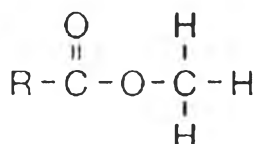


## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Biodiesel

Biodiesel can be chemically defined as a fuel composed of mono-alkyl esters of long chain fatty acids derived from renewable sources, such as vegetable oils and animal fats (Borges and Diaz, 2012). The structural formula of biodiesel is shown in Figure 2.1.



**Figure 2.1** Structural formula of biodiesel.

From Figure 2.1, R represents a chain of carbon atoms with hydrogen atoms attached. The difference of R in the structure results in difference of fatty acid methyl ester that leads to make different properties of biodiesel. R can be C<sub>12</sub> to C<sub>24</sub>.

Biodiesel, a renewable fuel with similar combustion properties to fossil diesel, is normally produced by transesterification of highly refined oils with short-chain alcohols. Biodiesel can significantly decrease the exhaust emission of CO, SO<sub>x</sub> and unburned hydrocarbons from motor vehicles (Clark *et al.*, 1984).

Today biodiesel fuels have been in commercial use in many countries, including Austria, Czech Republic, Germany, France, Italy, Slovakia, Spain, and USA for up to 20 years. Biodiesel is either used in pure form or as blends with diesel fuel, which in contrast to near vegetable oil/diesel blends – are stable in any concentration. Consequently, switching from one type of fuel to the other or to a blend of both does not pose any problems to the engine (Austrian Biofuels Institute, 2003). The advantages and disadvantages of biodiesel compared to diesel are shown in Table 2.1.

**Table 2.1** Biodiesel advantages and disadvantages compared to diesel(Austrian Biofuels Institute, 2003)

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>• Domestically produced from non-petroleum, renewable resources</li> <li>• Can be used in most diesel engines, especially newer ones</li> <li>• Less air pollutants (other than nitrogen oxides)</li> <li>• Less greenhouse gas emissions (e.g., B20 reduces CO<sub>2</sub> by 15%)</li> <li>• Biodegradable</li> <li>• Non-toxic</li> <li>• Safer to handle</li> </ul>	<ul style="list-style-type: none"> <li>• Use of blends above B5 not yet approved by many auto makers</li> <li>• Lower fuel economy and power (10% lower for B100, 2% for B20)</li> <li>• Currently more expensive</li> <li>• B100 generally not suitable for use in low temperatures</li> <li>• Concerns about B100's impact on engine durability</li> <li>• Slight increase in nitrogen oxide emissions possible in some circumstances</li> </ul>

## 2.2 Fats and oils

### 2.2.1 Traditional Raw Materials

A vegetable oil is a triglyceride extracted from a plant. Such oils have been part of human culture for millennia. The term "vegetable oil" can be narrowly defined as referring only to substances that are liquid at room temperature or broadly defined without regard to a substance's state of matter at a given temperature. Typical fatty acids compositions found in several vegetable oils are summarized in Table 2.2 (Demirbas, 2008).

**Table 2.2** Typical fatty acid composition (%) for different common oil source  
(Demirbas, 2008)

Sample	16:0	16:1	18:0	18:1	18:2	18:3	Others
Cottonseed	28.7	0	0.9	13.0	57.4	0	0
Poppy seed	12.6	0.1	4.0	22.3	60.2	0.5	0
Rapeseed	3.5	0	0.9	64.1	22.3	8.2	0
Safflower seed	7.3	0	1.9	13.6	77.2	0	0
Sunflower seed	6.4	0.1	2.9	17.7	72.9	0	0
Sesame seed	13.1	0	3.9	52.8	30.2	0	0
Linseed	5.1	0.3	2.5	18.9	18.1	55.1	0
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1
Corn marrow	11.8	0	2.0	24.8	61.3	0	0.3
Tallow	23.3	0.1	19.3	42.4	2.9	0.9	2.9
Soybean	13.9	0.3	2.1	23.2	56.2	4.3	0
Hazelnut kernel	4.9	0.2	2.6	83.6	8.5	0.2	0
Walnut kernel	7.2	0.2	1.9	18.5	56.0	16.2	0
Almond kernel	6.5	0.5	1.4	70.7	20.0	0	0.9
Olive kernel	5.0	0.3	1.6	74.7	17.6	0	0.8

### 2.2.1.1 Rapeseed Oil

Rapeseed oil was originally chosen for transesterification experiments by biodiesel pioneer because of its low price compared to other readily available vegetable oils (Mittelbach, 1989). However, it soon became apparent that with its high content of monounsaturated oleic acid and the low levels of both saturated and polyunsaturated acids, the oil is practically the ideal raw material regarding combustion characteristics, oxidative stability and cold temperature behavior. Due to its favorable properties, rapeseed oil still is the feedstock of choice in most European countries, including the world's largest biofuel producers, Germany and France.

### *2.2.1.2 Sunflower Seed Oil*

Sunflower seed oil (*Helianthus annuus*) comes second in the list of vegetable oil sources for biodiesel production in Europe. It is cultivated in Southern European countries, such as Italy, Spain, and Greece, because here the semi-arid climates prevent high oil yields for rapeseed. According to the European biodiesel standard (EN 14214), pure sunflower oil methyl ester cannot be used as a fuel for biodiesel engines, as it exceeds the limit for iodine value set at  $\leq 120$  g I<sub>2</sub>/100g. Moreover, unadditivated sunflower oil fuels will also give poor rating for oxidative stability.

### *2.2.1.3 Soybean Oil*

Soybean oil (*Glycine max*) is the most popular biodiesel feedstock in the USA, and it is by far the most frequently produced vegetable oil world-wide, mainly due to the utilization of soybean meal as a protein fodder. Similar to sunflower-oil regarding its fatty acid composition, soybean oil displays iodine values of 121-143 g I<sub>2</sub>/100g. Therefore, EN 14214 excludes pure soybean oil methyl ester from serving as a fuel, although this regulation is highly disputed by many experts.

### *2.2.1.4 Palm oil*

The oil palm (*Elaeis guineensis*) plays an important role for biofuel production in South Asia. Various parts of the palm fruits can be utilized for oil production for human consumption and industrial application. The mesocarp of the fruit yields palm oil, which is characterized by high amounts of medium-chain saturated (palmitic acid) and monounsaturated (oleic acid) fatty acids.

The main advantages of palm oil are outstandingly high hectare yield and moderate world-market prices compared to other edible vegetable oils. If biodiesel fuels are to be economically competitive with fossil diesel, even in the absence of tax concession programs, production costs have to be kept low. This poses considerable difficulty with most other highly refined vegetable oils, which could also be utilized for food purposes. The oil palm, however, is a low-value commodity crop (Murphy, 2003), so that the production of biodiesel from palm oil makes sense from an economic point of view. Nevertheless, its high contents of saturated fatty acid, leading to unacceptably high values for cold filter plugging point

(+11°C) and cloud point (+13°C), prevent winter operation on neat palm oil methyl esters in temperate climates. Moreover, high content of free fatty acids in the feedstock cause problems in traditional alkali catalyzed biodiesel production and thus necessitate decidification or acid catalyzed pre-esterification steps.

### 2.2.2 Non-edible Oils

One way of reducing the production costs for biodiesel fuels is the use of non-edible oils, which tend to be considerably cheaper than edible vegetable oils (Srivastava and Prasad, 2000). A number of plant oils contain substances which make them unsuitable for human consumption. In some cases these substances can be removed by refining.

#### 2.2.2.1 *Castor Oil*

Castor (*Ricinus communis*) is known as a house plant, although its seeds contain ricin, a highly toxic lectin. During oil recovery ricin remains within the press cake. Nevertheless, the recovered oil is not fit for nutritional purposes due to its laxative effect (Roth and Kormann, 2000). Castor oil ethyl ester are currently being discussed as a promising alternative fuel in Brazil (De Oliveira *et al.*, 2001).

#### 2.2.2.2 *Physic Nut Oil*

Physic nut (*Jatropha curcus*) oil cannot be used for food purposes because of its content of toxalbumine called "curcine" and the presence of various toxic phorbol ester, for some of which the structure has recently been elucidated (Haas *et al.*, 2002). Adaptable to a large variety of soils, altitudes and rain volumes, the plant yields seed oil rich in oleic and linoleic acid, which was discussed as a feedstock for biodiesel production in Nicaragua. Investigations on the fuel properties of *Jatropha* oil methyl and ethyl esters had brought promising results. Moreover, about 1000 hectares of the crop had already been cultivated and a pilot plant for the conversion of the oil had been established. Nevertheless, the project was abandoned due to political and economic reasons (Foidl *et al.*, 1996).

### 2.2.3 Animal Fats and Oils

Animal fats and fish oils are by-products of the meat packing and fishery industries, which are promising raw materials for fuel production due to their low prices. Fats and oils of animal origin, which have been tested as raw materials for alkyl ester production, include beef tallow (Nelson *et al.*, 1996; Zheng and Hanna, 1996; Foglia *et al.*, 1997; Hanna and Ali, 1997; Hsu *et al.*, 2001), lard (Lee, *et al.*, 2002) and fish oils. In a US patent application (Lee, *et al.*, 2002) also the direct acid-catalyzed esterification and trans-esterification of animal waste products (such as chicken skin, small bone and meat tissue) without previous fat extraction was reported.

Regarding their fatty acid compositions, all of these feedstocks have disadvantages. With their high amounts of saturated fatty acids, animal fats yield methyl ester with poor cold temperature properties, which poses problems in winter operation. On the other hand, their high degree of saturation makes animal fat methyl esters excellent fuels regarding heating value and cetane number.

### 2.2.4 Recycled or Waste Oils

Recycled or waste oils have evolved as very popular raw materials for the production of biodiesel, as they are inexpensive and offer the additional environmental benefit of using substances which would otherwise have to be disposed of. The first reference to the utilization of waste oil was made by Nye *et al.*, (1983), who reported on successful engine tests for methyl, ethyl and 1-butylesters produced from used frying oil. At the same time recycled frying oil was also studied as a raw material for biodiesel production by Mittelbach, who later developed a commercial process for converting waste oil from households and restaurants as well as fatty waste from slaughterhouses and sewage plants into biodiesel fuels (Mittelbach and Junek, 1988). Fatty acid methyl ester, FFA and water content of food-grade soybean oil, crude soybean oil, crude palm oil and waste cooking oil are shown in Table 2.5 (Yan, 2009).

**Table 2.3** Fatty acid methyl ester, FFA and water content of food-grade soybean oil, crude soybean oil, crude palm oil and waste cooking oil (Yan, 2009)

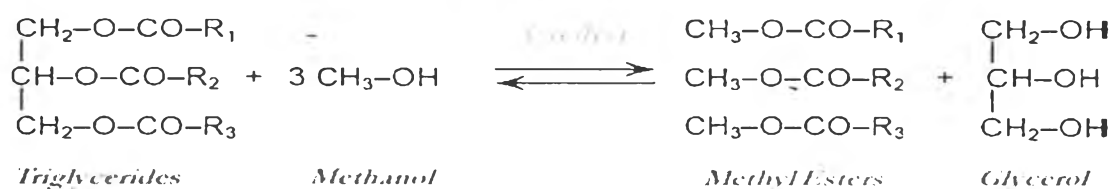
Fatty acid components	Food-grade soybean oil (%)	Crude soybean oil (%)	Crude palm oil (%)	Waste cooking oil (%)
C 14:0	0	0.27	0.21	0
C 16:0	11.07	13.05	41.92	11.58
C 16:1	0.09	0.39	0.23	0.18
C 18:0	3.62	4.17	3.85	4.26
C 18:1	20.26	22.75	42.44	24.84
C 18:2	57.60	52.78	11.30	53.55
C 18:3	7.36	6.59	0.04	5.6
FFA content	0.02	3.31	0.24	3.78
Water content	0.02	0.27	0.04	0.06

### 2.3 Derivatives of Triglycerides as Diesel Fuels

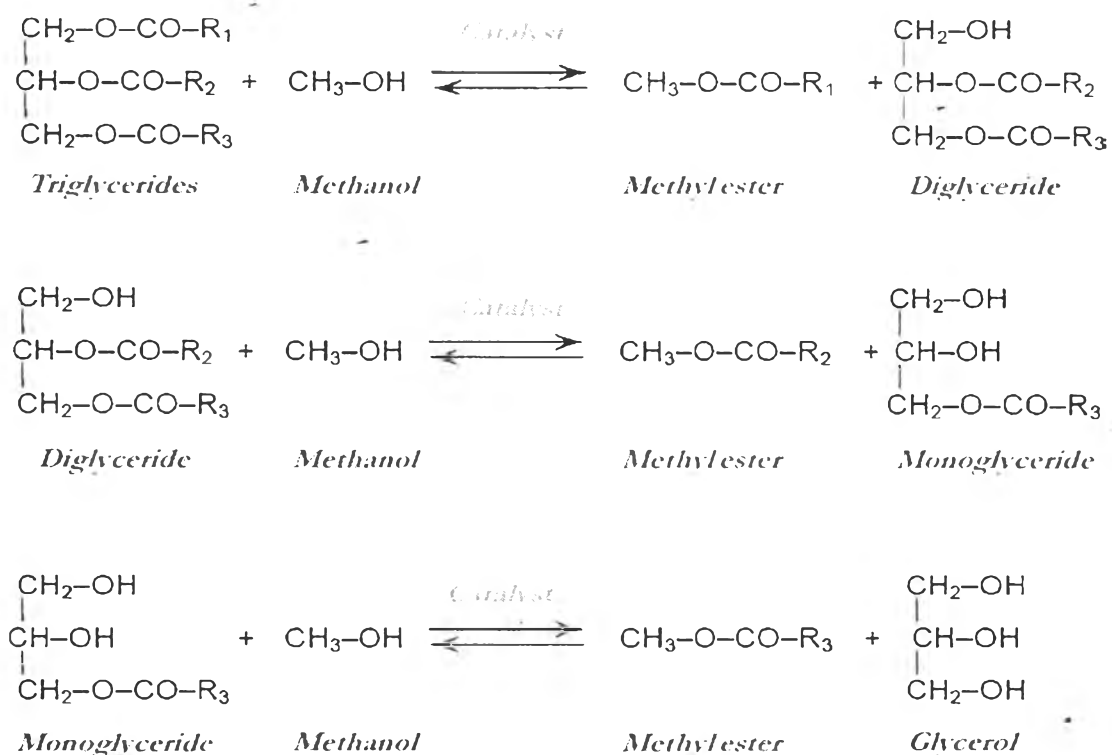
The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. Vegetable oil has too high viscosity for use in most existing diesel engines as a straight replacement fuel oil. There are many ways to reduce vegetable oils' viscosity. Dilution, microemulsification, pyrolysis, and transesterification are the four techniques applied to solve the problems encountered with high fuel viscosity. Biodiesel obtained from microemulsion and thermal cracking methods would lead to incomplete combustion due to a low cetane number. Transesterification is the most common method for biodiesel production due to its simplicity and it has been widely studied and industrially used to convert vegetable oil into biodiesel.

### 2.3.1 Transesterification

Transesterification is the reaction process by means of which triglyceride molecules present in animal fats or vegetable oils react with an alcohol in the presence of a catalyst to form esters and glycerol, as shown in Figure 2.2. When the transesterification reaction with alcohol proceeds, the first step is the triglycerides to diglycerides conversion, which is followed by the subsequent higher glycerides to lower glycerides conversion and then to glycerol, yielding one methyl ester molecule from each glyceride at each step, as shown in Figure 2.3 (Banerjee and Chakraborty, 2009)



**Figure 2.2** Triglycerides transesterification reaction with methanol.



**Figure 2.3** The transesterification reactions step.



Currently, transesterification reaction using basic catalysts is the most extended process to produce biodiesel. In this process, it is necessary to use feedstock (vegetable oils or animal fats) which present low free fatty acid content. When the raw materials contain high percentage of free fatty acids or water, the acid catalyst will be used in the reaction, it reacts with the free fatty acids to form biodiesel via esterification reaction.

### 2.3.2 Esterification

Esterification is the reaction process by means of which long chain carboxylic acids or free fatty acid (FFA) such as oleic acid in the context of biodiesel production react with an alcohol in the presence of a catalyst to form ester and water. FFA may be present in esterification of vegetable oils as well as recycled feedstocks as shown in Figure 2.4.



**Figure 2.4** The esterification reaction.

For a catalyst in biodiesel production is usually used to improve the reaction rate and yield because the reaction is reversible. There are many types of catalyst used in biodiesel production: homogeneous and heterogeneous catalysts.

## 2.4 Catalyst in Transesterification

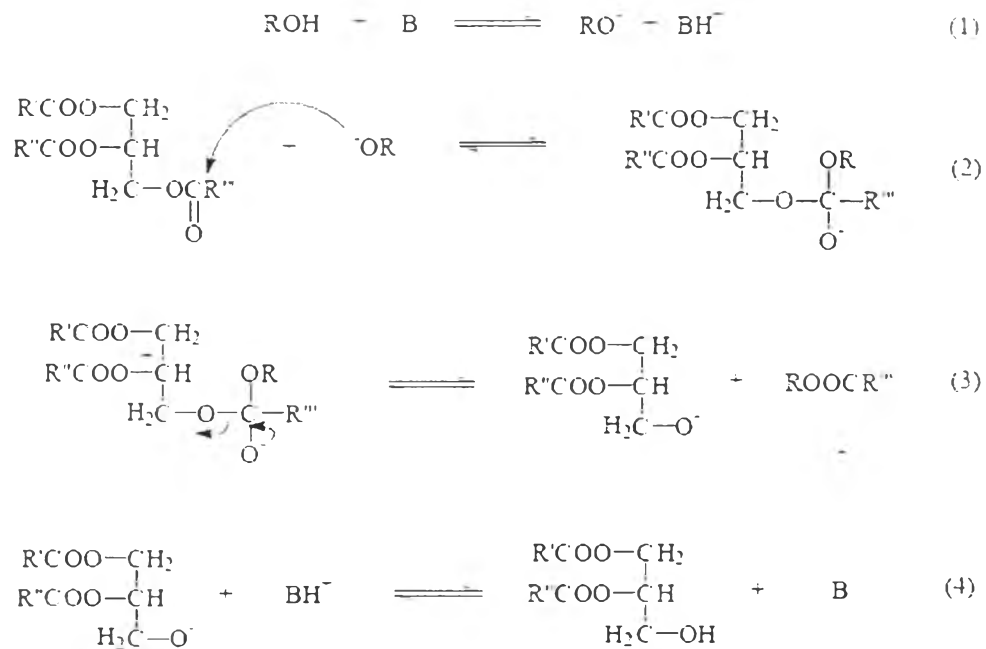
Catalysts in biodiesel production are divided into 2 types: basic catalyst and acid catalyst.

### 2.4.1 Homogeneous Catalyst

#### 2.4.1.1 *Homogeneous Basic Catalyst*

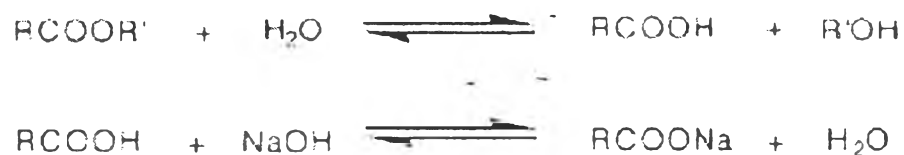
Homogeneous basic catalysts are commonly used in the industries due to several reasons, for example, able to catalyze reaction at low reaction temperature and atmospheric pressure. high conversion can be achieved in a minimal time, and widely available and economical (Lotero *et al.*, 2005). For this type of catalyst, sodium hydroxide (NaOH) and potassium hydroxide (KOH) are commonly used.

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Figure 2.5. The first step (1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (3). The latter deprotonates the catalyst, thus regenerating the active species (4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.



**Figure 2.5** Mechanism of the base-catalyzed transesterification of vegetable oils.

Although the base-catalyzed are widely used they have many limit conditions such as it is very sensitive to water and free fatty acid. Some water reacts with alcohol lead to soap formation, as shown in Figure 2.6 (Schuchardt *et al.*, 1998). This undesirable saponification reaction reduces the ester yields and considerably difficult to recover of the glycerol.



**Figure 2.6** Saponification of fatty acid alkyl ester.

Tomasevic and Siler-Marinkovic (2003) performed transesterification reaction of refined sunflower oil and used frying oils at 25 °C with homogeneous catalysts: KOH or NaOH. Transesterification reaction conditions that affect yield and purity of the product esters including oil quality, molar ratio of methanol to oil, type and catalyst concentration, temperature, and reaction time were

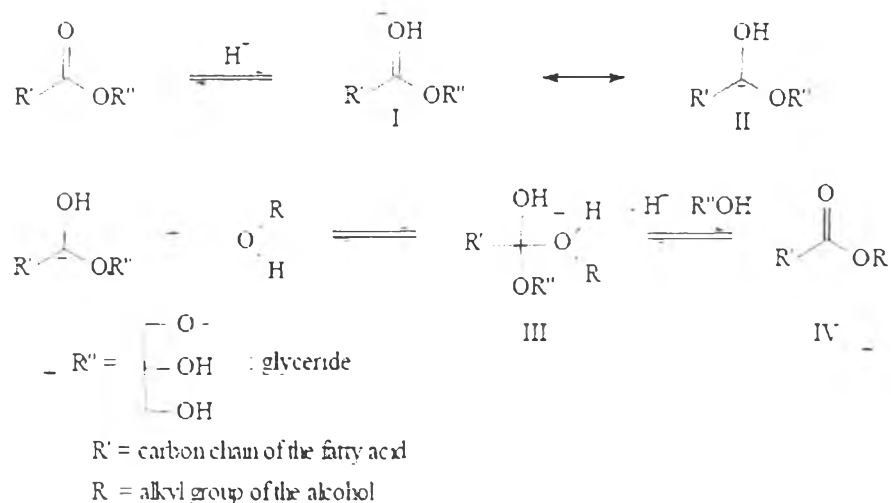
examined. They found that 1% KOH, temperature of 25 °C, methanol/oil ratio of 6 and reaction time of 30 min, all investigated oils were sufficiently transesterified and could be used as fuel in diesel engines.

Vicente *et al.* (2003) compared the catalytic activity of different basic catalysts (sodium methoxide, potassium methoxide, sodium hydroxide, and potassium hydroxide) for methanolysis of sunflower oil. All the reactions were carried out under the same experimental conditions in oil bath stirred reactor and the subsequent separation and purification stages in a decanter. They found that biodiesel purity was near 100 %wt for all catalysts; however, near 100 %wt biodiesel yields were only obtained with the methoxide catalysts. Although all the transesterification reactions were quite rapid and the biodiesel layers achieved nearly 100% methyl ester concentrations, the reactions using sodium hydroxide turned out the fastest.

#### 2.4.1.2 Homogeneous Acid Catalyst

The most widely used of catalysts for acid-catalyzed system are sulfuric acid ( $H_2SO_4$ ) and hydrochloric acid (HCl). Important advantages of acid-catalyzed reaction with respect to base-catalyzed reaction are insensitive to the presence of FFAs in the feedstock (Kulkarni and Dalai, 2006) and can catalyze esterification and transesterification simultaneously (Jacobson *et al.*, 2008). Therefore, acid-catalyzed process can occur in a one-step process for high FFAs feedstock that is more economical than the base-catalyzed process.

Schuchardt *et al.* (1997) studied the mechanism of the acid-catalyzed transesterification of vegetable oils (Figure 2.7) for a monoglyceride. However, it can be extended to di- and tri-glycerides. The protonation of the carbonyl group of the ester leads to the carbocation which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate, which eliminates glycerol to form the new ester, and to regenerate the catalyst  $H^+$ .



**Figure 2.7** Mechanism of the acid-catalyzed transesterification of vegetable oils.

According to this mechanism, carboxylic acids can be formed by reaction of the carbocation with water present in the reaction mixture and acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.

Because of slow reaction rate of acid-catalyzed process, requirement of high reaction temperature, high molar ratio of alcohol to oil, separation of the catalyst, serious environmental and corrosion related problem, this system is not a popular choice for commercial applications (Jacobson *et al.*, 2008, Wang *et al.*, 2006).

In a study of acid-catalyzed transesterification of waste cooking oil using  $H_2SO_4$ . Wang *et al.* reported that the yield of FAME increased with longer reaction time, higher methanol to oil ratio, and higher catalyst loading. The conversion of waste cooking oil was higher than 90% at a reaction time of 10 h with a ratio of methanol to oil of 20:1 and 4 wt.%  $H_2SO_4$  (with reference to weight of oil) (Wang *et al.*, 2006).

## 2.4.2 Heterogeneous Catalyst

### 2.4.2.1 Heterogeneous Basic Catalyst

Metal oxides are the basic heterogeneous catalysts group most studied. There are several metal oxides that have been studied: calcium oxide, magnesium oxide, strontium oxide, mixed oxides, and hydrotalcites.

CaO is the most widely used as a solid basic catalyst as it presents many advantages such as long catalyst life, high activity, and requires only moderate reaction conditions (Math *et al.*, 2010). Yoosuk *et al.* (2010) used a calcite natural source to produce CaO. This natural source is cheap, it shows high basicity and it is environmental friendly. They demonstrated that hydration and subsequent thermal decomposition is an effective method to increase the activity of calcined natural calcite. This technique generates a CaO with excellent textural properties and a large number of basic sites.

CaO has been mixed with other oxide compounds. Alba-Rubio *et al.* (2010) studied CaO supported on zinc oxide as a basic catalyst for transesterification processes. This supported CaO catalyst, thermally activated at 800 °C, can give biodiesel yields higher than 90% after 2 h of reaction at 60 °C.

Xie *et al.* (2006) studied the catalytic activity and base strength of Al<sub>2</sub>O<sub>3</sub> loaded with different potassium compounds (KF, KCl, KBr, KI, K<sub>2</sub>CO<sub>3</sub>, KNO<sub>3</sub>, KOH) in the soybean oil transesterification. The catalytic activity and base strength of KF supported on different carriers (ZrO<sub>2</sub>, ZnO, NaX zeolite, KL zeolite, and Al<sub>2</sub>O<sub>3</sub>), the effects of catalyst loading, molar ratio of methanol to oil, and reaction time were also studied. They indicated that KI/Al<sub>2</sub>O<sub>3</sub> was the most active catalyst, obtaining 96% conversion under the optimum conditions: amount of catalyst at 2.5 wt%, molar ratio of methanol/oil at 15:1, and reaction time at 8 h. Moreover, they suggested that the activity of catalyst was strongly affected not only by the strength of basic sites but also by the amount of basic sites. They found that the alumina loaded with potassium was a strong solid-base catalyst for the transesterification of soybean, having the highest basicity and the best catalytic activity for reaction. The catalytic activities of the heterogeneous base catalysts show a striking correlation with their corresponding basic properties. The decomposition

products of the loaded  $\text{KNO}_3$ , forming either  $\text{K}_2\text{O}$  species or Al-O-K group in the composite, were probably the active basic sites.

#### 2.4.2.2 Heterogeneous Acidic Catalyst

There are several reports on the use of heterogeneous catalyst for biodiesel production.

Yoo *et al.* (2010) carried out biodiesel production from rapeseed oil using supercritical methanol with transition metal oxides ( $\text{ZnO}$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ ).  $\text{ZnO}$  was reported as the best catalyst for the transesterification of rapeseed oil owing to its high activity and minimum weight loss in supercritical methanol. The optimal reaction conditions included a molar ratio of methanol to oil 40:1 in the presence of 1.0 wt.%  $\text{ZnO}$  and a reaction time of 10 min. The supercritical process with  $\text{ZnO}$  as a catalyst appeared economically viable.

Medina *et al.* (2012) prepared  $\text{ZnO}$  nanoparticles by chemical precipitation synthesis with the stoichiometric relation used of the  $\text{Zn}^{2+}:(\text{OH}^-)_2$  species was 1:1.  $\text{Zn}(\text{H}_3\text{C}_2\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$  was dissolved in distilled water and stirred at 40 °C. Then,  $\text{NaOH}$  solution was added to the  $\text{Zn}$ -solution. The  $\text{Zn}(\text{OH})_2$  was centrifuged, washed, and dried at room temperature. Finally, these samples were calcined at 500 °C for 60 min with a heating rate of 20 °C/min. They found that  $\text{ZnO}$  nanoparticles with hexagonal shape were produced. All hexagonal particles formed are of wurtzite crystal structure.

Yan *et al.* (2010) prepared  $\text{ZnO}$  nanoparticles by the urea hydrolysis method.  $\text{Zn}(\text{NO}_3)_2$  and  $\text{La}(\text{NO}_3)_3$  solutions with a 3:1 ratio of  $\text{Zn}:\text{La}$  were mixed with a 2 M urea solution. The mixture was boiled for 4 h, and then dried at 150 °C for 8 h, followed by step-rising calcination at 250, 300, 350, 400 °C, finally at 450 °C for 8 h. Then, using La modified  $\text{ZnO}$  nanoparticles as a catalyst for produced biodiesel by the transesterification of natural oils with methanol in a batch stirred reactor. This catalyst is a mixture of wurtzite  $\text{ZnO}$  nanoparticles and some amorphous materials and that the used catalysts have similar crystal structure to fresh catalyst. ICP results show that this catalyst does not dissolve in biodiesel, methanol, oil, and glycerine methanol solutions. It has a stable crystal structure under the reaction conditions. It was found that the catalyst was high catalytic activity, long

catalyst life and low leaching properties. The average yield of FAME was around 93.7% after were reused 17 times without any activity loss.

Jitputti *et al.* (2006) reported that  $\text{SO}_4^{2-}/\text{ZrO}_2$  could produce promising results in transesterification of palm kernel oil and crude coconut oil with methyl ester yield reaching as high as 90.3% and 86.3%, respectively. However, when unsulfated  $\text{ZrO}_2$  was used as catalyst instead of  $\text{SO}_4^{2-}/\text{ZrO}_2$ , only 64.5% (palm kernel oil) and 49.3% (crude coconut oil) of methyl ester yield were reported, respectively.

Transesterification from waste frying oil (WFO) in two steps catalyzed process was carried out by Corro *et al.* (2010). The free fatty acids (FFA) were first esterified with methanol catalyzed by  $\text{SiO}_2$  pretreated with HF. The catalyst was easy to recover; neither hydrated nor carbonated, did not dissolved by the reactants or the products of the reaction, showed high activity for the FFA esterification and presented high stability. After 10 esterification runs, the catalyst activity remained unchanged. During the second step, the triglycerides WFO were transesterified with methanol catalyzed by NaOH 96% methyl esters were obtained.

Mittelbach *et al.* (1996) compared the activities of a series of layered aluminosilicates loaded with  $\text{H}_2\text{SO}_4$  for the transesterification of rapeseed oil at used an initial oil/methanol molar ratio of 1:30 and 5 wt% catalyst. The solid catalysts showed a wide range of activities depending on the reaction conditions. The most active catalysts were those activated by sulfuric acid impregnation. For instance, sulfuric acid activated montmorillonite KSF showed 100% conversion after 4.h of reaction at 220 °C and 52 bar. However, leaching of the sulfate species made the reusability of this catalyst difficult. Thus, to maintain the catalyst activity at constant values, sulfuric acid re-impregnation had to be carried out after each run.

Recently, lignin is considered as the second-most abundant natural organic material after cellulose, and the richest aromatic organic biopolymer. It has high carbon content and should be usable as a precursor for activated carbon. The carbohydrate base biomass (for example, starch, glucose, and corncob) has been used as a raw material to make solid acid catalysts. Pua *et al.* (2011) synthesized solid acid catalyst prepared from Kraft lignin by chemical activation with phosphoric acid, pyrolysis, and sulfuric acid. It was shown to be useful for esterification and



one-step biodiesel production from low-qualified oils (Jatropha oil) due to its high acid density. Assessment for its catalytic activity via esterification proved that it was highly effective in converting oleic acid to ester. This catalyst was further successfully used for biodiesel production, with high yield (96.3%) from non-pretreated Jatropha oil was achieved at 5 wt% of catalyst, 120 °C, and molar ratio of oil to methanol of 1:12 within 5 h. Besides use in biodiesel production, a lignin derived solid acid catalyst may find other applications as a heterogeneous green catalyst.

Solid acid catalyst from glucose-starch mixture was synthesized by Chen *et al.* (2011). The starch with different amounts of amylopectin would affect the esterification activity of oleic acid with methanol. A catalyst with very high acid density and esterification activity was obtained from a mixture of glucose and corn powder. The catalyst composed of  $CS_{0.073}O_{0.541}$  has both Lewis acid sites and Bronsted acid sites which was caused by  $-SO_3H$  and  $-COOH$ . Under the optimized reaction conditions, catalyst for biodiesel production from high FFA (55.2 wt %) waste cottonseed oil afforded the methyl ester yield of about 90% after 12 h. It can be verified that the catalyst deactivated gradually after recycles usage, and regeneration of catalyst by  $H_2SO_4$  treatment was proposed.

Emrani and Shahbazi (2012) studied a single bio-based catalyst from glucose, sucrose, starch, activated carbon, and agricultural waste for biofuel and biodiesel. Biobased catalyst is non-toxic, cheap, based on renewable biomass, environmentally friendly. Moreover, it can use waste oil and grease as feedstock especially suited for trap grease and waste oil containing water and fatty acids.

Shu *et al.* (2009) synthesized a carbon-based solid acid catalyst for biodiesel production from cottonseed oil. A solid acid catalyst with good activity for transesterification has been prepared by sulfonating a composite material formed by the incomplete carbonization of vegetable oil asphalt. The resulting strong solid acid consists of a flexible carbon-based framework decorated with highly dispersed polycyclic aromatic hydrocarbons containing sulfonic acid groups. The high activity can be ascribed to the high acid site density, loose irregular network and large pores that can provide more acid sites for the reactants. The sulfonated

polycyclic aromatic hydrocarbons exert an electron-withdrawing force to keep the acid site stable.

## 2.5 Analysis of Esterification Products

Potential contaminants of biodiesel include unreacted triacylglycerides, residual alcohol, and catalyst may be present as well as intermediate mono- and di-acylglycerides, and glycerol co-product. Various methods have been investigated for analyzing biodiesel accordingly.

Gas chromatography (GC) is the most commonly used method for detailed analysis of transesterification and biodiesel. Analysis of reaction mixtures by capillary GC determining esters, mono-, di-, and tri-acylglycerols was carried out in one run (Freedman *et al.*, 1986). Cvengros *et al.* (1994) used GC to determine the conversion of TG to methyl esters, gave a correlation between the bound glycerol content determined by TLC/FID and the acyl conversion determined by GC.

As mentioned above, the raw materials for biodiesel production account for almost 75% of the total biodiesel cost. The production biodiesel from low cost raw materials which generally contain high amounts of free fatty acids is a valuable alternative that would make their production cost more competitive than petroleum-derived fuel. The biodiesel production using solid acid catalyst derived from biomass via esterification is very interesting because esterification is less affected by the presence of water and free fatty acids (FFA). In addition, biomass can be used as acid catalyst by sulfonation reaction.

Therefore, this research studied the biodiesel production via esterification using a solid acid catalyst derived from lignin in order to convert free fatty acid (FFA) to biodiesel and determine the optimum conditions for biodiesel production from oleic acid. Moreover, the effects of reaction time, molar ratio of methanol to oil, amount of catalyst and reaction temperature on the biodiesel yield were investigated. The prepared catalysts were characterized by using many techniques including FT-IR, SEM-EDS, XRD, BET, TPD-NH<sub>3</sub>, and titration method.