

**ULTRASONIC ASSISTED TRANSESTERIFICATION OF PALM OIL WITH  
METHANOL USING BARIUM OXIDE AS CATALYST**

**MOHD RUZAINI BIN ARIFFIN**

**A thesis submitted in the fulfillment of the  
requirements for the award of the degree of  
Bachelor of Chemical Engineers**

**Faculty of Chemical and Natural Resources Engineering  
Universiti Malaysia Pahang**

**JANUARY, 2012**

## ACKNOWLEDGEMENT

In the name of Allah S.W.T the Most Beneficent and the Most Merciful. The deepest sense of gratitude to the Almighty for the strength and ability to complete this project. Infinite thanks I brace upon Him.

I would like to take this opportunity to express my sincere appreciation to my supervisor Dr Chin Sim Yee, for encouragement, guidance, morale support, and critics in bringing this project fruition. Without her outstanding support and interest, this thesis would not been at the best it would right now.

I would also like to express my deepest appreciation to my mother whom always support me and motivate me to complete this final year project.

Last but not least, I am also in debt to Faculty of Chemical and Natural Resources Engineering for the usage of workstation lab for my research. My sincere appreciation also extends to all my colleagues, housemates, and friends whom had provided assistance at various occasions.

Finally to individuals who has involved neither directly nor indirectly in succession of this thesis. Indeed I could never adequately express my indebtedness to all of them. Thank you.

## ABSTRACT

The energy source which we rely on is in high demand than ever before and the solution for this is Biofuel. There are different processes which can be applied to synthesize biodiesel such as direct use and blending, micro emulsion process, thermal cracking process and the most conventional way is transesterification process. The homogenous catalyst is not environmental friendly, during the glycerol separation process it is complicated because of saponification process and when without ultrasonic, the reaction will take longer time. The ultrasonic-assisted transesterification of palm oil in the presence of alkaline earth metal oxide catalysts, Barium Oxide was investigated in this research. The objective of this research is to determine the feasibility of transesterification process by using heterogeneous catalyst, barium oxide (BaO) with ultrasonic bath. Ultrasonic was used to study on the reaction for effect of temperature at 40°C -60°C, alcohol to palm oil molar ratio (6:1–15:1), and catalysts loading (1–3%). The experimental procedure to produce biodiesel consist 2 major steps which were transesterification and settling. Optimum operating condition is at 50°C of temperature with molar ratio of alcohol to oil is 9:1 and 3 wt% of loading catalyst barium oxide. The highest conversion of methyl ester from this optimum operating condition is 91%

## ABSTRAK

Sumber tenaga yang digunakan sekarang mempunyai permintaan yang lebih tinggi daripada sebelumnya dan cara penyelesaian masalah ini adalah dengan menggunakan Biofuel. Terdapat proses yang berbeza yang boleh digunakan untuk menghasilkan biodiesel seperti penggunaan secara langsung dan mengadun, proses emulsi mikro, proses keretakan haba dan cara yang paling konvensional adalah proses transesterification. Pemangkin homogenus yang digunakan tidak mesra alam dan semasa proses pemisahan gliserol, ia begitu rumit disebabkan oleh terbentuknya buih-buih sabun dan tidak menggunakan ultrasonic, ia akan mengambil masa yang lebih lama. Objektif utama kajian ini adalah untuk mencari kesan optimum penggunaan pemangkin heterogenus, barium oksida (BaO) dengan bantuan ultrasonic. Dengan bantuan ultrasonic, kajian ini dijalankan pada suhu 40°C-60°C, nisbah antara alcohol dan minyak sawit pada (6:1-15:1), dan jumlah pemangkin pada (1-3%). Terdapat 2 langkah utama untuk menghasilkan biodiesel iaitu transesterification dan rehatkan. Hasil daripada kajian ini, keadaan yang optimum adalah pada suhu 50°C dengan nisbah alcohol dan minyak pada 9:1 dan berat pemangkin pada 3 wt%. Penghasilan methyl ester yang paling tinggi daripada keadaan optimum ini adalah 91%.

## CHAPTER ONE

### INTRODUCTION

#### 1.1. BACKGROUND OF RESEARCH

The energy source, fossil fuel, upon which we have come to rely on so heavily, is in higher demand than ever before that more energy is needed to fulfill this demand. Fossil fuel alone seems to be insufficient to cater to the needs of the global community. In light of this, it is in the world's best interest to devote a substantial amount of resources towards alternative forms of energy. Biofuel, as biodiesel in this context, is at the forefront of these alternatives due to its ability to fuel conventional diesel engines with minimum or no modifications, as well as form blends with fossil diesel.

Biodiesel is defined as fatty acid methyl esters prepared from any kind of feed stock including vegetable oils, animal fats, single cell oils, and waste material. Fatty acid ethyl esters can also be defined as and used to produce biodiesel. However, due to the relatively high price of ethanol compared to methanol, the use of ethyl esters has not been established to a level on par with methyl esters. The preparation of fatty acid methyl esters can be achieved by a process called transesterification, which is the exchange of alcohol or acid moiety of an ester. Alcoholysis is the transesterification of an ester with an alcohol, whereby methanolysis is the term used in the case of methanol.

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water (Srivatava and Prasad *et al.*, 2000). This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by the

general equation as in equation 1. Transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants. However, the presence of a catalyst (a strong acid or base) will accelerate the conversion.



Among the benefits of biodiesel is that there is no net output of carbon in the form of carbon dioxide (CO<sub>2</sub>). This is due to the fact that the same amount of carbon dioxide is absorbed during the growth period of oil crops as is emitted by fuel combustion. One ton of fossil fuel combusted releases 3 tons of carbon dioxide into the atmosphere while biodiesel only releases that which it has taken in while the plants it is made from were growing. Therefore, there is no negative impact on the carbon cycle. Biodiesel has many favorable emissions characteristics in comparison to conventional fossil diesel. It is known to have 100% reduction of net carbon dioxide, 100% reduction of sulphur dioxide, 40-60% reduction of soot emissions and 10-50% reduction of carbon monoxide. Biodiesel also exhibits a reduction of all polycyclic aromatic hydrocarbons (PAHs) and specifically the reduction of carcinogenic PAHs such as phenanthren by 97%, benxofloroanthen by 56%, benz-a-pyrene by 71%, aldehydes and aromatic compounds by 13% asl well as 5-10% reduction of nitrous oxide depending on the age and tuning of the vehicle concerned.

B-100, which represents 100% biodiesel, is as biodegradable as sugar and less toxic than conventional table salt. The rate of biodegradation of biodiesel is up-to four times higher than that of fossil diesel fuel. It has up to 98% biodegradation in three weeks. It also stores without letting up in completely full, cool, dark containers Therefore, spillages of biodiesel present a significantly lower risk compared to fossil diesel.

All feed stocks that contain fatty acids or glycerol can be used for biodiesel production including waste cooking oil. In European countries, rapeseed oil is used due to its widespread availability. Soybean oil is used in the Unites States of America, while

palm oil is used widely in tropical regions such as Malaysia. The use of methyl esters as fuel requires a low proportion of saturated fatty acids in order to make the fuel function at low temperatures. In colder climates, rapeseed oil and olive oil have proven to be one of the best options. The usage of palm oil is ideal in Malaysia due its abundant availability as well as its suitability in warm climates. Palm oil can also be used as blends with other types of oil. The type of feedstock chosen is also influenced by national and international specifications of biodiesel that need to be fulfilled.

## 1.2 PROBLEM STATEMENT

There are several methods used for biodiesel producing. These methods are microemulsion, pyrolysis, direct use and blending, and transesterification process. The regular method that always use was transesterification process. Based on the research of Hanna *et al.* (1999), the first method such as microemulsion and dilution method were unsuitable to use due to high viscosity of raw oils. Actually, these methods have such problems when use with the high viscosity oil. Using the biodiesel fuel from these methods will contribute to engines performance problem. Second method such as pyrolysis also is able to use. But it also has lack of problems which it will produce more biogasoline than biodiesel fuel. Thus, it wills lowers the product yield resulted low cost of sell. So, to overcome those problems using the transesterification process was found to be the most viable oil modification process.

Current commercial technology using homogeneous base catalyst was found not suitable for the transesterification of waste cooking oil due to its high FFA content. On the other hand, using homogeneous acid catalyst requires longer reaction time and could potentially cause corrosion on equipment. Unlike homogeneous catalyst, heterogeneous catalysis has many advantages: they are relatively non-corrosive, environmentally benign and present fewer removal problems. They are also much easier to be separated from liquid products and can be designed to give higher activity, selectivity and longer catalyst lifetimes.

To date, many solid base catalysts have been developed for biodiesel production, such as basic zeolites, alkaline earth metal oxides and hydrotalcites. On top of that, alkaline earth metal oxides especially calcium oxide, CaO have attracted much attention due to their relatively high basic strength, low solubility in methanol and can be synthesized from cheap sources like limestone and calcium hydroxide (Zabeti *et al.*, 2009).

Finally the conventional method that already use regularly was still in lack of technology. The reason is the time consuming in the process will affect high cost of production. So, to reduce the time consumed, the high technology that can shorten the time must be used such as ultrasonic technology. This concept of ultrasonic will increase the chemical reaction speed of the transesterification of palm oil into biodiesel fuel. The cavitation mixing in ultrasonic is an effective alternative means to achieve a better mixing in commercial processing. Ultrasonic cavitation provides the necessary activation energy for the industrial transesterification process. All those factors will reduce the operational costs and also can reduce the investment in production.

### **1.3 RESEARCH OBJECTIVES**

The aim of this study is to determine the feasibility of ultrasonic assisted transesterification process using heterogeneous catalyst, barium oxide (BaO).

### **1.4 SCOPE OF RESEARCH**

To achieve the objective of this research, there are three scopes have been identified:

- i. To study the effect of catalyst concentration of barium oxide (BaO) on the single step transesterification process of palm oil.
- ii. To study the effect of molar ratio of methanol on palm oil of single step transesterification process.
- iii. To study the effect of reaction temperature on single step transesterification process of palm oil



## 1.5 SIGNIFICANCE OF RESEARCH

This studies was been carried out to synthesise and develop new solid catalysts for transesterification reaction in order to overcome disadvantages of use of homogeneous catalyst and more likely to reduce the cost of biodiesel production. Advantage when using heterogeneous catalysis are they are relatively non-corrosive, environmentally benign and present fewer removal problems. Bournay et al. (2006) invented a new commercial continuous biodiesel production process, where a solid catalyst consists of zinc oxide and alumina was used and results showed that the process does not require any post treatment to remove the catalyst from biodiesel and methyl ester yields, close to theoretical value, were achieved at high pressure and temperature. Moreover, glycerol obtained through this process had a purity of approximately 98%.

The numerous advantages of using Ultrasonic transesterification would bring about volumes of significance in the biodiesel production industry. This is due to the fact that aside from giving relatively high yield, it would monumentally reduce the length of processing time needed for production, and this would go well to supply the ever increasing rate of demand for alternative liquid fuel. With Ultrasonic transesterification, the biodiesel production industry in Malaysia would be able to cater to the needs of Malaysians at a faster rate, thereby eliminating the need for any dependence on foreign alternative fuel that may arise in the future. Malaysia would be able to deal with its own fuel crisis, at an optimal rate using its abundant feedstock resources and ultrasonic transesterification.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 BIODIESEL

Rudolf Diesel (1858-1913) developed the first engine to run on peanut oil. He demonstrated this invention at the World Exhibition in Paris in 1900. A vegetable oil powered engine however, was not fully realized in his lifetime. He firmly believed that since the diesel engine can be fed with vegetable oils, it would help considerably in the development of agriculture of the countries which use it. Although the use of vegetable oils for engine fuels seemed insignificant during his day, such oils have come to be as important as the petroleum and coal tar products used at that time.

Canakci and Van Cerpen *et al.* (2003) have developed a pilot plant to produce biodiesel from feedstock with high FFAs content via two steps method; esterification and transesterification. The feedstock was first treated with  $H_2SO_4$  to reduce the level of FFAs to below 1 wt%, followed by transesterification process catalyzed by homogeneous base KOH. Although high FAME yield can be obtained, but the rate of FFA esterification reaction was relatively very slow. Thus, higher amount of acid catalyst are required to accelerate the rate of reaction. The drawback of this two-step process is even more pronounced due to the requirement of extra separation steps to remove the catalyst in both stages. Although problem of catalyst removal from the first stage can be avoided by using base catalyst from the second stage through neutralization process, the use of extra base catalyst will add to the cost of biodiesel production (Kulkarni *et al.*, 2006)

Kouzu *et al.* (2008) reported that CaO obtained from calcinations of pulverized limestone,  $\text{CaCO}_3$  at 900 °C for 1.5 h in the flow of helium gas exhibited substantially good result in transesterification of refined soybean oil. The yield of FAME was 93% after 1 h reaction time at methanol reflux temperature and methanol to oil ratio 12:1. However, the yield of FAME dropped to 66% when waste cooking oil with FFA content 2.6 wt.% was used under the same reaction condition. It is obvious that the basic sites of CaO were poisoned by strong adsorption of FFAs on the surface of the catalyst (Kouzu *et al.*, 2000). Consequently, a portion of the catalyst changed into calcium soap by reacting with the FFAs adsorbed, resulting in low recovery of catalyst. Kouzu *et al.* (2008) further reported that the concentration of Ca in reaction product was 3065 ppm which exceeded the basic standard of biodiesel; the concentration of mineral matter should be below 200 ppm (Kouzu *et al.*, 2008).

Wang *et al.* (2008) explored the potential of ultrasonic technology in enzymatic transesterification of high acid value waste oil. It was found that the enzymatic activity was enhanced with the assistance of low frequency and mild energy ultrasonic sound wave. Under the optimal ultrasonic assistant reaction conditions, such as 8% oil quantity of Novozym 435, molar ratio of propanol to oil 3:1, frequency of ultrasonic assistant 28 kHz occupied at power 100 W, reaction temperature at 40–45°C, an overall biodiesel (propyl oleate) conversion of 94.86% was achieved in only 50 min.

The rapid development of the petroleum industry produced a cheap byproduct called diesel fuel that eventually became the source of power to a modified diesel engine. As a result, vegetable oil was forgotten as a renewable source of power. Diesel engines today are designed to run on fuel that is less viscous than vegetable oil. However, times of fuel shortages saw cars and trucks were successfully run on biodiesel made from preheated peanut oil and animal fat. The upper rate for inclusion of rapeseed oil with diesel fuel is about 25% but crude vegetable oil as a diesel fuel extender induces poorer cold-starting performance compared with diesel fuel or biodiesel made with fatty esters (McDonnell *et al.*, 1999).

Present day diesel engines have need of a clean-burning, stable fuel that can operate under a variety of conditions. Biodiesel as fatty esters was developed as an alternative to petroleum diesel due to the fuel shortages of the mid 1970s and further interest spewed forth in the 1990s due the large pollution reduction benefits coming from the use of biodiesel.

The use of biodiesel is affected by legislation and regulations in all countries (Knothe *et al.*, 2002). In the Philippines, the Government directed all of its departments to incorporate one percent by volume coconut biodiesel in diesel fuel for use in government vehicles. The EU Council of Ministers adopted pan-EU rules for the detaxation of biodiesel and biofuels. In the United States, by 1995, percent of all federal vehicles were to be using alternative fuels to set an example for the private automotive and fuel industries. According to the AFP, Malaysia announced that it will build three plants to produce biodiesel from palm oil, as part of efforts to reduce its dependency on foreign oil and increase demand for domestically produced palm oil, Commodities Minister Peter Chin Fah Kui, September 26, 2005

Biofuel is at the forefront of the array of alternative energy sources that are being researched and developed today. Having physical and chemical properties that are compatible with its fossil counterpart has placed biodiesel as one of the most suitable alternatives to complement today, and perhaps even replace fossil diesel tomorrow. Its ability to fuel conventional diesel engines with minimum or no modifications, and to form blends with fossil diesel make it the most practical, and feasible alternative energy source to invest in.

There are many ways how biodiesel serves to benefit the environment more than fossil diesel. One major aspect of life cycle assessments is the potential of global warming, expressed as carbon dioxide, CO<sub>2</sub> equivalents. CO<sub>2</sub> is produced during the whole production process of fuels, biological based and fossil based alike. Due to the positive energy balance of biodiesel and the fact that biodiesel mainly consists of renewable material one could expect a large saving of greenhouse gases compared to fossil fuel. Now, while this remains true in the case of CO<sub>2</sub>, certain parties argue that if

other greenhouse gases like N<sub>2</sub>O and CH<sub>4</sub> are considered, which have higher global warming potential, the advantages of biodiesel are slightly diminished. Even so, the relative savings of greenhouse gases for the use of biodiesel over fossil diesel is 2.7kg of saved CO<sub>2</sub> equivalents for every kg of substituted fossil diesel fuel. Pure biodiesel is also completely free of sulfur and, this inadvertently reduces sulfur dioxide exhaust from diesel engines to virtually zero.

## **2.2 RAW MATERIALS**

The feedstock for biodiesel included virgin oil, waste vegetable oil and animal fat. The type of feedstock that is the most suitable varies from country to country and is dependent on an array of factors. These factors encompass the availability of the said feedstock, price, its suitability with the local climate and the adherence of the final product towards national and international specifications.

### **2.2.1 Soy Bean Oil**

Soybean oil is used as a major source of edible oil throughout the world. With about 222 million tonnes, soybean is the most important oil bearing plant cultivated world-wide and its production is seeing a further expansion, particularly in the USA, Brazil and Argentina (Bockey *et al.*, 2006). According to the National Board of Biodiesel (USA), soybean oil is the primary source for biodiesel production in US and an estimated 75 million gallons of biodiesel were to be produced in 2005. Soybeans can be produced without or nearly zero nitrogen. This makes soybeans advantageous for the production of biodiesel as nitrogen fertilizer is one of the most energy costly inputs in crop production. Pimental and Patzek *et al.* (2005) studied the energy estimation for producing soybean biodiesel. They reported that 5546 kg of soybeans were required for producing 1000 kg of oil and biodiesel production using soybean required 27% more fossil energy than the biodiesel fuel produced.

### **2.2.2 Palm and Pam Kernel Oil**

Oil is derived from both the flesh and the seed of the palm fruit. The fruit consists of an outer pulp, which is the source of crude palm oil and two or three kernels, which are the source of another oil type – palm kernel oil. Crude palm oil is semisolid at room temperature. Palm kernel oil is rich in lauric and myristic fatty acid with an excellent oxidative stability and sharp melting. Malaysia is the world's largest palm growing country and palm plantation covers two-third of its agricultural lands. Palm oil has been proved to be an efficient biodiesel source. The average yield of approximately 6000 l of palm oil/ha can produce 4800 l of biodiesel (Addison and Hiraga *et al.*, 2010). It has been stated that palm oil can have high levels of fatty acids, which require extra methanol transesterification before it can be used as biodiesel, thus increasing the cost of production somewhat (Crabbe *et al.*, 2001). Farmers in Ghana are producing biodiesel from palm kernel oil for powering their farm vehicles and generators.

### **2.2.3 Jatropha Oil**

Recently Jatropha is being considered as one of the most promising potential oil source to produce biodiesel in Asia, Europe and Africa. Jatropha can grow under a wide variety of climatic conditions like severe heat, low rainfall, high rainfall and frost. Jatropha is grown in marginal and waste lands with no possibility of land use competing with food production. Jatropha oil content varies depending on the types of species, climatic conditions and mainly on the altitude where it is grown. Various parts of the plant have medicinal values. Apart from supplying oils for diesel replacement, the growing of the tree itself effectively reduces CO<sub>2</sub> concentrations in the atmosphere. In developing countries like India it has been identified as the major source of biodiesel.

#### 2.2.4 Waste and Fat

Due to the high cost of crude and refined vegetable oil, cheaper animal fats and waste cooking oils available from restaurants and households are attracting attention as possible feedstocks. But unfortunately they contain large amount of FFAs. Refined vegetable oils contain generally less than 0.05% free fatty acid, while the FFA content in crude vegetable oil, restaurant waste grease, animal fat and trap grease are in the ranges of 0.3–0.7, 2–7, 5–30 and 40–100%, respectively (Van Gerpen *et al.*, 2004).

Any water and FFAs in feedstock will slow the alkali-catalyzed transesterification reaction. Ma *et al.* (1998) investigated the influence of FFA and water on transesterification of beef tallow. They reported that that for achieving best biodiesel conversion from beef tallow FFA content and water content of beef tallow should be kept within 0.06% w/w and 0.5% w/w. Waste oils and fats having low FFA and water content can be converted to biodiesel by traditional alkaline catalytic process. Since the FFA content of waste oils and fats is generally too high, it is impossible to convert those oils and fats to biodiesel using a single-alkaline catalyzed process. A pretreatment step is necessary to reduce the FFA content via an esterification reaction with methanol in presence of sulphuric acid. Canakci and Van Gerpen *et al.* (2003) developed a two-step process for producing biodiesel from brown grease having 40% FFA. In pretreatment step, the acid value was reduced to 2 mg KOH/g, and then the reaction was continued with alkali-catalyzed transesterification.

Even though acid catalytic process is able to esterify the FFAs present in waste cooking oil, it is not generally tried because methyl ester yield decreases due to the adverse effect of water which is produced when FFA reacts with the alcohol. Canakci and Van Gerpen *et al.* (1999) reported that methyl ester yield of acid catalytic process for soybean oil decreases from 90.54% to 58.77% when FFA level increases from 5% to 33%. Several researchers Demirbas *et al.* (2002) and Kudisana *et al.* (2004) investigated supercritical alcohol transesterification process which can efficiently convert triglycerides with high free fatty acid and water content and reported that it holds a good promise for the production of biodiesel from waste oils and fats.

There are other edible oils like safflower, linseed, olive oil, mustard oil, grape seed oil etc. which can be used as biodiesel feedstock. Babassu oil whose viscosity is quite less than castor oil is given much importance as a potential biodiesel resource in Brazil. Artichoke has been identified as a potential biodiesel crop in recent years for its oil which has a similar composition like sunflower and safflower oil. Other sources include Kukui nut, milk bush, and wild radish. Table 2.1 shows the past studies of biodiesel production via transesterification process using homogeneous, heterogeneous catalyst and different feed stock.



**Table 2.1:** Influence of feedstocks on biodiesel process selection and operating conditions

<b>Feedstock</b>	<b>Transesterification process</b>	<b>Alcohol to oil ratio</b>	<b>Catalyst to oil</b>	<b>Time</b>	<b>Temperature (°C)</b>	<b>Yield, %</b>	<b>References</b>
Sunflower	Alkali catalyzed	3:1	0.28% (w/w) KOH		70	<b>96</b>	Antolin <i>et al.</i> 2002
Soybean	Lipase catalyzed			2 h		<b>94</b>	Du <i>et al.</i> 2004
Palm	Alkali catalyzed	6:1	1% KOH	1 h	50	<b>75</b>	Darnoko and Cheryan <i>et al.</i> , 2000
Peanut	Alkali catalyzed	6:1		1 h	65	<b>82</b>	Ahmad <i>et al.</i> 2009
Jatropha	Alkali catalyzed	0.70 (w/w)	3.3% w/w NaOH to oil	2 h	60	<b>55</b>	Berchmans and Hirata <i>et al.</i> , 2008
Duck Fat	Alkali catalyzed	6:1	0.5% NaOH		60	<b>74</b>	Saydut <i>et al.</i> 2008
Cottonseed	Enzyme catalyzed	6:1	1% KOH	3 h	65	<b>97</b>	Chung <i>et al.</i> 2009

## 2.3 PROCESS OF SYNTHESIZING BIODIESEL

There are different processes which can be applied to synthesize biodiesel such as direct use and blending, micro emulsion process, thermal cracking process and the most conventional way is transesterification process. However, there are a lot of methods can be done through transesterification process such as based-catalyzed transesterification, acid-catalyzed esterification, intergrated acid-catalyzed preesterification of FFAs and based-catalyzed transesterification, enzyme-catalyzed transesterification, hydrolysis and supercritical alcohol transesterification (Saka et al., 2001).

### 2.3.1 Direct Use and Blending

The direct use of vegetable oils in diesel engine is not favorable and problematic because it has many inherent failings. The advantages of vegetable oils as diesel fuel are liquid nature-portability, heat content (80% of diesel fuel), ready availability and renewability. Then disadvantages are higher viscosity, lower volatility and the reactivity of unsaturated hydrocarbon chains (Pryde *et al.*, 1983). Problems appear only after the engine has been operating on vegetable oils for longer periods of time, especially with direct-injection engines.

The problems include coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged, oil ring sticking and thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils. Two severe problems associated with the use of vegetable oils as fuels were oil deterioration and incomplete combustion (Peterson *et al.*, 1983). Crude, degummed and degummed-dewaxed sun flower oils, as well as crude, degummed and alkali refined cottonseed oils, were tested using a single-cylinder precombustion chamber engine (Engler *et al.*, 1983). The results were negative. The processed oils which were slightly better than crude oils were not suitable for use as alternative fuels, even though they performed satisfactorily for a short time. The oils were not suitable because of carbon deposits and lubricating oil fouling.

Even though the vegetable oils have familiar properties as biodiesel fuel, it required some chemical modification before can be used into the engine. It has only been researched extensively for the past couple of decades, but has been experimented with for almost hundred years. Although some diesel engine can run pure vegetable oils, turbocharged direct injection engine such as trucks are prone to many problems. Energy consumption with the use of pure vegetable oils was found to be similar to that of diesel fuel. For short term use, ratio of 1:10 to 2:10 oil to diesel has been found to be successful (Ma and Hanna *et al.*, 1999).

### **2.3.2 Micro-emulsion Process**

Schwab *et al.* (1987) defined micro-emulsion as colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1 + 150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles. Micro-emulsion with solvents such as methanol, ethanol and 1-butanol has been studied to solve the problem of the high viscosity of vegetable oils. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles.

Ziejewski *et al.* (1984) prepared an emulsion of 53% (vol) alkali-refined and winterized sun flower oil, 13.3% (vol) 190-proof ethanol and 33.4% (vol) 1-butanol. This nonionic emulsion had a viscosity of 6.31 cSt at 40°C, acetane number of 25 and an ash content of less than 0.01%. Lower viscosities and better spray patterns (more even) were observed with an increase of 1-butanol. In a 200 h laboratory screening endurance test, no significant deteriorations in performance were observed, but irregular injector needle sticking, heavy carbon deposits, incomplete combustion and an increase of lubricating oil viscosity were reported.

### 2.3.3 Thermal Cracking (Pyrolysis)

Sonntag *et al.* (1979) defined pyrolysis as the conversion of one substance into another by means of heat or heating with the aid of a catalyst. Pyrolysis involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules (Weist *et al.*, 1979). Pyrolytic chemistry is difficult to characterize because of the variety of reaction path and the variety of reaction products that may be obtained from the reaction occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil (Ma and Hanna *et al.*, 1999).

Rapeseed oil was pyrolyzed to produce a mixture of methyl esters in a tubular reactor between 500 and 850°C and in nitrogen (Billaud *et al.*, 1995). A flow chart of the micro pilot pyrolysis plant for methyl esters from rapeseed oil and a design of the pyrolysis reactor were outlined. The conversion of methyl colzate increased with an increase of the temperature of pyrolysis. To illustrate the distribution of cracking products as a function of pyrolysis temperature, the selectivity of the products (hydrocarbons, CO, CO<sub>2</sub> and H<sub>2</sub>) obtained between 550±850°C with a constant residence time of 320 min and a constant dilution rate of 13 moles of nitrogen/mole of feedstock are provided in Table 8. The principal products were linear 1-olefins, n-paraffin and unsaturated methyl esters. High temperatures gave high yields of light hydrocarbons (66% molar ratio at 850°C).

The equipment for thermal cracking and pyrolysis is expensive for modest throughputs. In addition, while the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produced some low value materials and, sometimes, more gasoline than diesel fuel.

### 2.3.4 Transesterification Process

Transesterification of triglycerides with methanol and aid of catalyst produce methyl ester and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the forward reaction is first order reaction and the reverse reaction is found to be second order reaction. It was observed that transesterification is faster when catalyzed by alkali (Freedman *et al*, 1986).

A review from Hideki Fukuda *et al.* (2001), the activation energies of transesterification reactions of various triglycerides were calculated by Gaussian software to clarify the mechanism. The values show that the effects of the structure of the triglyceride on the reactivity are not particularly large. Moreover, formation of the fatty acid alkyl ester by the addition of an alkoxy group was considered by the activation energy. Ring formation involving the carbon of the carboxyl group and the alkoxy group at the transition state is essential for the transesterification reaction. Finally, the transesterification reaction was analyzed in detail. Ideally, the center ester bond in the triglyceride is transesterified before the outside ester bonds. Transesterification of monoglycerides and diglycerides is more difficult than for triglycerides by activation energy and ESP obtained from quantum computational chemistry.

A review from Xin Deng *et al.*, (2010), transesterification of high free fatty acid content *Jatropha* oil with methanol to biodiesel catalyzed directly by NaOH and high concentrated H<sub>2</sub>SO<sub>4</sub> or by two-step process were studied in an ultrasonic reactor at 60°C. If NaOH was used as catalyst, biodiesel yield was only 47.2% with saponification problem. With H<sub>2</sub>SO<sub>4</sub> as catalyst, biodiesel yield was increased to 92.8%. However, longer reaction time (4 h) was needed and the biodiesel was not stable. A two-step, acid-esterification and base-transesterification process was further used for biodiesel production. It was found that after the first-step pretreatment with

H<sub>2</sub>SO<sub>4</sub> for 1 h, the acid value of Jatropha oil was reduced from 10.45 to 1.2 mg KOH/g, and subsequently, NaOH was used for the second-step transesterification. Stable and clear yellowish biodiesel was obtained with 96.4% yield after reaction for 0.5 h. The total production time was only 1.5 h that is just half of the previous reported. The two-step process with ultrasonic radiation is effective and time-saving for biodiesel production from Jatropha oil.

## 2.4 CATALYST

A catalyst is a substance that accelerates the rate of reaction by lowering its activation energy. A catalyst recovered unchanged and it does not appear in the product. Catalyst used in the transesterification of triglycerides can be classified as homogeneous, heterogeneous and enzyme catalyst. Hanna *et al.* (1999), stated that excess amount of catalyst would lead to the higher amount of production cost and reduce product yield.

### 2.4.1 Homogeneous Catalyst

Homogeneous catalyst involves processes in which catalyst is in solution with at least one of the reactant. Basically, in this transesterification process, there are two types of homogeneous catalyst which is acid catalyst (H<sub>2</sub>SO<sub>4</sub> or HCl) and alkali catalyst (KOH or NaOH). Homogeneous basic catalyst provides much faster reaction rates than heterogeneous catalyst, but it is difficult to separate homogeneous catalyst from the reaction mixture (Du *et al.*, 2004).

Currently, biodiesel is commonly produced using homogeneous base catalyst, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) (Felizardo *et al.*, 2006) and (Kulkarni and Dalai *et al.*, 2006). These catalysts are commonly used in the industries due to several reasons like able to catalyze reaction at low reaction temperature and atmospheric pressure, high conversion can be achieved in a minimal time, and widely available and economical (Lotero *et al.*, 2005). In fact, it was reported that the rate for base-catalyzed reaction would be 4000 times faster compared to acidic

catalyst (Felizardo *et al.*, 2006) and (Kulkarni and Dalai *et al.*, 2006). However, the use of this catalyst is limited only for refined vegetable oil with less than 0.5 wt.% FFA (Wang *et al.*, 2006) or acid value less than 1 mg KOH/g (Felizardo *et al.*, 2006). Nevertheless, it is clear that the FFA content in oil feedstock should be as low as possible (ranging from less than 0.5 wt% to less than 2 wt%) for base-catalyzed transesterification reaction. Thus, if waste cooking oil with an average FFA content more than 6 wt%, base catalyst is definitely not suitable to be used (Loterio *et al.*, 2005 )

#### **2.4.2 Heterogeneous Catalyst**

A heterogeneous catalytic process involves more than one phase, usually the catalyst is a solid and the reactant and product are in liquid or gaseous form. There are many advantages of using heterogeneous catalyst such as non-corrosive, environmental friendly present fewer disposal problems, easier in separation from liquid product and they can be design to give higher activity, selectivity and longer catalyst lifetime (Gryglewicz *et al.*, 1999). There are many types of heterogeneous catalyst such as alkaline earth metal oxides, anion exchange resins, various alkali metal compounds supported on alumina and various type of zeolite that can be use in various type of chemical reaction including transesterification process. However, most anion exchange resins and supported alkali metal catalyst are easily corroded by methanol and they exhibit short catalyst lifetime in catalyst transesterification. The alkaline earth metal oxides compound is very favorable used in transesterification process because it is slightly soluble in organic solvents (Supes *et al.*, 2004).

To date, many solid base catalysts have been developed for biodiesel production, such as basic zeolites, alkaline earth metal oxides and hydrotalcites. On top of that, alkaline earth metal oxides especially calcium oxide, CaO have attracted much attention due to their relatively high basic strength, low solubility in methanol and can be synthesized from cheap sources like limestone and calcium hydroxide (Zabeti *et al.*, 2009). Kouzu *et al.* (2008) reported that CaO obtained from calcinations of pulverized limestone, CaCO<sub>3</sub> at 900 °C for 1.5 h in the flow of helium gas exhibited substantially good result in transesterification of refined soybean oil. The yield of FAME was 93%

after 1 h reaction time at methanol reflux temperature and methanol to oil ratio 12:1. However, the yield of FAME dropped to 66% when waste cooking oil with FFA content 2.6 wt% was used under the same reaction condition. It is obvious that the basic sites of CaO were poisoned by strong adsorption of FFAs on the surface of the catalyst (Kouzu *et al.*, 2008). Consequently, a portion of the catalyst changed into calcium soap by reacting with the FFAs adsorbed, resulting in low recovery of catalyst. Kouzu *et al.* (2008) further reported that the concentration of Ca in reaction product was 3065 ppm which exceeded the basic standard of biodiesel; the concentration of mineral matter should be below 200 ppm (Kouzu *et al.*, 2008a).

### 2.4.3 Enzyme Catalyst

There also have a different way of synthesizing biodiesel by using bio-catalyst such as lipase enzyme instead of chemically catalyst. Bio-catalyst such as enzyme is a high molecular weight protein or protein-like substance that acts on substrate (reactant molecule) to transform it chemically at a greatly accelerate rate than the uncatalyzed rate (Shuler nad Kargi *et al.*, 2002).

Chen *et al.* (2006) investigated the enzymatic conversion of waste cooking oil using immobilized *R. oryzae* lipase. A three-step batch transesterification reactor was used and stepwise process was introduced in the reactor to reduce the poisoning of enzyme by methanol. The optimum reaction condition was reported at 40 °C, methanol to oil molar ratio of 4, immobilized lipase to oils weight ratio of 30%, pressure of 1 atm and reaction time of 30 h. Biodiesel yield in the range of 88–90% can be obtained under these conditions. Table 2.2 shows the past study of biodiesel production



**Table 2.2:** Summary of biodiesel production

<b>Reaction</b>	<b>Catalyst</b>	<b>Finding</b>	<b>Author</b>
Transesterification of edible and non-edible oils over basic solid	Mg–Zr catalysts with varying Mg to Zr ratios	An environmentally friendly, inexpensive, reusable and highly active Mg/Zr catalyst for transesterification of both edible and non-edible oils at room temperature in short reaction times is demonstrated	Sree <i>et al.</i> (2008)
Transesterification of soybean oil	Calcium oxide	At 1 hour of reaction time, yield of FAME was 93% for CaO	Masahiko Tajika, <b>et al 2008</b>
Transesterification of soybean oil to biodiesel	Strontium oxide	SrO demonstrated excellent catalytic activity and stability due to its strong basicity and long catalyst lifetime. The biodiesel yield exceeded 95% within 30 minit	Xuejun Liu, <b>et al 2007</b>
Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification	Lewis acids (AlCl <sub>3</sub> or ZnCl <sub>2</sub> )	Optimum conditions with AlCl <sub>3</sub> that achieved 98% conversion were 24:1 molar ratio at 110 C and 18 h reaction time. ZnCl <sub>2</sub> was far less effective as a catalyst compared to AlCl <sub>3</sub>	Soriano <i>et al.</i> (2007)
Ultrasonic transesterification of <i>Jatropha curcas</i> L. oil to biodiesel by a two-step process	NaOH and H <sub>2</sub> SO <sub>4</sub>	Either NaOH or H <sub>2</sub> SO <sub>4</sub> alone was not suitable as catalyst for biodiesel because NaOH produce low biodiesel yield and H <sub>2</sub> SO <sub>4</sub> catalyst needed long reaction time. Both H <sub>2</sub> SO <sub>4</sub> and NaOH were used as catalysts for the two-step, acid esterification and base-transesterification and this process only needed 1.5 hour to achieve 96.4% diesel yield.	Xin Deng, <i>et al</i> 2010

Reaction	Catalyst	Finding	Author
Transesterification of sunflower oil to biodiesel	ZrO <sub>2</sub> supported La <sub>2</sub> O <sub>3</sub> catalyst	After calcined at 600 °C for 4 hour, the catalyst with 21 wt% La <sub>2</sub> O <sub>3</sub> loaded on ZrO <sub>2</sub> was found to be with highest basicity and catalytic activity for the transesterification reaction. The catalytic activities showed a correlation with their basic properties towards biodiesel production, which is that, the stronger basicity, the higher biodiesel yield we achieved.	Hui Sun, <i>et al</i> 2009
Transesterification of sunflower oil to biodiesel	ZrO <sub>2</sub> supported La <sub>2</sub> O <sub>3</sub>	La <sub>2</sub> O <sub>3</sub> loaded on ZrO <sub>2</sub> was found to be with highest basicity and catalytic activity for the transesterification reaction and the catalytic activities showed a correlation with their basic properties towards biodiesel production, which is that, the stronger basicity, the higher biodiesel yield we achieved.	Hui Sun, <i>et al</i> 2009
Transesterification of Jatropha oil	Alumina loaded with potassium nitrate as a solid base catalyst	Alumina loaded with potassium was found to be strong solid base catalyst for the transesterification of Jatropha oil with methanol.	Vyas <i>et al.</i> 2008
Transesterification of palm oil	K <sub>y</sub> Mg <sub>1-x</sub> Zn <sub>1+x</sub> O <sub>3</sub> catalyst: Effect of Mg-Zn interaction	In particular, for a specific case of K <sub>2</sub> Mg <sub>0.34</sub> Zn <sub>1.66</sub> O <sub>3</sub> with Mg-Zn ratio of 1:4.81, calcination at temperature of 460 °C gave the highest activity during the transesterification of palm oil with 73% FAME content above all the other formulations under the same experimental conditions. The catalyst demonstrated a good activity to FAME yield and provided minimum leaching of about 4%.	B.H. Hameed <i>et al</i> 2010