

CHAPTER II

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel refers to a diesel-equivalent that is defined as the monoalkyl esters, especially (m)ethyl ester, of long-chain fatty acids derived from renewable biolipids. The structural formula of biodiesel is shown in Figure 2.1.

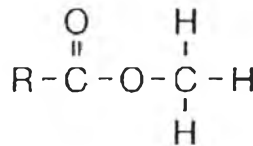


Figure 2.1 Structural formula of biodiesel.

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 C₁₄ to C₂₄.

Biodiesel is typically produced through the reaction of a vegetable oils or animal fats with methanol or ethanol in the presence of a catalyst to yield methyl or ethyl esters (biodiesel) and glycerin (Demirbas, 2008). Generally, methanol is preferred for transesterification because it is low cost and industrial availability.

The advantages of biodiesel as diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, lower sulfur, and aromatic content (Ma and Hanna, 1999; Knothe *et al.*, 2006), higher cetane number, and higher biodegradability (Zhang *et al.*, 2003). The main advantages of biodiesel given in the literature include its domestic origin, which would help reduce a country's dependency on imported petroleum, its biodegradability, high flash point, and inherent lubricity in the neat form (Mittelbach and Remschmidt, 2004; Knothe *et al.*, 2005). Technical properties of biodiesel shown in Table 2.1 and Table 2.2 show some fuel properties of six methyl ester biodiesels given by different researchers.

Table 2.1 Technical properties of biodiesel

Common name	Biodiesel (bio-diesel)
Common chemical name	Fatty acid (m)ethyl ester
Chemical formula range	C ₁₄ -C ₂₄ methyl esters or C ₁₅₋₂₅ H ₂₈₋₄₈ O ₂
Kinematic viscosity range (mm ² /s, at 313 K)	3.3-5.2
Density range (kg/m ³ , at 288 K)	860-894
Boiling point range (K)	>475
Flash point range (K)	430-455
Distillation range (K)	470-600
Vapor pressure (mm Hg, at 295 K)	<5
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

Table 2.2 Some fuel properties of six methyl ester biodiesel

Source	Viscosity cSt at 313.2 K	Density g/mL at 288.7 K	Cetane number	Reference
Sunflower	4.6	0.880	49	Pischinger <i>et al.</i> , 1982
Soybean	4.1	0.884	46	Schwab <i>et al.</i> , 1987
Palm	5.7	0.880	62	Pischinger <i>et al.</i> , 1982
Peanut	4.9	0.876	54	Srivastava and Prasad, 2000
Babassu	3.6	-	63	Srivastava and Prasad, 2000
Tallow	4.1	0.877	58	Ali <i>et al.</i> , 1995

2.2 Derivatives of Triglycerides as Diesel Fuels

Because of vegetable oils and animal fats have too high viscosity for use in most existing diesel engines as a straight replacement fuel oil. There are several ways to reduce vegetable oils' viscosity.

2.2.1 Dilution of Oils

The high viscosity of vegetable oil can be minimized by blending it with diesel or solvents. The vegetable oil-diesel fuel blend is a simple way to reduce the viscosity of neat vegetable oil that can solve some engine performance problems such as injector coking and carbon deposits, etc. Dilution method does not require any chemical process.

Ziejewski *et al.* (1986) decreased the viscosity of sunflower oil by blending with conventional diesel. Blending of 25 % of sunflower oil and 75 % of diesel were blended as diesel fuel. The viscosity was 4.88 cSt at 40 °C, while the maximum specified ASTM value was 4.0 cSt at 40 °C. But this mixture was not suitable for long-term use in a direct injection engine.

2.2.2 Micro-emulsification of Oils

Micro-emulsification is the formation of microemulsions that can solve the high viscosity of vegetable oils. Microemulsions are clear, or translucent thermodynamically-stable dispersions of oil, water, surfactant, and often a small amphiphilic molecule, called a co-surfactant.

To solve the high viscosity of vegetable oils, microemulsions with immiscible liquids such as methanol, ethanol and ionic or non-ionic amphiphiles have been studied (Billaud *et al.*, 1995). They found that short-term performances of both ionic and non-ionic microemulsions of aqueous ethanol in soybean oil are nearly as well as that of No.2 diesel fuel.

Ziejewski *et al.* (1986) decreased the viscosity by prepared a microemulsion of 53% (v/v) sunflower oil, 13.3% (v/v) ethanol, and 33.4%(v/v) 1-butanol which this non-ionic microemulsion had a viscosity of 6.31 cSt at 40 °C , a

cetane number of 25 and an ash content of less than 0.01%. Lower viscosities and better spray patterns were observed with an increase of 1-butanol.

2.2.3 Pyrolysis and Catalytic Cracking

Pyrolysis is a thermochemical decomposition of one substance into another at elevated temperatures. It involves heating in the absence of air or oxygen to decompose chemical bonds and yield smaller molecules. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids, and methyl esters of fatty acids. The fuel properties of the liquid product fractions of the thermally decomposed vegetable oil or animal fat are likely to approach diesel fuels.

Srivastava *et al.* (2000) pyrolyzed soybean oil, for instance, contains 79% carbon and 11.88% hydrogen. It has low viscosity and a high cetane number compared to pure vegetable oils. Soybean oil pyrolyzed distillate, which consisted mainly of alkanes, alkenes and carboxylic acids had a cetane number of 43.

For catalytic cracking, several vegetable oils (e.g. palm, canola, soybean) have been employed in the process that involves conversion of the oils into bio-fuels suitable for gasoline engines using acid catalysts such as transition metal catalysts (that yield bio-fuels enriched in diesel fraction over 50% by weight) and zeolites and mesoporous materials that give bio-fuels with higher gasoline fractions over 40% with higher aromatic content. The reaction is normally performed at moderate to high temperatures (300–500 °C) using different oils to catalyst ratios depending on the oil and the catalyst. Catalytic cracking not only increases the yield of gasoline by breaking large molecules into smaller ones, but also improves the quality of the gasoline: this process involves carbocations and yields alkanes and alkanes with the highly branched structures desirable in gasoline.

2.2.4 Transesterification

Transesterification reaction seems to be the common and best choice as the physical characteristics of biodiesel are very close to those of diesel fuel and the process is relatively simple. This reaction is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol in the presence of a catalyst. Many types of alcohols can be used such as methanol, ethanol, propanol, and butanol

but the most common used is methanol because it gives a proper viscosity and boiling point and a high cetane number. To complete a transesterification stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is needed. In practice, the ratio needs to be higher to shift the equilibrium to a maximum ester yield (Fangrui and Hanna, 1999). The transesterification reaction of triglyceride is shown in Figure 2.2.

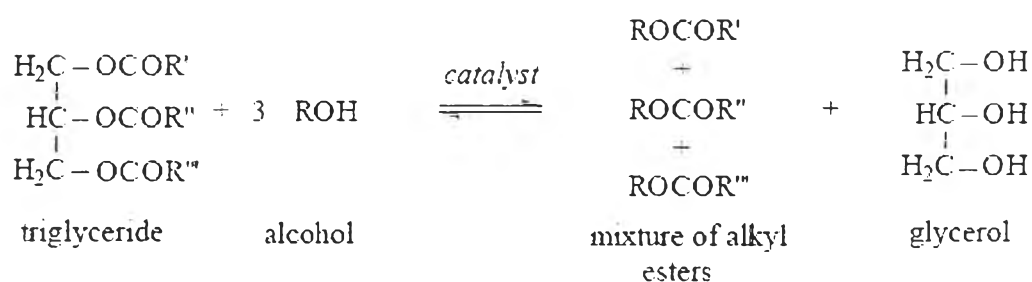


Figure 2.2 Transesterification reaction of triglyceride with alcohol.

The transesterification reaction shown in Figure 2.3 is indeed the overall reaction for three stepwise reaction with intermediate formation of diglyceride and monoglyceride (Figure 2.3). In the first reaction, triglyceride (TG) react with alcohol to produce diglyceride (DG), then in the second reaction, diglyceride (DG) react with alcohol to form monoglyceride (MG). Finally, in the third reaction, monoglyceride (MG) react with alcohol to give glycerol.

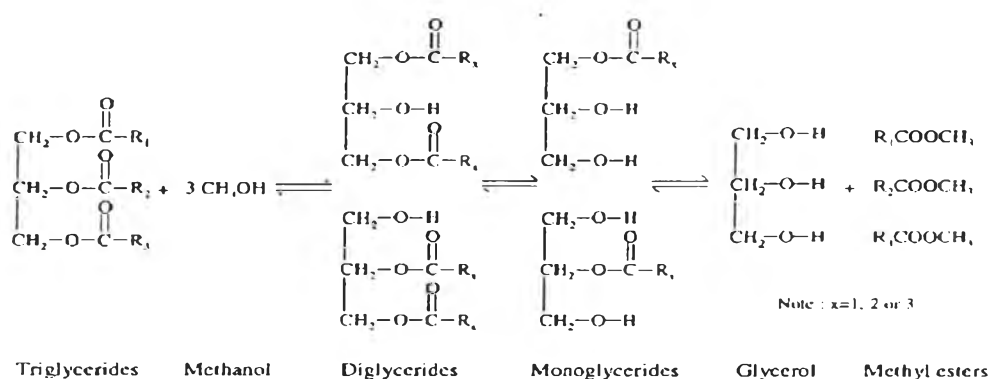


Figure 2.3 The transesterification reactions of vegetable oil with alcohol to esters and glycerol (Abdullah *et al.*, 2007).

For a catalyst in transesterification reaction is usually used to improve the reaction rate and yield because the reaction is reversible. There are many types of catalyst used in transesterification reaction: homogeneous and heterogeneous catalysts that were shown in the next part.

2.3 Vegetable Oils

Vegetable oils are lipid materials derived from plants such as coconut, corn, cotton seed, palm, soybean etc. There are primarily water-insoluble, hydrophobic substances in the plant kingdom that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides. Vegetable oils are renewable and potentially inexhaustible source of energy, with energy content close to that of diesel fuel. They have become more attractive recently because of their environmental benefits and the fact that they are made from renewable resources. The advantages of vegetable oils as diesel fuel are liquidity, ready availability, renewability, lower sulfur and aromatic content, and biodegradability. The main problems of the direct use of vegetable oils in fuel engines are higher viscosity, lower volatility and the reactivity of unsaturated hydrocarbon chains.

Vegetable oils is triglyceride molecules in which three fatty acid groups are esters attached to one glycerol molecule, as shown in Figure 2.4. R_1 , R_2 and R_3 represent a chain of hydrocarbon attached which the differences of R_1 , R_2 and R_3 result in different of vegetable oil characteristics. Vegetable oils comprise of 90 to 98% triglycerides and small amounts of mono- and di-glycerides. They contain free fatty acids (generally 1 to 5%) and traces of water (Srivastava and Prasad, 2000).

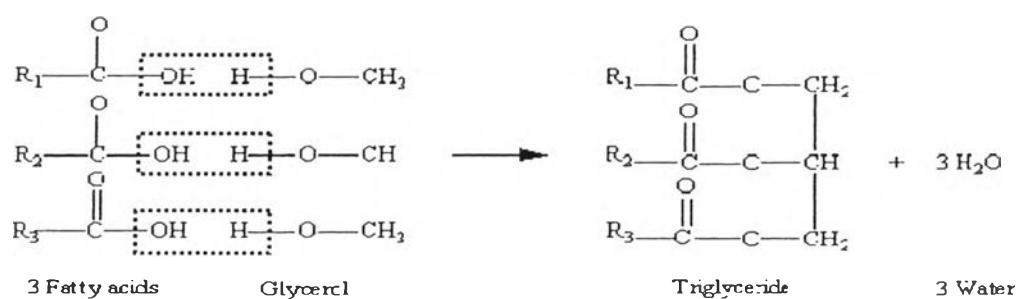


Figure 2.4 Formation of triglyceride. (Srivastava and Prasad, 2000)

The common fatty acids found in vegetable oils are stearic, palmitic, oleic, linoleic, and linolenic. Name and chemical structure of common fatty acids are shown in Table 2.3. Typical fatty acids compositions found in several vegetable oils are summarized in Table 2.4 (Demirbas, 2008).

Table 2.3 Chemical composition of vegetable oils (Srivastava and Prasad, 2000)

Fatty acid	Systematic name	Structure ^a	Formula
Lauric	Dodecanoic	12:0	C ₁₂ H ₂₄ O ₂
Myristic	Tetradecanoic	14:0	C ₁₄ H ₂₈ O ₂
Palmitic	Hexadecanoic	16:0	C ₁₆ H ₃₂ O ₂
Stearic	Octadecanoic	18:0	C ₁₈ H ₃₆ O ₂
Arachidic	Eicosanoic	20:0	C ₂₀ H ₄₀ O ₂
Behenic	Docosanoic	22:0	C ₂₂ H ₄₄ O ₂
Lignoceric	Tetracosanoic	24:0	C ₂₄ H ₄₈ O ₂
Oleic	cis-9-Octadecenoic	18:1	C ₁₈ H ₃₄ O ₂
Linoleic	cis-9,cis-12-Octadecadienoic	18:2	C ₁₈ H ₃₂ O ₂
Linolenic	cis-9,cis-12,cis-15-Octadecatrienoic	18:3	C ₁₈ H ₃₀ O ₂
Erucic	cis-13-Docosenoic	22:1	C ₂₂ H ₄₂ O ₂

^axx:y indicates x carbons in fatty acid chain with y double bonds

Table 2.4 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

2.4 Catalyst in Transesterification

Catalysts in transesterification reaction such as alkalis (basic), acids, or enzymes help to increase the rate of reaction and yield of alkyl esters. Sodium hydroxide and potassium hydroxide are used most frequently as alkali catalysts. Sulfuric acid and hydrochloric acid are usually used as acid catalysts. The main types of catalysts are divided into 2 types: homogeneous catalyst and heterogeneous 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.

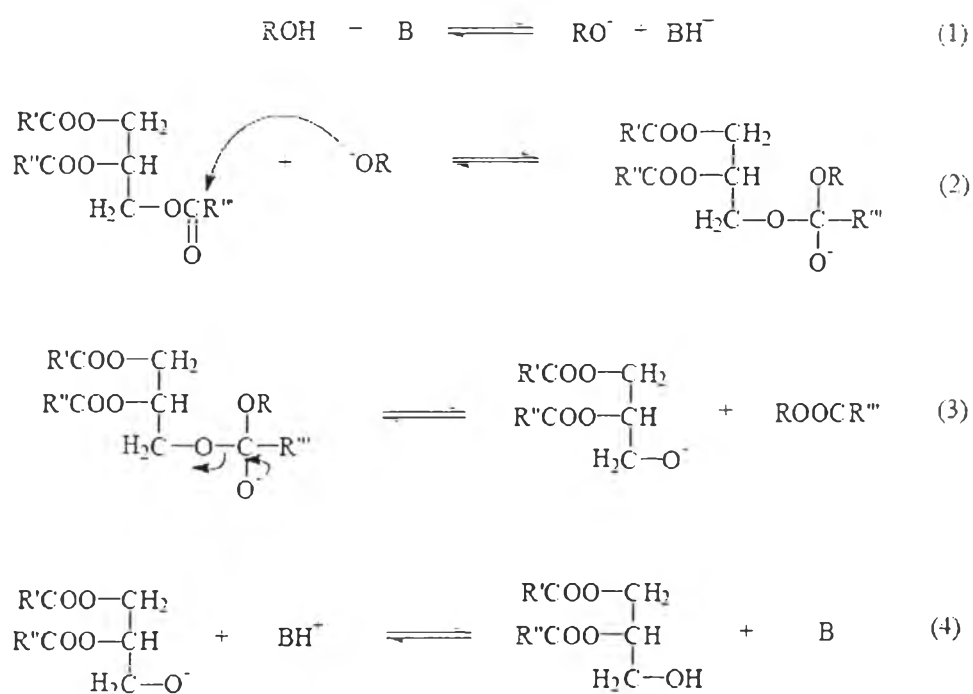


Figure 2.5 Mechanism of the base-catalyzed transesterification of vegetable oils.

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 the 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 at 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 NaOH turned out the fastest.

2.4.1.2 Homogeneous Acid Catalyst

The most widely used of catalysts for acid-catalyzed system are sulfuric acid (H₂SO₄) 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* (1998) 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⁺.

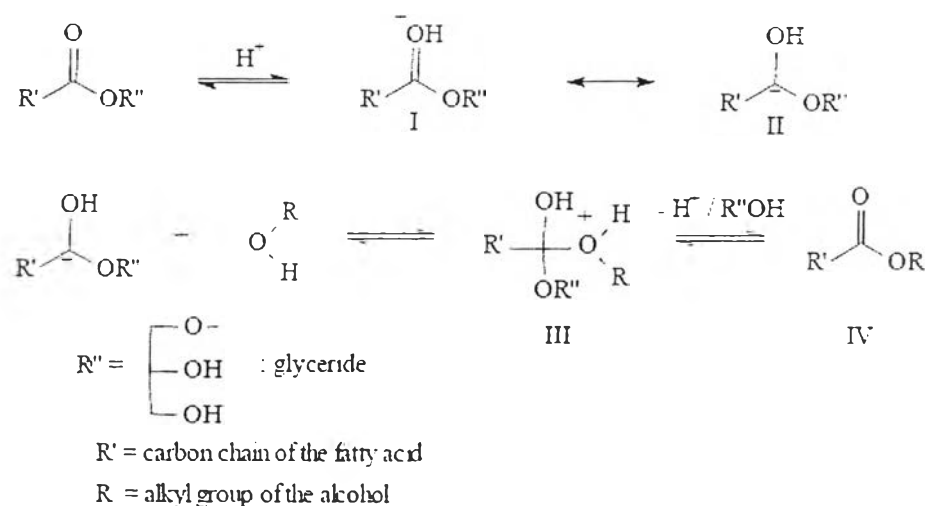


Figure 2.7 Mechanism of the acid-catalyzed transesterification of vegetable oils.

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 more than 90% at a reaction time of 10 h with ratio of methanol to oil at 20:1 and 4 wt.% H_2SO_4 (with reference to weight of oil) (Wang *et al.*, 2006).

Freedman *et al.* (1984) reported that 99 % oil conversion by using 1 mol% of H_2SO_4 and methanol to oil ratio 30:1 for 69 h reaction time. These data indicates that acid-catalyzed transesterification process requires more severe reaction conditions (such as longer reaction time) than base-catalyzed reaction.

2.4.2 Heterogeneous Catalyst

Although, homogeneous catalysts are the most widely used in industrial because they give high conversions under mild conditions and reaction generally takes about an hour for completion, homogeneous catalyzed process face difficulties to handle feed stocks with higher fatty acid or water content lead to formation of soap and consequent loss of oil and problems of product separation. So, biodiesel production using heterogeneous catalysts instead of homogeneous catalysts could potentially lead to cheaper production costs because it is possible to reuse the catalysts and to carry out both transesterification and esterification simultaneously (Furuta *et al.*, 2004).

2.4.2.1 Heterogeneous Acidic Catalyst

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

Serio *et al.* (2007) studied catalytic activity of vanadyl phosphate (VOP) as a catalyst in the transesterification of soybean oil. This catalyst was prepared from the suspension of V_2O_5 in diluted phosphoric acid and then calcined at 500 °C for 2 h. They found that the catalyst was active in transesterification reaction with 80% methyl ester yield obtained only after 1 h reaction time even though the specific surface area of catalyst was low (2–4 m²/g). The catalytic activity was increased with increasing the calcination temperature, which helped in removing the hydration water of the sample and thus, increasing the concentration of the coordinatively unsaturated VO group and resulted in increased Lewis acidity of solids.

Garcia *et al.* (2008) studied sulfated zirconia solid acid catalyst for transesterification reaction of soybean oil and simultaneous esterification of oleic acid with methanol and ethanol in a high pressure reactor. This catalyst was prepared by either solvent free method (S-ZrO₂) or standard precipitation method (SZ). In solvent free method, ZrOC₁₂.8H₂O and (NH₄)₂SO₄ are mixed in molar ratio of 1:6 for 20 min at room temperature and calcined at 600 °C for 5 h. Whereas, in standard precipitation method, SZ was prepared by precipitation of zirconium oxychloride hydrate (ZrOC₁₂.8H₂O) with ammonium hydroxide at pH 8.5 and then washed, dried, and after that powder was sulfated by impregnated H₂SO₄ and then calcined at 650 °C for 4 h. It was found that sulfated zirconia prepared by solvent free method was very active in the transesterification as well as esterification reaction. The conversion in alcoholysis catalyzed by S-ZrO₂ obtained under optimized conditions at 120 °C, 5 wt.% of catalyst (w/w) was 98.6% (methanolysis) and 92% (ethanolysis), respectively, after 1 h. The performance of ethanolysis was not as good as in methanolysis due to the higher water content of ethanol (0.44%) compared to methanol (0.08%). S-ZrO₂ was an amorphous material while SZ are crystalline (tetragonal and monoclinic phases of zirconia).

2.4.2.2 Heterogeneous Basic Catalyst

High basicity catalysts show good catalytic activity in the transesterification of vegetable oils. Gryglewicz (1999) studied the behavior of a series of catalysts based on alkaline earth metal oxides, hydroxides, and methoxides for methyl ester production from rapeseed oil. They found that the transesterification of rapeseed oil by methyl alcohol can be catalyzed effectively by basic alkaline-earth metal compounds: CaO, CH₃OCa and BaOH. The basicity of alkaline-earth metal hydroxides increases in the order Mg(OH)₂ < Ca(OH)₂ < Ba(OH)₂ because the ionic radii of alkaline-earth metals increase and their electronegativity decreases in this order. According to Lewis theory, the oxides of alkaline-earth metals are stronger bases than their hydroxides and alkaline-earth metal methoxides are even more basic. Thus, calcium compounds, and similarly magnesium and barium compounds, can be ordered according to their alkaline power as follows: Ca(OH)₂ < CaO < Ca(CH₃O)₂. For transesterification of rapeseed oil, BaOH was high active which the yield was 75% after 30 min. CH₃OCa was medially active which the yield was 55% after 30 min, 80% after 1 h, and the state of reaction equilibrium (93%) was reached after 2.5 h. The rate of the reaction was lowest when CaO powder was used as the catalyst. But even in this case, a close-to-equilibrium state was reached after 2.5 h of reaction. Magnesium oxide and calcium hydroxide showed no catalytic activity in the rapeseed oil methanolysis.

In addition, Hameed *et al.* (2009) studied the effect of methanol/oil molar ratio, reaction time, and amount of catalyst for the production of biodiesel from palm oil using KF/ZnO catalyst. The biodiesel yield was found to increase with increasing catalyst amount, methanol/oil molar ratio, and reaction time within the range studied. The maximum biodiesel yield was 89.23% with the optimum reaction conditions were found as follows: methanol/oil ratio of 11.43, reaction time of 9.72 h and catalyst amount of 5.52 wt.%. The biodiesel yield from transesterification of soybean oil using KF/ZnO catalyst is strongly dependent upon the catalyst applied. The conversion to methyl esters increased to 87% when the amount of loaded catalyst increased to 3% that the catalytic activities showed a correlation with their corresponding basic properties towards palm oil transesterification.

Zhu *et al.* (2006) showed the basic strength of calcium oxide was more than 26.5 that the sufficient for the transesterification of oil from *Jatropha curcas*. This catalyst gave 93% oil conversion with the optimum conditions of catalyst calcination temperature of 900 °C, reaction temperature of 70 °C, reaction time of 2.5 h, catalyst dosage of 1.5%, and methanol/oil molar ratio of 9:1

CaO is the most widely used as a heterogeneous basic catalyst as it presents many advantages such as long catalyst life, high activity, and requires only moderate reaction conditions. Besides, CaO has attracted much attention due to the fact that there are several natural calcium sources and calcium sources are cheap.

Liu *et al.* (2008) studied the catalytic activity of CaO as a solid catalyst used in transesterification of soybean oil to biodiesel. The BET surface area of the CaO catalyst was 0.56 m²/g. The optimum condition was 12:1 molar ratio of methanol to oil, 8 wt.% catalyst concentration at 65 °C and reaction time 3 h. Biodiesel yield was 95% when reaction was carried out for 3 h. They compared the activity of CaO with K₂CO₃/γAl₂O₃ and KF/γAl₂O₃ catalysts prepared by an impregnation method and calcined at 550 °C for 5 h. They found that CaO maintained sustained activity for 20 cycles after reused and biodiesel yield was also not affected. On the other hand, K₂CO₃/γAl₂O₃ and KF/γAl₂O₃ catalysts were not able to maintain activity and biodiesel yield also got affected after every use because the alkali metal compounds dissolved in methanol, which reduced the active ingredients and thereby decreasing biodiesel yield in the subsequent experiments.

Kouzu *et al.* (2008) used CaO catalyst for transesterification of soybean oil. The reaction conditions were 12:1 molar ratio methanol to oil, at 500 rpm and at reflux temperature for 2 h in a glass batch reactor and gave 93% biodiesel yield. CaO was obtained by calcination of pulverized lime stone at 900 °C for 1.5 h. Calcium diglyceride and calcium methoxide were used as reference samples. The BET surface area of fresh CaO was 13 m²/g, whereas the surface area of CaO collected after conversion was 11 m²/g. While the BET surface area of reference samples such as calcium diglyceroxide and calcium methoxide were 11.3 m²/g and 44 m²/g, respectively.

Because of the leaching problem of active phase from the catalyst to the reaction medium is the main problem for using as heterogeneous

catalyst which would force to introduce additional stage of neutralization and elimination of these species. Under this condition, the catalytic process operating in the transesterification will be mixed with contribution of both homogeneous and heterogeneous catalysis that losing the advantages of a purely heterogeneous process for biodiesel production. Rubio *et al.* (2010) solved this problem by filling CaO to the mesoporous network of ZnO obtained by thermal decomposition of zinc oxalate. This supported CaO catalyst thermally activated at 800 °C can give rise to biodiesel yield higher than 90% after 2 h of reaction, when a methanol:oil molar ratio of 12 and 1.3 wt% of the catalyst with a 16 wt% CaO. CaO seems to be stabilized by filling the mesoporous of ZnO, thus avoiding the leaching of the active phase in the reaction medium.

Ngamcharussrivichai *et al.* (2008) studies transesterification of palm kernel oil with methanol over mixed oxides of Ca and Zn. This catalyst was prepared via a conventional co-precipitation at calcination temperature 800 °C. The results indicated that the mixed oxides possess relatively small particle sizes and high surface areas, compared to pure CaO and ZnO. Moreover, the combination of Ca and Zn reduced the calcination temperature. Under the suitable transesterification conditions at 60 °C (catalyst amount = 10 wt.%, methanol/oil molar ratio = 30, reaction time = 1 h), the FAME content of >94% can be achieved over CaO-ZnO catalyst with the Ca/Zn ratio of 0.25. This catalyst can be reused up to 3 times with maintaining the FAME content > 90%.

Yan *et al.* (2010) prepared Ca-La metal oxide catalysts by four different preparation methods: ammonia-ethanol-carbon dioxide precipitation, physical mixing, impregnation, and co-precipitation. Three types of Ca structures were observed: (1) Ca species segregated on the surface in the samples prepared by the ammonia-ethanol-carbon dioxide precipitation method and the physical mixing method. Crystal size of Ca species for Ca₃La₁ was smaller than of the CaO-La₂O₃; (2) Ca incorporated into the La(OH)₃ lattice prepared by the impregnation method; and (3) Ca stayed as a non-crystal structure prepared by the co-precipitation method. Segregated and highly dispersed Ca species were obtained by the ammonia-ethanol-carbon dioxide precipitation method. Also, the ammonia-ethanol-carbon dioxide precipitation method resulted in the highest BET specific surface area, base strength

and base site concentration that are characteristics of an active transesterification catalyst.

Surface area and morphology of catalyst are the main parameters that affect to catalytic activity of heterogeneous catalysts. There are several methods for preparing ZnO support to get different morphology and surface areas.

Medina *et al.* (2012) prepared ZnO nanoparticles by chemical precipitation synthesis with the stoichiometric relation used of the $Zn^{2+}:(OH^-)_2$ species was 1:1. $Zn(H_3C_2O_2)_2 \cdot 2H_2O$ was dissolved in distilled water and stirred at 40 °C. Then, NaOH solution was added to the Zn-solution. The $Zn(OH)_2$ 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 ZnO nanoparticles with hexagonal shape were produced. All hexagonal particles formed are of wurtzite crystal structure.

Zhang *et al.* (2011) synthesized nanoparticle-assembled ZnO micro-octahedrons by a facile homogeneous precipitation method. 0.05 M of $Zn(CH_3COO)_2 \cdot 2H_2O$ was mixed with aqueous ammonia (25–28 wt.%) until the pH value was adjusted to 10. After 2 h stirring, the white precipitation was filtered, washed with deionized water, dried at 80 °C for 12 h, and finally calcined at 500 °C for 1 h. The ZnO are composed of octahedral crystals with very rough surfaces and mean edge length about 4.5 μm which is self-assembled of nanoparticles with diameters of 200–300 nm.

Yan *et al.* (2010) prepared ZnO nanoparticles by the urea hydrolysis method. $Zn(NO_3)_2$ and $La(NO_3)_3$ solutions with 3:1 ratios of Zn: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 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 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. The high catalytic activity, long catalyst life and low leaching properties. It was found that the average yield of FAME was around 93.7% after were reused 17 times without any activity loss.

Yakuphanoglu (2010) prepared ZnO by sol-gel method. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$ is the starting material, deionized water is the solvent, and monoethanolamine is stabilizer. Equal concentrations of monoethanoamine and Zn^{2+} were used. The precursor solution was mixed with a magnetic stirrer for 2 h in 60 °C and then aging for 24 h resulting in a clear and homogeneous sol. The acid sol (pH 1) was prepared by adding nitric acid (HNO_3). The sample was stood on a hot plate at 150 °C for 2 h for evaporating the solvent. Then, the dried sample was annealed at 600 °C in a furnace under air atmosphere. The ZnO exhibits a polycrystalline grown with a hexagonal wurtzite-type.

2.5 Analysis of Transesterification Products

Potential contaminants of biodiesel including 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 and Povazanec (1996) 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.

Glycerol was also analyzed by high-performance liquid chromatography (HPLC) using pulsed amperometric detection, which offers the advantage of higher sensitivity compared to refractometry and being suitable for detection of small amounts for which GC may not be suitable.