CHAPTER II

LITERATURE REVIEW

2.1 Vegetable Oils

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 first use of vegetable oils as a fuel was in 1900. The advantages of vegetable oils as diesel fuel are liquidity, ready availability, renewability, lower sulfur and aromatic content, and biodegradability. The main disadvantages of vegetable oils as diesel fuel are higher viscosity, lower volatility, and the reactivity of unsaturated hydrocarbon chains.

Vegetable oils and animal fats are triglyceride molecules in which three fatty acid groups are esters attached to one glycerol molecule. Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdoms that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides. 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). The general formation of triglyceride is shown in Figure 2.1
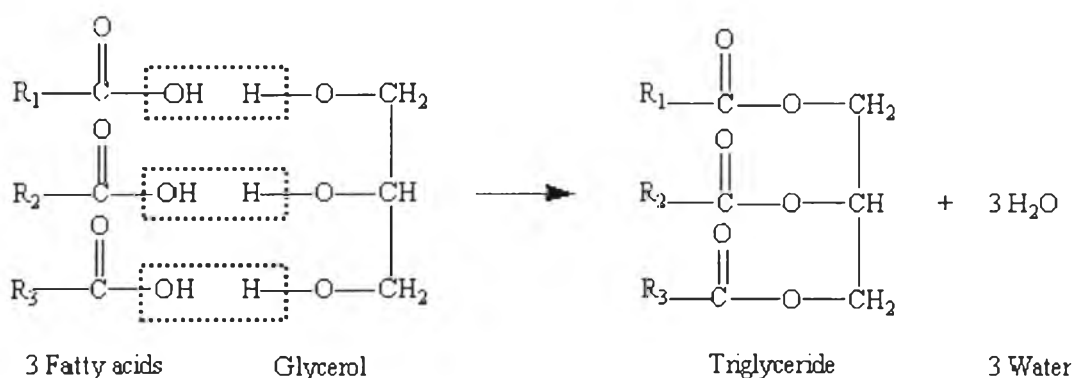

Figure 2.1 Formation of triglyceride. (Srivastava and Prasad, 2000)

From Figure 2.1, R_1, R_2 and R_3 represent a chain of carbon atoms with hydrogen atoms attached. The differences of R_1, R_2 and R_3 result in differences of fatty acids which glycerol backbone will be combined. Fatty acids vary in their carbon chain length and in the number of double bonds. This reason leads to make different characteristics of vegetable oil. 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 2.1. Typical fatty acids compositions found in several vegetable oils are summarized in Table 2.2 (Ma and Hanna, 1999).

Table 2.1 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	$C_{22}H_{42}O_2$

[a]xx:y indicates x carbons in fatty acid chain with y double bonds

Table 2.2 Typical fatty acid composition (%) for different common oil sources. (Ma and Hanna, 1999).

Fatty acid	Soybean	Cottonseed	Palm	Lard	Tallow	Coconut
Lauric (C12:0)	0.1	0.1	0.1	0.1	0.1	46.5
Myristic (C14:0)	0.1	0.7	1.0	1.4	0.8	19.2
Palmitic (C16:0)	0.2	20.1	42.8	23.6	23.3	9.8
Stearic (C18:0)	3.7	2.6	4.5	14.2	19.4	3.0
Oleic (C18:1)	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic (C18:2)	53.7	55.2	10.1	10.7	10.7	2.2
Linolenic (C18:3)	8.6	0.6	0.2	0.4	0.4	0.0

2.2 Biodiesel

Biodiesel (Greek, bio, life + diesel from Rudolf Diesel) refers to a diesel-equivalent, processed fuel derived from biological sources. Chemically, biodiesel is defined as the monoalkyl esters, especially (m)ethyl ester, of long-chain fatty acids derived from renewable biolipids. Biodiesel is typically produced through the reaction of 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 *et al.*, 2002). Generally, methanol is preferred for transesterification because it is less expensive than ethanol, can give a proper viscosity and boiling point, and a high cetane number. Technical properties of biodiesel are shown in Table 2.3.

Table 2.3 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 40 °C)	3.3-5.2
Density range (kg/m^3, at 15 °C)	860-894
Boiling point range (°C)	>202
Flash point range (°C)	157-182
Distillation range (°C)	197-327
Vapor pressure (mm Hg, at 22 °C)	<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

Biodiesel is technically competitive with or offers technical advantages over conventional petroleum diesel fuel. The advantages of biodiesel as diesel fuel are portability, ready availability, renewability, higher combustion efficiency, and 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). Table 2.4 shows some fuel properties of six methyl ester biodiesels given by different researchers.

Table 2.4 Some fuel properties of six methyl ester biodiesels

Source	Viscosity cSt at 313.2 K	Density g/mL at 288.7 K	Cetane number	Reference
Sunflower	4.6	0.880	49	Pischinger *et al.*, 1982
Soybean	4.1	0.884	46	Schwab *et al.*, 1987
Palm	5.7	0.880	62	Pischinger *et al.*, 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 *et al.*, 1995

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.

2.3.1 Dilusion of Oils

Dilusion of oils with solvents and microemulsions of vegetable oils lowers the viscosity and mitigates some engine performance problems such as injector coking and carbon deposits, etc. To dilute vegetable oils the addition of 4% ethanol to the oils increases the brake thermal efficiency, break torque, and brake power while decreasing brake-specific fuel consumption. Since the boiling point of ethanol is less than that of vegetable oils, it could assist in the development of the combustion process through an unburned blend spray (Bilgin *et al.*, 2002).

The viscosity of oil can be lowered by blending with pure ethanol. Twenty-five parts of sunflower oil and 75 parts of diesel were blended as diesel fuel (Ziejewski *et al.*, 1984). The viscosity was 4.88 cSt at 40 °C, while the maximum specified ASTM value was 4.0 cSt at 40 °C. This mixture was not suitable for long-term use in a direct injection engine.

2.3.2 Microemulsion of Oils

Microemulsions are isotropic, clear, or translucent thermodynamically-stable dispersions of oil, water, surfactant, and often a small amphiphilic molecule, called a co-surfactant.

To reduce the high viscosity of vegetable oils, microemulsions with immiscible liquids such as methanol and ethanol and ionic or non-ionic amphiphiles have been studied (Billaud *et al.*, 1995).

Ziejewski *et al.* (1984) prepared an emulsion of 53% (vol) alkali-refined and winterized sunflower oil, 13.3% (vol) 190-proof ethanol, and 33.4% (vol) 1-butanol. This non-ionic emulsion 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 (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 in lubricating oil viscosity were reported (Ma and Hanna, 1999)

2.3.3 Pyrolysis and Catalytic Cracking

Pyrolysis is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst. It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids, and methyl esters of fatty acids.

Catalytic cracking of vegetable oils to produce biofuels has been studied (Pioch *et al.*, 1993). Copra oil and palm oil stearin were cracked over a standard petroleum catalyst SiO_2/Al_2O_3 at 450 °C to produce gases, liquids, and

solids with lower molecular weights. The condensed organic phase was fractionated to produce biogasoline and biodiesel fuels.

2.3.4 Transesterification

Among all these alternatives, transesterification seems to be the best choice as the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel and the process is relatively simple.

Transesterification (also called alcoholysis) is the reaction of a fat or oil triglyceride with an alcohol to from esters and glycerol. Many types of alcohol can be used such as methanol, ethanol, propanol, and butanol. The most common used is methanol because it gives a proper viscosity and boiling point and a high cetane number. In the transesterification of vegetable oils, triglyceride reacts with methanol producing glycerine and a mixture of fatty acid methyl esters (biodiesel). Figure 2.2 shows the transesterification reaction of triglyceride.
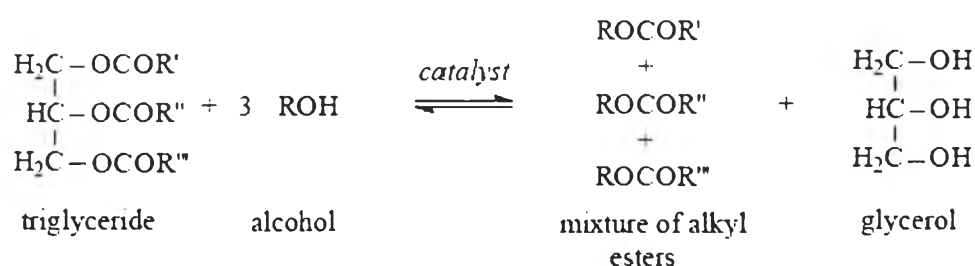
$$
\begin{array}{ccccccc}
& & & & ROCOR' & & \\
H_2C-OCOR' & & & & + & & H_2C-OH \\
| & & & catalyst & & & | \\
HC-OCOR'' & + & 3\ ROH & \rightleftharpoons & ROCOR'' & + & HC-OH \\
| & & & & + & & | \\
H_2C-OCOR''' & & & & ROCOR''' & & H_2C-OH \\
\text{triglyceride} & & \text{alcohol} & & \text{mixture of alkyl} & & \text{glycerol} \\
& & & & \text{esters} & &
\end{array}
$$

Figure 2.2 Transesterification reaction of triglyceride with alcohol.

From Figure 2.2, a catalyst is usually used to improve the reaction rate and yield because the reaction is reversible. 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 shown in Figure 2.2 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 monoglyeride (MG). Finally, in the third reaction, monoglyceride (MG) react with alcohol to give glycerol.
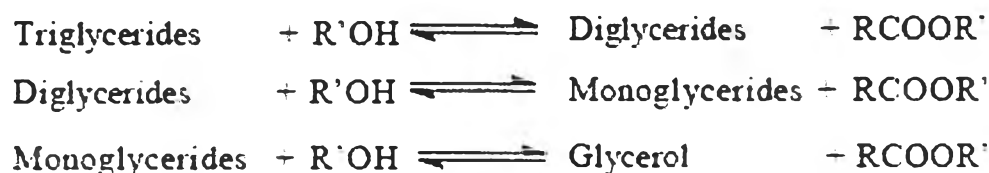
Triglycerides   + R'OH ⇌ Diglycerides   + RCOOR'

Diglycerides   + R'OH ⇌ Monoglycerides + RCOOR'

Monoglycerides + R'OH ⇌ Glycerol   + RCOOR'

Figure 2.3 The transesterification reactions of vegetable oil with alcohol to esters and glycerol (Freedman *et al.*, 1986).

2.4 Catalyst in Transesterification

Vegetable oils can be transesterified by heating them with a large excess of anhydrous methanol and a catalyst. The transesterification reaction can be catalyzed by alkalis (basic), acids, or enzymes in order 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. Moreover, the transesterification reaction can be achieved without a catalyst, by the supercritical method.

2.4.1 Homogeneous Base-catalyzed Transesterification

Currently, biodiesel is commonly produced by using homogeneous base catalyst, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). These catalysts are commonly used in the industries due to several reasons: (i) able to catalyze reaction at low reaction temperature and atmospheric pressure, (ii) high conversion can be achieved in a minimal time, and (iii) widely available and economical (Lotero *et al.*, 2005). In fact, it was reported that the rate for base-catalyzed reaction would be 4,000 times faster compared to acidic catalyst (Fukuda *et al.*, 2001, Kulkarni and Dalai, 2006).

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Figure 2.4. The first step (Eq. 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 (Eq. 2), which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 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.
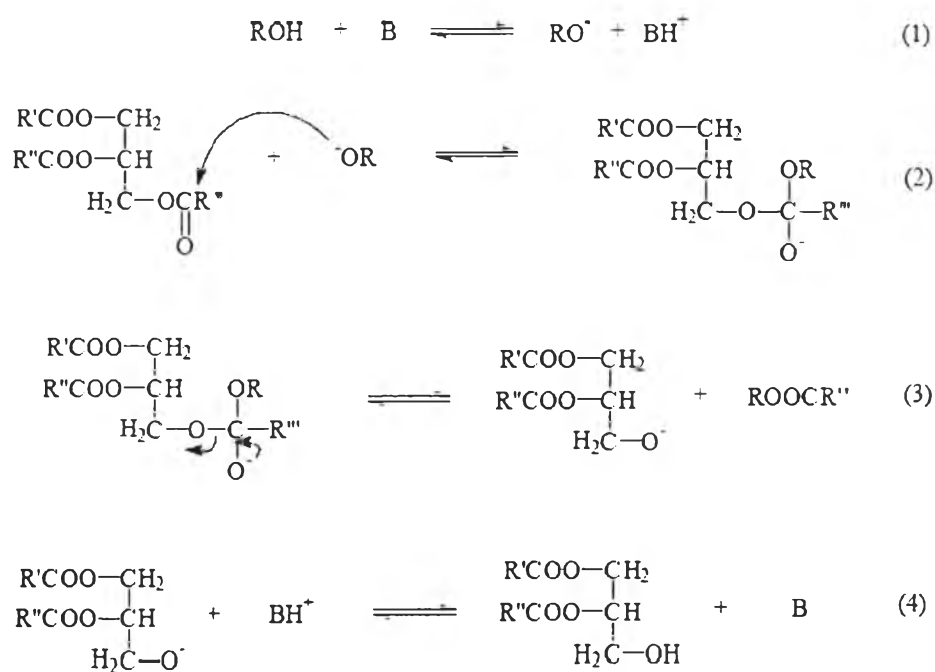
$$ROH + B \rightleftharpoons RO^- + BH^+ \qquad (1)$$

$$
\begin{array}{l}
R'COO-CH_2 \\
R''COO-CH \\
\quad H_2C-OCR''' \\
\qquad \parallel \\
\qquad O
\end{array}
\; + \; {}^-OR \;\rightleftharpoons\;
\begin{array}{l}
R'COO-CH_2 \\
R''COO-CH \quad OR \\
\quad H_2C-O-C-R'' \\
\qquad\qquad \mid \\
\qquad\qquad O^-
\end{array}
\qquad (2)
$$

$$
\begin{array}{l}
R'COO-CH_2 \\
R''COO-CH \quad OR \\
\quad H_2C-O-C-R''' \\
\qquad\qquad \parallel \\
\qquad\qquad O
\end{array}
\;\rightleftharpoons\;
\begin{array}{l}
R'COO-CH_2 \\
R''COO-CH \\
\quad H_2C-O^-
\end{array}
\; + \; ROOCR'' \qquad (3)
$$

$$
\begin{array}{l}
R'COO-CH_2 \\
R''COO-CH \\
\quad H_2C-O^-
\end{array}
\; + \; BH^+ \;\rightleftharpoons\;
\begin{array}{l}
R'COO-CH_2 \\
R''COO-CH \\
\quad H_2C-OH
\end{array}
\; + \; B \qquad (4)
$$

Figure 2.4 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 2.5 (Schuchardt *et al.*, 1997). This undesirable saponification reaction reduces the ester yields and considerably difficult to recover of the glycerol.
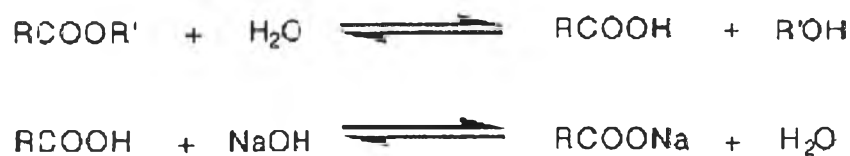
$$RCOOR' \; + \; H_2O \; \rightleftharpoons \; RCOOH \; + \; R'OH$$

$$RCOOH \; + \; NaOH \; \rightleftharpoons \; RCOONa \; + \; H_2O$$

Figure 2.5 Saponification of fatty acid alkyl ester.

Tomasevic *et al.* (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 1wt% KOH, temperature of 25 °C, a 1:6 molar ratio of oil to methanol 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, NaOH, and KOH) for methanolysis of sunflower oil. All the reactions were carried out under the same experimental conditions in a batch 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 transesterification reactions were quite rapid and the biodiesel layers achieved nearly 100% methyl ester concentrations, the reactions using sodium hydroxide turned out the fastest.

Felizardo *et al.* (2006) studied transesterification of waste frying oils with methanol using NaOH as a catalyst. Methanol/oil molar ratios and catalyst/oil weight ratios were varied. For oils with an acid value of 0.42 mg KOH/g, the results showed that a methanol/oil ratio of 4.8 and a catalyst 0.6% gave the highest yield of methyl esters for 1 h. Furthermore, an increase in the amount of methanol or catalyst quantity seems to simplify the separation or purification of the methyl esters phase, as shown by a viscosity reduction and an increasing purity to values higher than 98% for methyl esters phase.

2.4.2 Homogeneous Acid-catalyzed Transesterification

Since liquid base-catalyzed transesterification process poses a lot of problems especially for oil or fat with high FFAs concentration, liquid acid catalysts are proposed in order to overcome the limitations. To date, the most investigated catalysts for acid-catalyzed system are sulfuric acid (H_2SO_4) and hydrochloric acid (HCl). Acid-catalyzed transesterification holds an important advantage with respect to base-catalyzed process: acid catalyst is insensitive to the presence of FFAs in the feedstock (Kulkarni and Dalai, 2006) and can catalyze esterification and transesterification simultaneously (Jacobson *et al.*, 2008).

In addition, economic analysis has proven that acid-catalyzed procedure, being a one-step process, is more economical than the base-catalyzed process, which requires an extra step to convert FFA to methyl esters (Zhang *et al.*, 2003).

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 2.6 (Schuchardt *et al.*, 1997). However, it can be extended to di- and tri-glycerides. The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H^+.
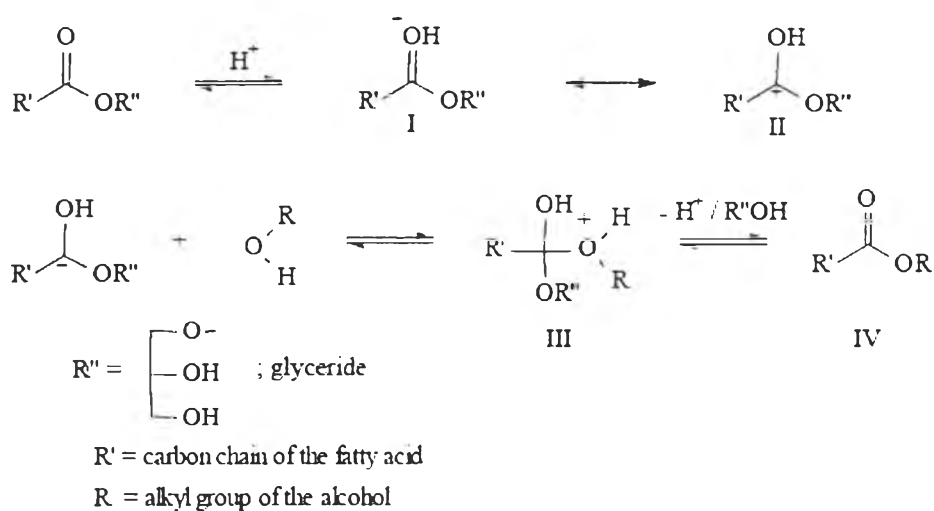
Figure 2.6 Mechanism of the acid-catalyzed transesterification of vegetable oils.

According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an 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.

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

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 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.

2.4.3 Heterogeneous Catalyst

Generally, homogeneous catalyzed biodiesel processes are relatively fast and give high conversions with minimal side reaction but they still have several problems. For example: (i) the catalyst cannot be recovered and must be neutralized at the end of the reaction, (ii) there is limited use of continuous process, and (iii) the processes are very sensitive to the presence of water and FFA which give rise to competing hydrolysis and saponification reaction. So, heterogeneous reaction is being considered in which the liquid catalyst is replaced by solid catalysts. This process could potentially lead to cheaper production costs because it is possible to reuse the catalysts and to carry out both transesterification and esterification simultaneously (Lopez *et al.*, 2005).

There are several reports on using heterogeneous catalyst for biodiesel production.

Jitputti et $al.$ (2006) studied several acid and base solid, such as ZrO_2, ZnO, SO_4^{2-}/SnO_2, SO_4^{2-}/ZrO_2, KNO_3/KL zeolite and KNO_3/ZrO_2 as heterogeneous catalysts for crude palm kernel oil (PKO) and crude coconut oil (CCO) transesterification with methanol. They found that ZnO and SO_4^{2-}/ZrO_2 exhibited the highest activity for both PKO and CCO transesterification. In the case of SO_4^{2-}/ZrO_2, only 1 wt% of this acidic solid was needed to catalyze the reaction, and resulted in fatty acid methyl esters content higher than 90%. Moreover, a study of the catalyst's recyclability indicated that the spent SO_4^{2-}/ZrO_2 cannot be directly reused for the transesterification. However, this spent catalyst can be easily regenerated and the same activity can be obtained.

Xie et $al.$ (2006) studied the catalytic activity and base strength of Al_2O_3 loaded with different potassium compounds (KF, KCl, KBr, KI, K_2CO_3, KNO_3, and KOH) in the soybean oil transesterification, the catalytic activity and base strength of KI supported on different carriers (ZrO_2, ZnO, NaX zeolite, KL zeolite, and Al_2O_3), the effect of catalyst loading, the molar ratio of methanol to oil, and the reaction time. They indicated that KI/Al_2O_3 was the most active catalyst, obtaining 96% conversion of soybean oil under the optimum condition: 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 oil, 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 KNO_3, forming either K_2O species or Al–O–K group in the composite, were probably the active basic sites.

Furthermore, Xie et $al.$ (2007) studied the effect of using NaX zeolite loaded with KOH as a solid base catalyst in transesterification of soybean oil with methanol to methyl esters. They found that NaX zeolite loaded with 10% KOH, 10:1 molar ratio of methanol to soybean oil, a reaction time of 8 h and a catalyst amount

of 3 wt%, gave the conversion of soybean oil of 85.6%. Moreover, they discovered that of KOH/NaX zeolite has basic strength higher than the parent NaX zeolite. After being loaded with KOH, the pore structure of zeolite which is necessary for catalysis could be retained. This approach was successfully used in an attempt to increase the catalytic activity of NaX zeolite towards the transesterification reaction.

Shu *et al.* (2007) tested the catalytic activity of zeolite beta modified with La (La/zeolite beta) as a heterogeneous catalyst for methanolysis of soybean oil. They found that La/zeolite beta showed higher conversion and stability than zeolite beta for the production of biodiesel, which may be correlated to the higher quantity of external Bronsted acid sites available for the reactants. The product consists of a mixture of monoalkyl esters primarily, and when the methanol/soybean oil molar ratio was 14.5, reaction temperature at 60 °C, reaction time 4 h and catalyst/soybean oil mass ratio of 0.011, the conversion of triglyceride 48.9 wt% was obtained from this optimal reaction condition.

Kawashima *et al.* (2008) investigated thirteen different kinds of metal oxides containing calcium, barium, magnesium, or lanthanum as catalysts for biodiesel production. They found that calcium-containing catalysts — $CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, and $CaO\text{-}CeO_2$ — showed high activities and gave approximately 90% methyl ester. Moreover, they tested the catalytic durability by repeating the transesterification reaction several times with the calcium-containing catalysts recovered from the previous reaction mixture. It was found that $CaZrO_3$ and $CaO\text{-}CeO_2$ showed high durability and have the potential to be used in biodiesel production processes as heterogeneous base catalysts.

Noiroj *et al.* (2009) studied the catalytic activity of KOH/Al_2O_3 and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. They suggested that 25 wt% KOH/Al_2O_3 and 10 wt% KOH/NaY catalysts are the best formula due to their biodiesel yield of 91.07% at temperatures below 70 °C within 2–3 h at a 1:15 molar ratio of palm oil to methanol and a catalyst amount of 3–6 wt%. Moreover, about 51.26 and 3.18% of the K were leached from 25 wt% KOH/Al_2O_3 and 10 wt% KOH/NaY, respectively, by using the optimum conditions. The 10 wt% KOH/NaY should be proper for the transesterification reaction as a heterogeneous catalyst since the amount of K in the fresh catalyst is about the same

as in the spent catalyst. It is reasonable to conclude that the type of support strongly affects the activity and leaching of the active species of the catalyst.

Kansedo *et al.* (2009) investigated the optimum four-variable, reaction temperature (50–190°C), reaction period (60–300 min), methanol/oil molar ratio (4–12), and amount of catalyst (1–5 wt%) in the transesterification of palm oil using montmorillonite KSF as a heterogeneous catalyst. The transesterification reactions were carried out in a batch reactor and the magnetic stirrer was set at 190–200 rpm. Based on the experimental result obtained, they found that the yield of palm oil fatty acid methyl esters (FAME) could reach up to 79.6% using the following reaction conditions: reaction temperature of 190 °C, reaction period at 180 min, molar ratio of methanol/oil at 8:1 and amount of catalyst at 3%.

Hameed *et al.* (2009) studied the effect of methanol/oil molar ratio, reaction time, and amount of catalyst for production of biodiesel from palm oil using KF/ZnO catalyst. The optimum reaction conditions for transesterification of palm oil to biodiesel were found as follows: methanol/oil ratio of 11.43, reaction time of 9.72 h and catalyst amount of 5.52 wt%. The optimum biodiesel yield was 89.23%. Besides, the catalytic activities showed a correlation with their corresponding basic properties towards palm oil transesterification.

Soetaredjo *et al.* (2010) studied the effects of various reaction variables on the yield of biodiesel using KOH/bentonite as a heterogeneous catalyst. They found that the highest yield of biodiesel over KOH/bentonite catalyst was 90.70±2.47%. It was obtained at KOH/bentonite ratio 1:4, reaction time of 3 h, 3 wt% catalyst, methanol to oil ratio of 6, and at 60 °C. In addition, a heterogeneous catalyst KOH/bentonite can be used as a solid based catalyst for biodiesel production via transesterification of palm oil.

Zhang *et al.* (2010) studied the transesterification of palm oil with dimethyl carbonate (DMC) for preparing biodiesel in solvent-free system at the catalysis of potassium hydroxide (KOH) as a heterogeneous catalyst. The effects of reaction conditions (molar ratio of DMC and palm oil, catalyst amount and time) were investigated on FAMEs yield. The highest FAMEs yield could reach 96.2% at refluxing temperature for 8 h with molar ratio of DMC and oil 9:1 and 8.5% KOH

(based on oil weight). Moreover, the kinetics of the KOH-catalyzed transesterification of palm oil and DMC was investigated over a temperature range of 65 – 75 °C. A pseudo first-order model was proposed. The activation energy (Ea) was 79.1 kJ mol^{-1} and the pre-exponential factor (k$_o$) was 1.26 x 109 min^{-1} from Arrhenius equation.

Hamad *et al.* (2010) prepared zirconia promoted with Cs by cationic exchange of zirconium hydroxide with Cs. They found that ZrOCs was obtained via cationic exchange between zirconium hydroxide with Cs$^+$ in basic conditions followed by calcination at high temperature. ZrOCs oxide has an excellent activity for vegetable oil transesterification with ethanol and methanol in mild conditions, while Cs-free ZrO$_2$ is not active in their standard conditions. Moreover, it was demonstrated that ZrOCs gives higher turnover rate than soluble NaOH. ZrOCs is a potential catalyst due its basic features and thermal stability since this catalyst was formed via calcination at temperature of 550 °C.

2.5 Analysis of Transesterification Products

Potential contaminants of biodiesel include unreacted triacylglycerides, residual alcohol, and catalyst may be presented 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 triacylglycerols 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.

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 (Lozano *et al.*, 1996).