea_i	Activation Energy, i = 1,2,3,4,5 and 6 (J/mol)
F-value	Ratio of model mean square to residuals mean square
k_i	Reaction rate constants, i = 1,2,3,4,5 and 6 (dm^3/mol.s)
MR_i	Molar ratio of solvent to oil
n	Number of experiment
R	Gas constant (J/mol.K)
R^2	Correlation coefficient
T	Reaction temperature (K)
t	Reaction time (seconds)
x	Independent variable
Y	Response (Yield)
y_i	Concentration, i = 1,2,3,4,5 and 6 (mol/dm^3)
β	Constants in quadratic model
α	CCD rotatable value

LIST OF ABBREVIATION

ASTM	American Society of Testing and Materials
CCD	Central Composite Design
DMC	Dimethyl carbonate
DOE	Design of Experiment
DAG	Diacetylglycerides
EU	European Union
FAEE	Fatty acid ethyl esters
FAME	Fatty acid methyl esters
FFA	Free fatty acids
GC	Glycerol carbonate
GHG	Greenhouse gas
GL	Glycerol
MA	Methyl acetate
MAG	Monoacetylglycerides
ROH	Alcohol
RSM	Response Surface Methodology
SCA	Supercritical alcohol
SCDMC	Supercritical dimethyl carbonate
SCE	Supercritical ethanol
SCF	Supercritical fluid
SCM	Supercritical methanol
SCMA	Supercritical methyl acetate
TAG	Triacetylglycerol
TG	Triglycerides

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SINTESIS ASID LEMAK METIL ESTER DARIPADA MINYAK KELAPA SAWIT MELALUI TINDAKBALAS BENDALIR LAMPAUGENTING TANPA MANGKIN

ABSTRAK

Minyak kelapa sawit terdapat dengan banyaknya di Malaysia dan telah dibukti merupakan bahan mentah yang berpotensi tinggi dalam penghasilan asid lemak metil ester (FAME) atau biodiesel jika dibandingkan dengan minyak yang lain. Dalam kajian ini, minyak kelapa sawit digunakan sebagai sumber trigliserida dalam tindakbalas bendalir lampaugenting (SCF). Pelarut yang diselidiki dalam kajian ini adalah metanol, metil asetat dan dimetil karbonat. Sistem eksperimen telah berjaya direka dan dibina untuk tindakbalas SCF. Tindakbalas SCF tanpa mangkin tersebut dilakukan dengan suhu tindakbalas dari 300°C hingga 400°C, nisbah molar pelarut berbanding minyak dari 10 hingga 50 mol/mol dan masa tindakbalas dari 5 hingga 60 minit. Analisis statistik kaedah rekabentuk eksperimen telah digunakan untuk menyelidik pengaruh suhu tindakbalas, masa tindakbalas dan nisbah molar pelarut berbanding minyak terhadap hasil biodiesel. Keadaaan operasi optimum untuk 3 tindakbalas SCF tersebut telah ditentukan dengan menggunakan kaedah respon permukaan untuk mencari hasil biodiesel yang optimum.

Keputusan kajian menunjukkan bahawa 3 tindakbalas SCF tersebut mempunyai ciri-ciri tersendiri. Sebagai contoh, tindakbalas metanol lampaugenting (SCM) menunjukkan prestasi yang baik jika dibandingkan dengan tindakbalas konvensional bermangkin dalam aspek masa tindakbalas dan hasil biodiesel. Tindakbalas tanpa mangkin ini hanya memerlukan 16 minit masa tindakbalas dan suhu tindakbalas 372°C untuk mencapai hasil biodiesel yang tinggi sekitar 82%. Di samping itu, tindakbalas metil asetat lampaugenting (SCMA) memerlukan tempoh

tindakbalas yang lebih lama (59 minit) dan suhu tindakbalas yang lebih tinggi (399°C) untuk mencapai hasil biodiesel 98% yang mengandungi FAME dan triacetin. Keputusan kajian menunjukkan bahawa triacetin tidak menyebabkan kesan buruk terhadap ciri-ciri biodiesel tetapi sebaliknya meningkatkan ciri-ciri aliran sejuk seperti takat tuang dan takat berawan. Untuk tindakbalas dimetil karbonat lampaugenting (SCDMC), hanya keadaan operasi yang biasa sahaja diperlukan (380°C suhu tindakbalas dan 30 minit masa tindakbalas) untuk mencapai keputusan hasil biodiesel melebihi 91%. Selain itu, penghasilan gliserol karbonat (GC) sebagai hasil sampingan dalam tindakbalas tersebut membolehkan pemprosesan biodiesel yang lebih ekonomik.

Di samping itu, semua proses SCF telah ditunjukkan mempunyai toleransi yang tinggi terhadap bendasing seperti asid lemak bebas dan sebatian air yang umum dijumpai dalam sisa minyak/lemak. Maka, dengan toleransi yang tinggi tesebut membolehkan penggunaan bahan mentah murah seperti minyak masak terpakai selain minyak terproses yang lebih mahal dan seterusnya membolehkan penghasilan biodiesel yang kos efektif. Selain itu, model matematik berdasarkan kajian kinetik yang mencukupi dan signifikan telah berjaya dihasilkan untuk tindakbalas SCF untuk mempredik hasil produk pada semua keadaan eksperimen. Tambahan pula, parameter kinetik yang penting seperti tenaga pengaktifan dan langkah penentu kadar untuk tindakbalas SCF telah diperolehi melalui model matematik tersebut. Akhirnya, biodiesel yang dihasilkan telah menjalani beberapa ujian dan telah ditunjukkan bahawa biodiesel tersebut memenuhi piawaian antarabangsa iaitu criteria EN and ASTM. Oleh sebab itu, dapat disimpulkan bahawa tindakbalas SCF adalah teknologi baru yang berpotensi dan berkemampuan dalam penghasilan biodiesel.

SYNTHESIS OF FATTY ACID METHYL ESTERS (FAME) FROM PALM OIL VIA NON-CATALYTIC SUPERCRITICAL FLUID REACTION

ABSTRACT

Palm oil is abundantly available in Malaysia and has been shown to be a promising feedstock in fatty acid methyl esters (FAME) or biodiesel production compared to other vegetable oils. In the present study, palm oil was utilized as the source of triglycerides in supercritical fluid reactions. The solvents that were investigated in this study were methanol, methyl acetate and dimethyl carbonate. An experimental system was successfully designed and fabricated for supercritical fluid (SCF) reaction. The non-catalytic SCF reactions were carried out with reaction temperature varying from 300°C to 400°C, molar ratio of solvent to oil from 10 to 50 mol/mol and reaction time of 5 to 60 minutes. Statistical analysis method of design of experiment (DOE) was employed to investigate the effects of temperature, reaction time and molar ratio of solvent to oil on the yield of biodiesel. The optimum operating conditions for the 3 supercritical fluid reactions were determined by using response surface methodology (RSM) in order to find the optimum yields of biodiesel.

It was found that the 3 SCF reactions have their own characteristics. For instance, supercritical methanol (SCM) reaction showed superior performance compared to conventional catalytic reaction in terms of reaction time and yield. This non-catalytic reaction only required 16 minutes of reaction time and 372°C reaction temperature to achieve high yield of approximately 82%. On the other hand, supercritical methyl acetate (SCMA) reaction required longer reaction time (59 minutes) and higher reaction temperature (399°C) to accomplish 98% yield of biodiesel mixture comprising of FAME and triacetin. It was shown that the presence of triacetin did not cause adverse effect on the properties of biodiesel but instead led to improvement in cold flow properties such as pour point and cloud point. For supercritical dimethyl carbonate (SCDMC) reaction, only milder operating conditions (380°C of reaction temperature and 30 minutes of reaction time) were necessary to achieve a high yield more than 91%. Besides, the formation of glycerol carbonate (GC) as co-product in the reaction leads to more economical processing costs of biodiesel.

Furthermore, the SCF processes were shown to have high tolerance towards impurities such as free fatty acids and water compounds which are common in waste oils/fats. Hence, the high tolerance allows the utilization of inexpensive feedstock such as waste cooking oils rather than the costly refined oils and subsequently leads to cost-effective biodiesel production. In addition, mathematical models based on kinetics study were successfully developed for the SCF reactions which are adequate and significant to predict the yield of reactants and products at any designated experimental conditions. Besides, important kinetic parameters such as activation energy and rate limiting step of the SCF reactions were obtained via the mathematical model. Finally, the produced biodiesel were subjected to several characterization tests and they were found to fulfil the international standard of EN and ASTM criteria. Hence, it can be concluded that SCF reaction is a highly potential and promising new technology in biodiesel production.

CHAPTER 1

INTRODUCTION

1.1 Global Energy Scenario

Fossil fuels such as petroleum, natural gas and coal have been the main source of energy supply around the world for the past few decades. Most countries depend heavily on fossil fuels to generate energy in terms of electricity, transportation fuels and heat which is essential for continuous development and economic growth of a country. For instance, as shown in Figure 1.1, the demand for petroleum and coal in the world market have been increasing steadily over the past 20 years and is projected to escalate substantially within the next three decades (EIA, 2010). However, these fossil fuels are non-renewable and will be depleted in the future which prompted concerns of energy security and sustainability. Moreover, uncertainty over petroleum reserves and volatile political scenario in Middle East countries, which are the main producers of petroleum in the world have led to unstable supply of petroleum in the world market. Hence, with high demand and limited supply of fossil fuels, the prices of these energy sources have been escalating to unprecedented heights lately. For instance, the price of crude petroleum oil has been increasing significantly for the past several years with record high of US$ 130 per barrel in 2008.

On the other hand, utilization of these expensive energy sources is also one of the main causes of environmental pollution. The combustion process of these non-renewable fossil fuels emits excessive toxic gases which include carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxide (NO), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2). These harmful gases, particularly CO_2 are responsible for green house effect phenomenon as it can trap enormous amount of heat in the atmosphere and subsequently leads to global warming scenario. Besides, extensive exposure to elevated amount of these poisonous gases has been found to be hazardous to human beings as well as affecting ecological stability. Consequently, it is vital to replace these fossil fuels with alternative energy which are economical, renewable and sustainable.

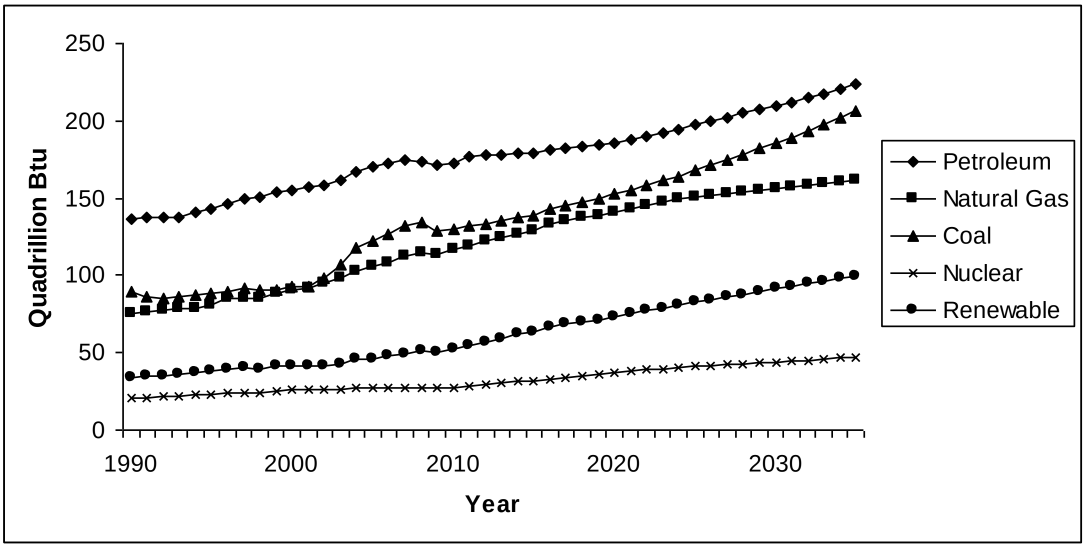


Figure 1.1: World marketed energy use by fuel type (EIA, 2010)

1.2 Renewable Energy

For the past two decades, the search for alternative energy which is renewable and environmental-friendly has been carried out extensively over the world. Renewable energy is derived by utilizing inexhaustible natural resources including sunlight, wind, geothermal and biomass to produce energy in terms of liquid fuels, electricity and heat. Hence, renewable energy sources do not emit excessive harmful gases or particulates to the environment as in non-renewable fossil fuels. Instead, it has the potential to mitigate climate change and solve environmental pollution crisis in the world. For instance, renewable energy such as biofuels is produced from crops and biomass, which absorb carbon from the atmosphere as they grow. Subsequently, the carbon will be released during combustion of biofuels and return to the atmosphere. Hence, biofuels is a carbon neutral source of energy as no additional emission is discharge to the environment during the carbon cycle. Apart from being environmental-friendly, renewable energy also offer a promising solution for energy security and sustainable development in the long term due to the renewable feedstock used in the production.

Currently, there are many types of renewable energy that are being heavily researched and developed in the world, namely solar, wind, hydrothermal, geothermal and biofuels. However, apart from biofuels, all these renewable energy are only able to generate electricity and thermal energy from infinite sources while 40% of total energy consumption in the world is in the form of liquid fuels such as diesel or gasoline. Hence, the most attractive and practical choice to replace fossil fuels as the main source of energy would be biofuels, which are mostly in liquid forms. Generally, biofuels can be divided into a few categories such as biodiesel, bioethanol, biomethanol and biohydrogen. Among all, biodiesel has been receiving a lot of attention due to similarity between biodiesel and conventional diesel in terms of chemical structure and energy content. Besides, no modification in diesel engine is required as biodiesel is compatible with existing engine model and has been commercially blended with diesel as transportation fuel in several countries including Germany, Italy and Japan. In addition, biodiesel is better than diesel as far as sulfur content, flash point, aromatic content and biodegradability are concerned (Saka and Kusdiana, 2001)

Biodiesel is defined as fatty acid alkyl ester and is derived from triglycerides via transesterification reaction with alcohols such as methanol and ethanol (Yin *et al.*, 2008). In this reversible reaction, 1 mol of triglycerides will react with 3 mol of alcohol to produce 1 mol of glycerol and 3 mol of fatty acid alkyl esters. If methanol is used as the source of alcohol, fatty acid methyl ester (FAME) will be formed. On the other hand, if ethanol is used, fatty acid ethyl ester (FAEE) will be produced. Both of these alkyl esters are commonly known as biodiesel. Generally, the sources of triglycerides are obtained from oil-bearing crops, namely rapeseed, soybean and palm as well as animal fats such as tallow (Demirbas, 2008b). Transesterification reaction can proceeds with or without the presence of catalyst. However, without any catalysts the reaction proceeds in an extremely slow rate due to immiscibility between oil and alcohol. Thus, catalysts are normally introduced into the reaction medium to increase the reaction rate.

The transesterification reaction can be catalyzed by both homogeneous and heterogeneous catalysts. In addition, the catalysts can be either acidic or alkaline such as sulfuric acid, hydrochloric acid, sodium hydroxide and potassium hydroxide which are all homogeneous catalysts. In fact, most of the conventional commercial plants producing biodiesel from vegetable oils have been using these homogenous catalysts. However, it was found that separation and purification of products and catalysts required complicated procedures due to the homogenous phase of the mixture. Consequently, the production cost and energy consumption in the process become unattractive and impractical from economic considerations. Apart from that, the catalyst will react with free fatty acids (FFA) available in vegetable oils and subsequently produce unwanted side product such as soap (Marchetti and Errazu, 2008). Consequently, other alternative technologies were developed in order to solve the problems arise from homogeneous reaction.

Subsequently, heterogeneous catalytic reactions were extensively developed and carried out by using acidic or alkaline catalysts in transesterification reaction. The potential catalysts that have been proposed include alkaline metal oxides, solid resins, enzymes and zeolites. Application of heterogeneous catalysts simplifies separation and purification processes as the product is in different phase from the catalysts. Besides, the presence of high FFA content in vegetable oils will not affect the yield of alkyl esters as no soap formation will occur. Nevertheless, application of heterogeneous catalysts in biodiesel production has been found to suffer from low yield and longer reaction time. Besides, utilization of expensive solid catalysts also increased the total production costs in this process.

1.3 Supercritical Fluid (SCF) Technology

Due to the limitations of homogeneous and heterogeneous catalytic reaction in biodiesel production, there have been a lot of alternative technologies that have been proposed in order to solve the problems. One of them which have been widely reported lately is by employing non-catalytic supercritical fluid (SCF) technology. In this method, the reactants are subjected to supercritical conditions of the solvent/ reactant (i.e. alcohol) without the presence of any catalysts. During supercritical state, the properties of the solvent do not fulfil the definition of neither liquid nor gas but in between these two phases. It possesses unique solvating and transport properties which could solve the problems associated with the two-phase nature of alcohol and oil mixture by forming a single phase solution during supercritical conditions. Hence, the presence of catalyst to enhance the reaction rate is not required in SCF reaction which makes separation and purification of products to become simpler and cost-effective procedures compared to catalytic reactions (Saka and Kusdiana, 2001). Furthermore, it was reported that transesterification reaction in SCF method could be completed in a shorter amount of time compared to conventional catalytic reactions. Besides, no side products such as soap will be formed as FFA in vegetable oils will be esterified simultaneously during transesterification reaction to become fatty acid alkyl esters (Warabi *et al.*, 2004). Table 1.1 summarizes the critical properties for several solvents commonly employed in SCF reactions.

Table 1.1: Critical properties for selected solvent

Solvent	**Critical Temperature (°C)**	**Critical Pressure (MPa)**
Methanol	239	8.09
Ethanol	243	6.38
Carbon dioxide	31	7.39
Methyl acetate	234	4.69
Dimethyl carbonate	275	4.63

1.4 Palm Oil in Malaysia

Palm oil (*Elaeis guineensis*) is one of the most important vegetable oils in the world market. This is due to versatility of palm oil as source of triglycerides which is the major component in producing edible and non-edible products including cooking oil, margarine, soap and cosmetics. Besides, the high yield of palm oil per hectare also makes this crop an attractive choice of vegetable oil in term of economic consideration. Generally, palm oil consists of myristic acid, $C_{14:0}$ (1%), palmitic acid, $C_{16:0}$ (46%), stearic acid, $C_{18:0}$ (3%), oleic acid, $C_{18:1}$ (44%) and linoleic acid, $C_{18:2}$

(6%). Therefore, palm oil consists of mainly saturated and mono-unsaturated fatty acids only with negligible amount of poly-unsaturated fatty acids.

Malaysia has always been one of the major producers of palm oil in the world for the past few decades. For instance, as shown in Figure 1.2, Malaysia contributed approximately 39% of the total production of palm oil in the world which was 45.1 million ton in 2009 (MPOB, 2009). In recent years, palm oil was not only seen as a valuable source of consumer products, but also as potential renewable energy source such as biodiesel. Moreover, with the huge demand of palm oil in the world market, it was not surprising to note that palm oil has surpassed soybean oil as the largest source of vegetable oils since 2007, consisting more than 25% of total vegetable oils produced. However, escalating palm oil production has leads to concerns regarding the sustainability of oil palm plantation with arising environmental issues such as deforestation and animal extinction. Nevertheless, the issues have been addressed and with strong collaboration between non-governmental organizations and government authorities particularly in Malaysia, measurements have been implemented to ensure sustainable development in terms of palm oil production and environmental conservation.

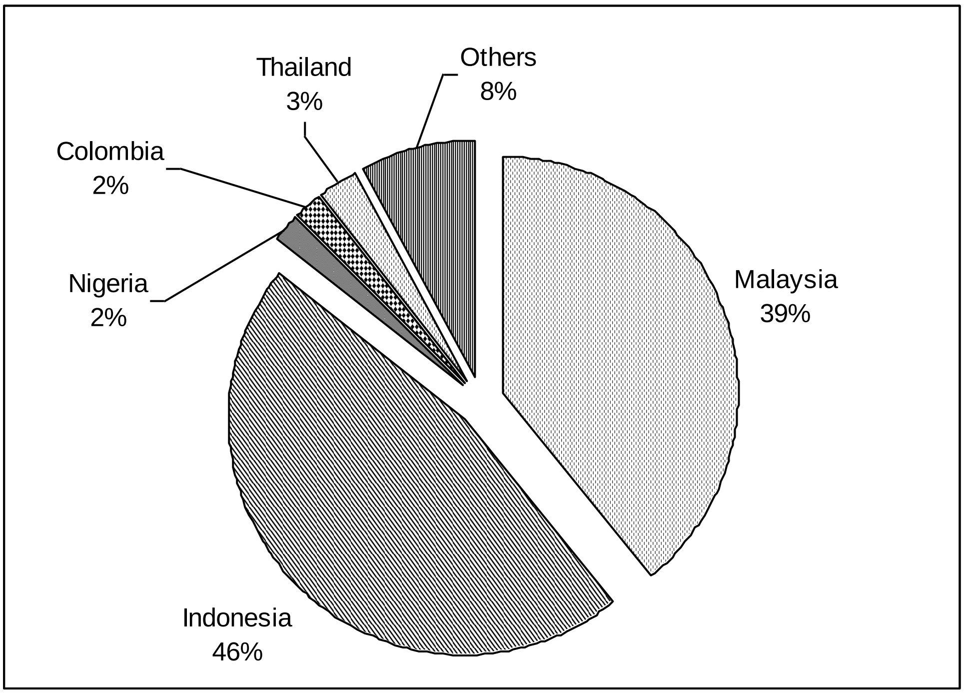


Figure 1.2: World major producers of palm oil in 2009 (MPOB, 2009)

1.5 Problem Statement

The escalating demand of renewable and environmental-friendly source of energy has prompted many researchers to focus on the production of biodiesel from vegetable oils such as rapeseed oil, soybean oil and sunflower oil. Most of the studies concentrate on developing catalytic transesterification reactions which have several limitations and drawbacks in terms of biodiesel yield, reaction time and cost. Hence, there is a growing interest in alternative processes which can solve the problems arise in catalytic reactions such as non-catalytic supercritical fluid technology.

Currently, most reported studies in supercritical reactions for biodiesel production involved alcohol as the solvent. However, there is limited literature on biodiesel production from palm oil via supercritical alcohol technology. Therefore, it is very beneficial to conduct a comprehensive process study for biodiesel production from palm oil for better understanding of supercritical alcohol technology.

Palm oil is abundantly available in Malaysia and therefore is an attractive source of triglycerides to be used as biodiesel feedstock. Besides, palm oil has the highest yield per hectare among all vegetable oils in the world market. Hence, it has the potential to be the major source of triglycerides for biodiesel production throughout the world. Moreover, biodiesel derived from palm oil will be an environmental-friendly and sustainable source of renewable energy since it is essentially free of sulfur and nitrogen compounds.

On the other hand, employment of alcohol in transesterification reaction with triglycerides inevitably produces glycerol as side product which has low economic value and leads to uneconomical biodiesel production. Hence, it is interesting to investigate the potential of glycerol-free processes involving non-alcohol solvents such as methyl acetate and dimethyl carbonate. In these glycerol-free methods, valuable side products of triacetin and glycerol carbonate will be produced, instead of unwanted glycerol. Consequently, it will makes biodiesel production to be more economical and cost-competitive compared to petroleum-derived diesel.

Apart from that, there are limited researches on developing a suitable mathematical model for SCF reaction. Currently, most studies only reported a simplified kinetics model to represent the SCF transesterification by considering the overall transesterification reaction while ignoring the intermediate reactions. Therefore, there are inadequate knowledge on the 3 sequential and reversible reactions in SCF reaction such as rate limiting step and activation energy for each step in transesterification reaction. Therefore, it is vital to develop a comprehensive model which considered all intermediate reactions and subsequently provide useful information on SCF reaction.

1.6 Objectives

1. To optimize the yield of fatty acid methyl esters (FAME) from palm oil and various solvents via SCF reaction by response surface methodology.
2. To investigate the potential of co-solvent in reducing the various operating conditions of SCF reaction.
3. To develop mathematical models suitable for SCF reaction.
4. To analyze the properties of FAME produced in the study.

1.7 Scope of Study

Employment of non-catalytic SCF reaction is one of the major breakthroughs in biodiesel processing in recent years. The absence of catalyst in this method reduces processing cost substantially compared to conventional catalytic reaction. Therefore, it is of major importance to investigate the potential of producing FAME by SCF methods.

In this study, FAME from palm oil will be produced in a batch-type tube reactor via SCF reaction. Various operating conditions which include temperature, molar ratio of solvent to oil and reaction time will be investigated in order to obtain the optimum conditions for FAME production. Information on optimum operating conditions of SCF reaction is valuable and vital for commercialization and industrial applications.

Generally, methanol is utilized in transesterification reaction with triglycerides to produce FAME and glycerol as side product. Therefore, it is interesting to investigate the potential of non-alcohol solvents in FAME production which leads to other side products rather than glycerol. Hence, in this study, palm oil will react with 3 different solvents in transesterification reaction to produce FAME.

The solvents that will be employed are methanol, methyl acetate and dimethyl carbonate. Therefore, 3 dissimilar side products will be formed which are glycerol, triacetin or glycerol carbonate, depending on the type of solvent utilized. The performance of the solvents in terms of FAME yield will be compared and analyzed thoroughly.

The SCF reaction will be conducted at temperature beyond critical temperature of the solvents. For methanol, the critical temperature is 239°C while for methyl acetate and dimethyl carbonate they are 234°C and 275°C, respectively. Besides, the molar ratio of solvent to oil will be in the range of 10 to 60 mol/mol and reaction time between 10 to 60 minutes. Furthermore, the effects of impurities commonly found in waste oils/fats such as FFA and water on FAME yield in supercritical reaction will be investigated as well. Excellent tolerance towards impurities is vital to allow utilization of inexpensive waste oils/fats rather than refined oils as feedstock in order to minimize total production costs.

Apart from that, the potential of co-solvent in reducing the operating conditions required in SCF reaction will be examined. Heptane was chosen as potential co-solvent due to its excellent miscibility with polar and non-polar compounds. In addition, mathematical models will be developed which are adequate to represent SCF reaction. Several important kinetics parameters such as activation energy, reaction rate constant and pre-exponential factor will be determined for SCF reaction.

Finally, the FAME produced via SCF reaction will be characterized according to methods which fulfil international standards of ASTM-D6751 or EN-14214. The physico-chemical properties of FAME produced by the 3 different solvents will be analyzed and compared with international ASTM and EN criteria.

1.8 Organization of Thesis

Generally, this thesis consists of five chapters. Chapter 1 gives an outline of the whole thesis which covers the current global energy scenario, definition of renewable energy, potential of palm oil as the source of biodiesel and brief introduction on SCF technology. Besides, problem statement illustrates the problems faced and the necessity of carrying out the current research study. Apart from that, the research objectives highlight the aims and purposes of this study. The scope of study elaborates the objectives in details and provides the focus and limitations of the study. On the other hand, organization of thesis provides brief information on the content of every chapter in this thesis.

Subsequently, Chapter 2 compiled all literature reviews conducted which include definition and mechanism of transesterification reaction, types of catalytic transesterification reaction and progress in non-catalytic transesterification reaction. Updated literature covering a wide range of feedstock for biodiesel production is summarized and presented in details. Apart from that, advantages of SCF technology compared to conventional catalytic reactions are covered as well.

Chapter 3 presents the experimental methodology and analysis. The details of chemicals and materials used throughout the study are listed in details. Besides, this chapter also provides the details of experimental set-up, application of statistical analysis tool, operating procedures of the SCF system, product analysis and characterization methods.

Chapter 4 comprises of results and discussion of the research study. It is divided into several parts which include (a) Design of Experiments (DOE) to find the optimum conditions for SCF reaction involving palm oil and 3 different solvents of methanol, methyl acetate and dimethyl carbonate (b) effects of impurities on the yield of FAME produced in SCF reaction (c) potential of co-solvent in reducing the severe conditions of supercritical reaction (d) development of mathematical models which could represent transesterification supercritical reaction (e) characterization of FAME produced via supercritical reaction to obtain their physico-chemical properties and subsequently compared with international ASTM and EN criteria.

Chapter 5 provides a summary of the results obtained in the research study. Besides, conclusion remarks and recommendations for future works in SCF technology were discussed as well.

CHAPTER 2

LITERATURE REVIEW

2.1 Palm Oil as Biodiesel Feedstock

Oil palm industry in Malaysia has emerged from a small plantation area into a well developed and diversified industry to accommodate the demand of human beings over the past few decades. From a mere exporter of crude palm oil and edible products such as cooking oil and margarine, it has evolved to become a major component in other industries producing non-edible products such as soap and detergent and oleochemical compounds including biodiesel and glycerol. Recently, palm oil application in oleochemical industries has been expanding with mounting interest from biodiesel producers due to its high productivity and inexpensive cost. Currently, the main source of triglycerides employed as biodiesel feedstock is rapeseed oil which comprised approximately 84% of global biodiesel production as shown in Table 2.1 (Thoenes, 2007). Rapeseed oil is extensively utilized as biodiesel feedstock in the European Union (EU) particularly Germany which is the main producer of biodiesel in the world with annual production of nearly 2.8 million ton from 6 million ton worldwide (Martinot, 2008). However, rapeseed suffers from high processing cost as well as low oil yield per ha which leads to expensive biodiesel production.

On the other hand, palm-based biodiesel production only consists of 1% from global biodiesel production but the high yield of palm oil/ha makes it an attractive choice to be employed as biodiesel feedstock. Figure 2.1 shows annual oil yield per hectare for major vegetable oils in the world (Thoenes, 2007). From the figure, it is obvious that the average annual yield of palm oil is the highest with approximately 4.2 ton/ha, far exceeding the average yield of rapeseed oil of 1.2 ton/ha while soybean only produces 0.4 ton of oil per ha annually. Being a perennial crop, oil palm has the advantage of producing consistent yield of oil for at least 20 years after maturation period compared with annual crops such as rapeseed and soybean which require replanting activities yearly. Hence, the yields of rapeseed and soybean are substantially lower, allowing palm oil to be an attractive and major feedstock for biodiesel production.

Table 2.1: Percentage of biodiesel produced worldwide from various vegetable oils (Thoenes, 2007)

Source of Biodiesel	**Percentage**
Rapeseed Oil	84%
Sunflower Oil	13%
Palm Oil	1%
Soybean Oil and others	2%

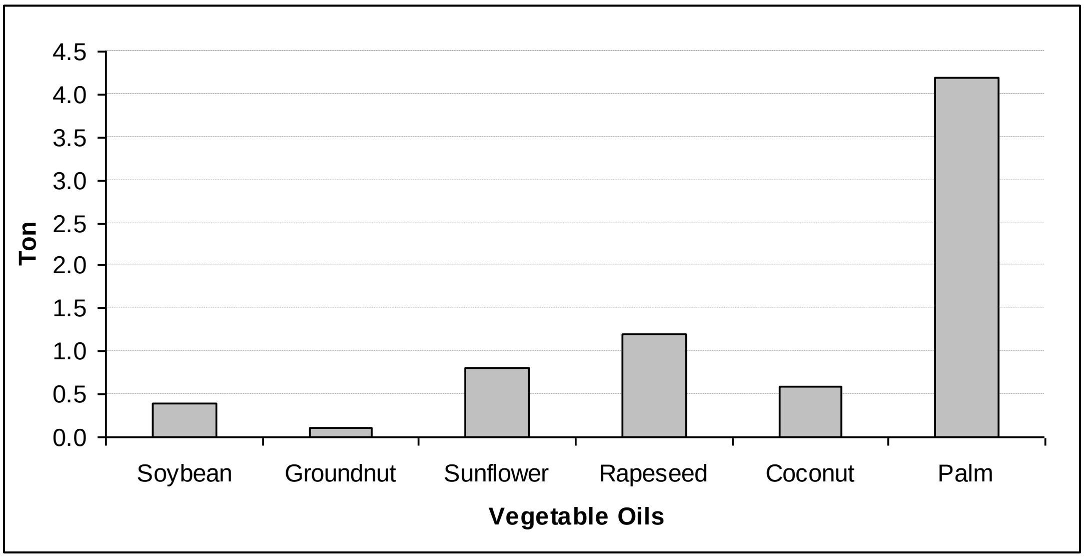
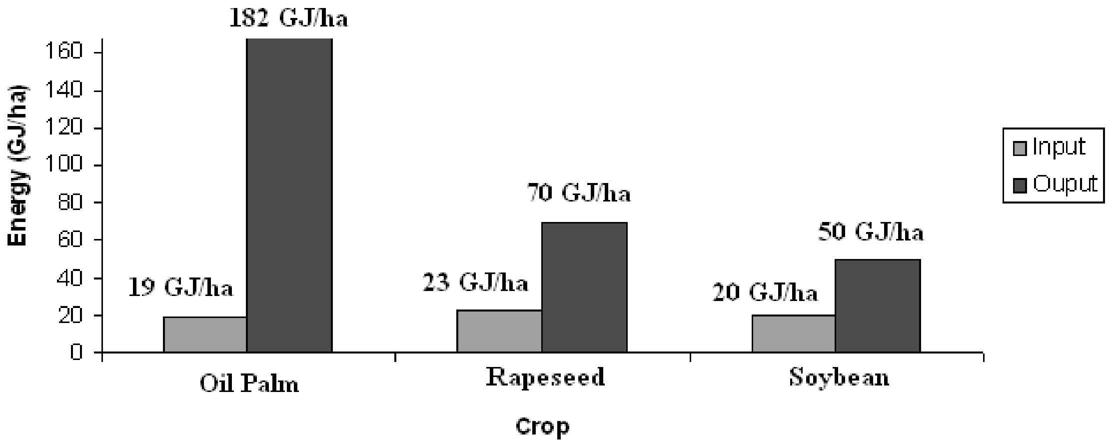


Figure 2.1: Annual oil yield per ha for selected vegetable oils (Thoenes, 2007)

In addition, the production cost of palm oil is the least expensive among all vegetable oils. For instance, the production cost for palm oil is approximately US$ 228/ ton while the cost to produce an equivalent amount of rapeseed oil would cost nearly 3 times of palm oil at US$ 648. For soybean oil, the price is also costlier with production rate of US$ 400/ ton (Lam *et al.*, 2009). Hence, utilization of palm oil as biodiesel feedstock has the potential to reduce the cost of biodiesel, leading it to be an economical and cost-effective biofuels compared with petroleum-derived diesel. On the other hand, in terms of energy output to input (O/I) ratio, oil palm was found to be superior to other major oil-bearing crops as shown in Figure 2.2 (Lam *et al.*, 2009). For instance, the energy ratio (O/I) of oil palm is the highest at 9.6 compared with rapeseed and soybean, which only have ratios of 3.0 and 2.5, respectively. In other words, oil palm only consumes 1 unit of energy to produce 9.6 unit of energy which is important to address the issue of energy sustainability in biodiesel. In this context, the energy input includes fertilizer, fuel for machinery, sunlight and others which are essential to produce energy output such as oil and biomass. As mentioned previously, rapeseed and soybean are annual crops which require energy input for ploughing, sowing and fertilizing yearly, leading them to require higher energy input compared with perennial crop like oil palm.

Furthermore, oil palm tree has the potential to mitigate carbon dioxide (CO_2) emission due to its high efficiency in absorbing this harmful greenhouse gas during photosynthesis compared with tropical rainforest. It was reported that annual net assimilation of CO_2 for oil palm plantation and tropical rainforest is 64.5 and 42.4 ton CO_2 per hectare, respectively (MPOC, 2007). This proves that oil palm is superior in terms of carbon sequestration and thus has the ability to alleviate greenhouse effect and global warming. Besides, oil palm tree is also competent in biomass production as well, with an annual increment of 8.3 ton compared with 5.8 ton for rainforest (MPOC, 2007). Biomass generated by oil palm has several applications and usage, ranging from natural fertilizer derived from empty fruit bunch to renewable energy sources such as bioethanol and biohydrogen.



Output/Input Ratio (O/I)	Oil Palm	Rapeseed	Soybean
GJ/ha	9.6	3.0	2.5

Figure 2.2: Comparison of energy ratio of output to input for palm oil, rapeseed and soybean (Lam *et al.*, 2009)

At present, oil palm is grown on less than 5 % of the world's agriculture land for major edible oils production but it accounts for a massive 25 % of the global market share. With high yield of oil per ha and inexpensive cost of production, palm oil has become the largest source of vegetable oil in the world, surpassing soybean oil which was the main supply of vegetable oil for the past few decades. For instance, in 2007, the global production of palm oil was 38.5 million ton, exceeding the total productivity of soybean oil by 1.6 million ton. On top of that, oil palm only utilized a mere 10.5 million ha to produce this enormous amount of palm oil, while soybean requires a massive plantation area of nearly 95 million ha which is approximately 10 times more than oil palm. This proves that oil palm is more efficient than soybean in terms of land utilization, thus ensuring optimized productivity to cater the mounting demand of oils as food and fuel feedstock in the world market. Hence, as the largest source of oil in the world, palm oil has proven its capacity to be the major feedstock for biodiesel production without compromising its supply to other edible and non-edible industries. This is important as the demand for biodiesel in the world market has been escalating particularly in the EU which is the main consumer of biodiesel in the world. Furthermore, the EU commission has set a target of employing 5.75 % of biofuels in 2010 and palm oil has been seen as the ideal feedstock to meet the mounting demand for biodiesel.

Apart from economic consideration, palm-based biodiesel was reported to be superior to biodiesel produced from other type of oils in terms of energy sustainability. In this context, the sustainability of biodiesel produced from various oils was investigated by conducting a life cycle assessment (LCA) analysis which is vital to determine the energy ratio (O/I) for biodiesel production. This cradle-to-grave analysis covers the lifespan of biodiesel which begins from crop cultivation to the production of biodiesel. It was reported that palm-based biodiesel requires substantially lower amount of energy to produce 1 ton of biodiesel compared with rapeseed-based biodiesel with the total energy consumed of 17.2 GJ and 74.7 GJ, respectively. Furthermore, the energy ratio (O/I) for the production of 1 ton of palm-based biodiesel is significantly higher at 3.53, far superior to rapeseed-based biodiesel with the value of only 1.44 (Yee *et al.*, 2009). Hence, it can be concluded that palm-derived biodiesel only requires a small amount of energy input in the production process, thus ensuring its sustainability in terms of energy utilization.

Biodiesel from biomass such as palm oil is an environmental-friendly source of energy. The carbon released during the combustion process of biodiesel was absorbed by the biomass from the atmosphere during cultivation period of the crop. Hence, palm oil can be considered as a carbon neutral source of energy because no additional carbon is released to the atmosphere. In addition, palm oil is essentially free of hazardous compounds such as sulfur and nitrogen which contribute significantly towards global warming and acid rain phenomenon. Consequently, displacement of petroleum-derived diesel with renewable biodiesel will be able to mitigate environmental pollution as well as addressing the issues of energy security and sustainability. Furthermore, palm-based biodiesel was reported to have similar fuel properties compared to petroleum-derived diesel (May *et al.*, 2005b). Hence, engine modification is not required to employ biodiesel in existing diesel-powered vehicles. In addition, biodiesel has higher flash point and cetane number, leading it to offer enhanced safety for air-fuel mixture and excellence ignition property, respectively. Besides, field trials of palm-based biodiesel involving different types of vehicle such as taxis, buses and trucks have been successfully carried out and no major difference in engine performance was detected. On top of that, palm-based biodiesel has been proven to fulfil international benchmark such as American Society of Testing and Materials (ASTM) standards which is important for commercialization purposes throughout the world (Al-Widyan and Al-Shyoukh, 2002; Kalam and Masjuki, 2002).

2.2 Transesterification Reaction

Generally, the overall reaction between triglycerides and alcohol is as shown in Figure 2.3. In this reaction, the alcohol is hydrolyzed and reacts with another ester compound, leading it to be known as alcoholysis reaction as well. In this reaction, alcohol is the acyl acceptor of (R_nCO-) group found in triglycerides to form fatty acid alkyl esters (FAAE) and glycerol. Alternatively, it is also possible to utilize other compounds as acyl acceptor to replace alcohol such as carboxylic acid and ester. If ester is employed as acyl acceptor, the reaction is known as interesterification which involved exchange of acyl group between two different ester compounds. On the other hand, acidolysis reaction takes place when an ester compound reacts with carboxylic acid. These three reactions of alcoholysis, interesterification and acidolysis are often grouped together and known as transesterification reaction.

In biodiesel production, transesterification reaction is the main reaction that occurs between triglycerides and alcohol to produce FAAE and glycerol (GL). Transesterification is an equilibrium reaction which consists of three consecutive and reversible reactions where diglycerides (DG) and monoglycerides (MG) are formed as intermediates as shown in Figure 2.4 (Schuchardt et al., 1998; Song et al., 2008). In this reaction, one of the alkoxy groups in the triglycerides (TG) is replaced by another alkoxy group in the alcohol (ROH) to form a new ester compound of FAAE (Demirbas, 2005). Finally, after all the three alkoxy groups available in triglycerides have been replaced, 3 mol of FAAE and 1 mole of GL molecule will be formed. As these reactions are reversible, a larger amount of alcohol than stoichiometry requirement is commonly employed to shift the reaction equilibrium to produce more alkyl esters.

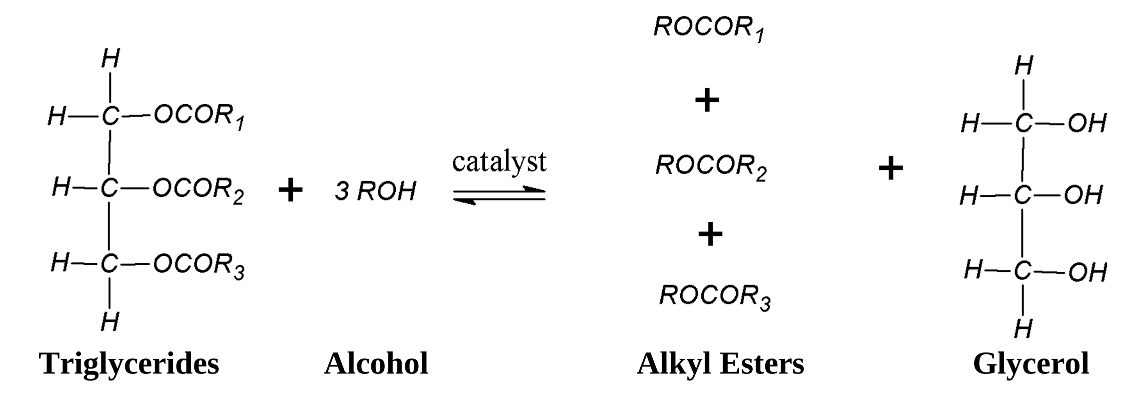


Figure 2.3: General transesterification reaction between triglycerides and alcohol (Song *et al.*, 2008)

Triglycerides (TG)	+	ROH	⇌	Diglycerides (DG)	+	FAAE
Diglycerides (DG)	+	ROH	⇌	Monoglycerides (MG)	+	FAAE
Monoglycerides (MG)	+	ROH	⇌	Glycerol (GL)	+	FAAE

Figure 2.4: The three reversible and consecutive reactions in transesterification of triglycerides (Schuchardt *et al.*, 1998; Song *et al.*, 2008)

The main objective of transesterification reaction is to alter the properties of vegetable oils to values similar to petroleum-derived diesel. Neat vegetable oils could not be used directly in the diesel engine due to its high viscosity and low volatility (Demirbas, 2005). Besides, it will also cause some carbon deposition and injector coking in the diesel engine. Hence, transesterification reaction is employed to solve these problems. Table 2.2 shows comparison between vegetable oils and their respective methyl esters in terms of physical and chemical properties such as viscosity, density and flash points. From the table, it is obvious that neat vegetable oils have significant high values of viscosity, ranging from 32.6 to 39.6 mm^2/s while their respective methyl esters have substantially lower values from 3.7 to 4.6 mm^2/s

which is approximately similar with the viscosity of diesel (4.3 mm^2/s). Besides, the high values of flash point in vegetable oils (246-274°C) make them an unsuitable fuel source with the low volatility characteristic. On the other hand, the flash points of methyl esters are relatively lower (155-174°C), offering excellent combustion quality which is comparable with diesel.

Table 2.2: Comparison of properties for selected vegetable oils and their respective methyl esters (Barnwal and Sharma, 2005; Demirbas, 2005)

Fuel Type	**Viscosity (mm^2/s (at 40°C))**	**Density (kg/m^3(at 15°C))**	**Flash Point (°C)**
Palm oil	39.6	918.0	267
Palm methyl ester	3.7	870.0	170
Rapeseed oil	37.0	911.5	246
Rapeseed methyl ester	4.6	885.0	155
Soybean oil	32.6	913.8	254
Soybean methyl ester	4.1	885.0	174
Sunflower oil	33.9	916.1	274
Sunflower methyl ester	4.2	880.0	170

In general, alcohol and oil are not miscible to form a single phase of solution at room temperature. Consequently, the reaction rate of transesterification is relatively slow at low temperature due to poor contact area between these two reactants. Hence, vigorous mixing and stirring are usually carried out to enhance the solubility and subsequently improve the reaction rate substantially. Apart from that, temperature also plays a crucial role in determining the reaction rate as well. For instance, the reaction requires up to 8 hours of reaction time to reach completion at ambient temperature. On the other hand, if the reaction temperature was conducted at

60°C, only a mere 120 minutes of reaction time will be needed. Nevertheless, catalysts are commonly introduced in the reaction medium to improve the reaction rate and yield of biodiesel. The presence of catalysts will be able to solve the problem of immiscibility between alcohol and oil as it acts as an intermediate compound in the reaction and subsequently induced rapid reaction rate. There are two types of catalysts commonly employed in biodiesel production which are homogeneous and heterogeneous catalysts. In brief, catalysts which are in the same phase as the reactants are classified as homogeneous catalysts while those in different phase are known as heterogeneous catalysts. Hence, liquid catalysts such as sodium hydroxide and sulfuric acid are categorized as homogeneous whereas solid catalysts including enzymes are regarded as heterogeneous catalysts. Furthermore, the catalysts are also classified as either acid or base, depending on the nature of active compound found in the catalysts.

2.3 Catalytic Homogeneous Reaction

2.3.1 Base-Catalyzed Reaction

Homogeneous catalysts such as sodium hydroxide and potassium hydroxide are commonly and widely used in commercial biodiesel plant throughout the world. These soluble catalysts are inexpensive and effectively enhanced biodiesel production by producing intermediate of methoxide which will react with oil to produce biodiesel and glycerol. A lot of researches have been reported in the literature involving homogeneous base catalysts with refined oils, animal fats or waste oils as the source of triglycerides. Animal fats and waste oils are cheap sources of triglycerides which has the potential to reduce the cost of biodiesel substantially since the cost of feedstock contributes more than 70% of the total production expenditures (Haas *et al.*, 2004). However, these waste oils/fats commonly have high percentage of impurities such as free fatty acids (FFA) and water which could cause soap formation and reduce catalyst efficiency. Hence, waste oils/fats usually undergone pre-treatment procedure to remove these impurities prior to reaction to avoid undesirable side reactions.

Ma and co-workers studied base-catalyzed transesterification reaction by using beef tallow as the source of triglycerides with sodium hydroxide and sodium methoxide as homogeneous catalysts (Ma *et al.*, 1998). The experiments were carried out with and without the presence of FFA and water content in the waste oils. The results obtained show that the yield of methyl esters was optimum when no FFA or water was added. Besides, it was found that sodium hydroxide and sodium methoxide attained maximum conversion of triglycerides at 0.3% and 0.5% weight of catalyst compared to beef tallow, respectively. However, with the presence of FFA or water in the reaction medium, the yields reduced significantly due to saponification reaction between sodium hydroxide and FFA. In addition, it makes separation and purification procedures of biodiesel to become more complicated. Hence, it was concluded that FFA and water contents should be kept below 0.5% and 0.05% (weight), respectively for effective transesterification reaction involving sodium hydroxide as homogeneous catalyst.

Apart from beef tallow, another source of waste which has the potential to be used as biodiesel feedstock is waste cooking oil. Waste cooking oil is a growing problem throughout the world. It is usually discharge by pipelines and drains which subsequently create nuisance for wastewater treatment plants. Hence, it is a very attractive solution to utilize this waste cooking oil as biodiesel feedstock which can also resolve environmental problems due to improper disposal. Several researchers have embarked on a few experiments in utilizing waste cooking oil as biodiesel feedstock. For instance, Felizardo and co-workers carried out an experimental study on waste cooking oil transesterification (Felizardo *et al.*, 2006). Initially, the waste cooking oil was subjected to pre-treatment steps to alleviate the percentage of water and FFA content to avoid saponification reaction. In their work, the best conditions for biodiesel production from waste cooking oil were investigated by using sodium hydroxide as base catalyst and 1 hour reaction time. Besides, various molar ratio of alcohol to oil were studied as well at 65°C of reaction temperature. It was found that the optimum conditions were methanol to oil molar ratio of 4.8 and catalyst to oil ratio of 0.6% which produced more than 96% of biodiesel yield. Furthermore, it was reported that increment in methanol or catalyst content helped to increase the yield to 98% and reduced the viscosity of biodiesel.

Recently, there are several researchers that carried out experiments by using basic alkaline-earth metal compounds in transesterification reaction. One of them is Arzamendi and co-workers who utilized alkaline-earth metal hydroxides such as sodium, potassium, lithium, rubidium and cesium to investigate the effect of different metal hydroxides on transesterification reaction. The experiments were carried out by using sunflower oil as the source of triglycerides, temperature at 50°C, ratio of alcohol to oil of 12:1 and catalyst concentration equivalent to 0.1% NaOH for comparison purposes. It was reported that except for lithium hydroxide, all the hydroxides produce relatively similar yield of biodiesel which is approximately 90% after 90 minutes of reaction time. For lithium hydroxide, it was observed that there was an induction period occurred during the early stages but the reaction achieved a comparatively high conversion of 85% after 90 minutes. Generally, alkaline-earth metals are strong bases which can easily dissolve in methanol to produce methoxide