



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Biodiesel

Biodiesel refers to any diesel-equivalent biofuel made from renewable biological materials such as vegetable oils or animal fats. In general, biodiesel consists of mono alkyl-esters. It is usually produced by transesterification and esterification reactions of vegetable or waste oil, respectively, with a low molecular weight alcohol, such as ethanol and methanol. During this process, the triglyceride molecule from vegetable oil is removed in the form of glycerin (soap). Once the glycerin is removed from the oil, the remaining molecules are similar to those of petroleum diesel fuel. Although, there are some noble difference. While the petroleum and other fossil fuel contain a lot of sulfurs, ring molecules and aromatics, the biodiesel molecules are very simple hydrocarbon chains, containing no sulfur, ring molecules or aromatics. Thus biodiesel is essentially free of sulfur and aromatics. Biodiesel is made up of almost 10% oxygen, making it a naturally "oxygenated" fuel.

The advantage of biodiesel is when use in diesel engine, it can substantially reduces emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter. The use of biodiesel decreases the solid carbon fraction of particulate matter which the oxygen in biodiesel enables more complete combustion to CO_2 and reduces the sulfate fraction, while the soluble, or hydrocarbon, fraction stays the same or increases. Therefore, biodiesel works well with emission control technologies such as diesel oxidation catalysts. Emissions of nitrogen oxides increase with the concentration of biodiesel in the fuel. The general properties of biodiesel are shown in Table 2.1.

Table 2.1 The general properties of biodiesel (Alternative Fuel Data Center)

Biodiesel's Physical Characteristics:	
Specific gravity	0.87 to 0.89
Kinematic viscosity @ 40°C	3.7 to 5.8
Cetane number	46 to 70
Higher heating value (btu/lb)	16,928 to 17,996
Sulfur, wt. %	0.0 to 0.0024
Cloud point °C	-11 to 16
Pour point °C	-15 to 13
Iodine number	60 to 135
Lower heating value (btu/lb)	15,700 to 16,735

2.2 Vegetable Oil

Vegetable oils are substances derived from plants which are composed of triglycerides. Normally, oils are liquid at room temperature and fats are solid; a dense brittle fat is called wax. Although many different parts of plants may yield oil, in actual commercial practice oil is extracted primarily from the seeds of oilseed plants. Vegetable oil comes in many shapes and sizes with varying properties. The most important consideration is the melting point. The actual vegetable oil molecule is composed of three long carbon chains on a glycerol 'backbone' and the properties are determined by the individual 'fatty acid' chains. Vegetable oils comprise 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).

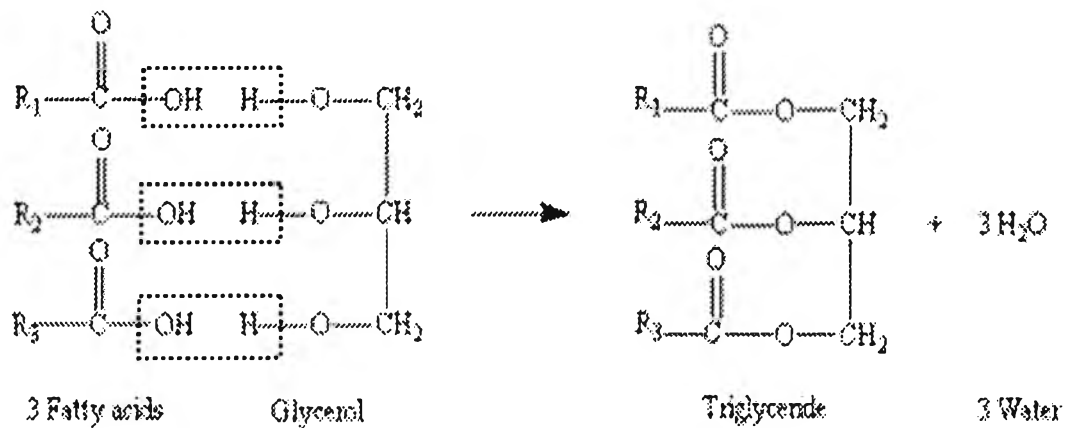


Figure 2.1 Formation of triglyceride.

From Figure 2.1 (Srivastava and Prasad, 2000), R_1 , R_2 and R_3 represent the chains 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 the 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 2.2.

Table 2.2 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

2.3 Transesterification

Transesterification or alcoholysis is the reaction of fats or oils with an alcohol to form esters and glycerol. A catalyst (a strong acid or base) is usually used to improve the reaction rate and yield. This process has been widely used to reduce the high viscosity of triglycerides (Meher *et al.*, 2006). The transesterification reaction is represented by the general equation, as shown in Figure 2.2. The alcohols used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are most frequently used, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides and NaOH can easily dissolve into it. Because transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants; therefore, the excess alcohol is required to use shift the equilibrium to forward (Fangrui and Hanna, 1999). To complete transesterification stoichiometrically, 3:1 molar ratio of alcohol to triglycerides is

needed. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield.

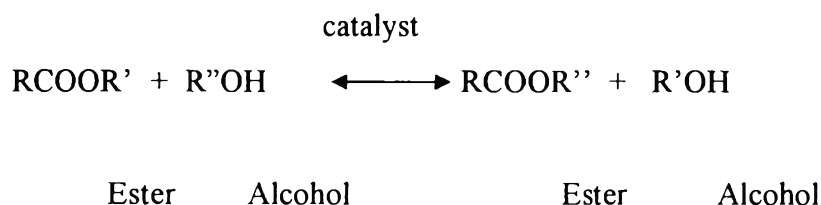


Figure 2.2 General equation for a transesterification reaction.

2.3.1 Transesterification of Vegetable Oils

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base producing a mixture of fatty acids alkyl esters and glycerol as shown in Figure 2.3 (Fangrui and Hanna, 1999). The overall process is a sequence of three consecutive and reversible reactions, in which di- and mono-glycerides are formed as intermediates. The stoichiometric reaction requires 1 mole of a triglyceride and 3 mole of alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed. Several aspects including the type of catalyst (alkaline or acid), alcohol/vegetable oil molar ratio, temperature, stirrer speed, purity of the reactants (mainly water content) and free fatty acid content can influence on the yield of product of the transesterification.

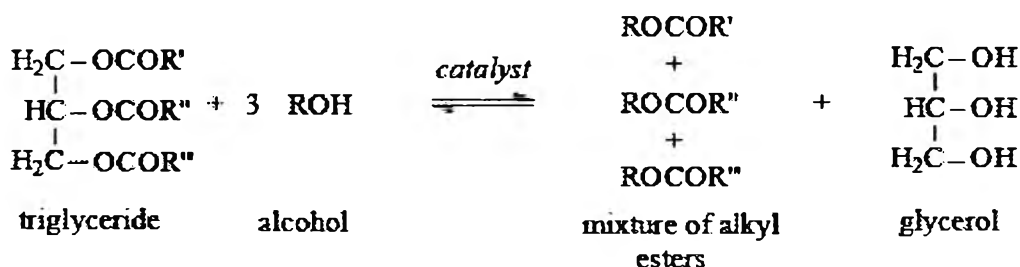


Figure 2.3 Transesterification reaction of triglyceride with alcohol.

Catalyst in transesterification

In general, transesterification of triglyceride with lower alcohol can proceed but it requires high energy input and long reaction time. To achieve satisfactory ester yield under mild condition, biodiesel production is generally conducted in the presence of catalysts. The catalyst can be divided in two types; homogeneous and heterogeneous catalyst. Nowadays, commercial biodiesel production uses homogeneous catalyst in the process, because homogeneous catalyst gives high conversion and short reaction time. Homogeneous catalyst can be divided in two types.

2.3.2 Homogeneous Acid Catalyst

The transesterification is often catalyzed by Brønsted acids, sulfonic and hydrochloric acids (Ebiurá *et al.*, 2005). These catalysts give very high yields in alkyl esters but acid-catalyst reaction requires higher temperature and pressure as well as higher amount of alcohol. Moreover, the reaction rate is very slow. It takes more than 3 hours. Freedman *et al.* (1984) studied the methanolysis of soybean oil by using H_2SO_4 as a catalyst. They discovered that in the presence of 1 mole % with an alcohol/oil molar ratio of 30:1 at $65^\circ C$, it took 50 hours to reach complete conversion. Furthermore, Schuchardt *et al.* (1998) studied the ethanolysis ($78^\circ C$) and butanolysis ($117^\circ C$) at the same quantities of catalyst and alcohol. They found that the reaction took 3 and 18 hours for ethanolysis and butanolysis, respectively.

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 2.4 (Schuchardt *et al.*, 1998), for a monoglyceride. However, it can be extended to di- and triglycerides. 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^+ .

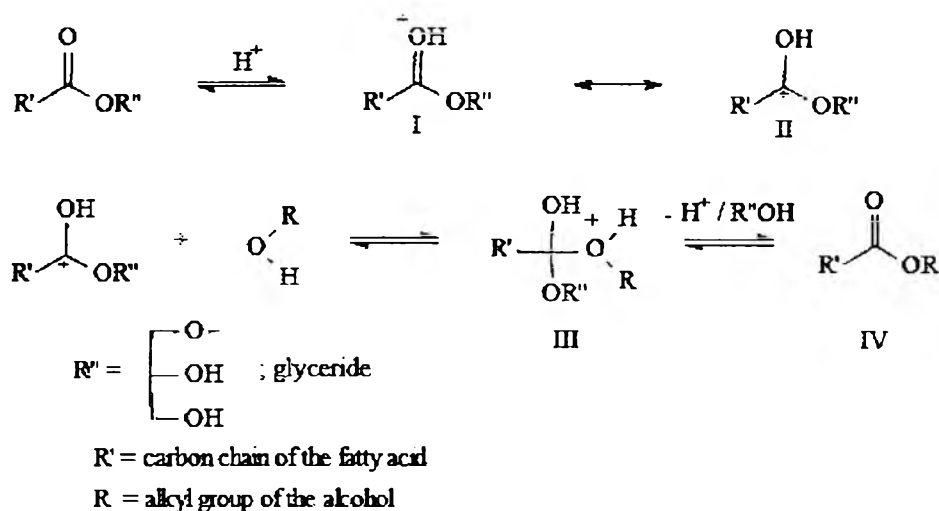


Figure 2.4 Mechanism of the acid-catalyzed transesterification of vegetable oils.

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.

Besides, acid catalyst have many drawbacks such as high free fatty acid content, very long reaction time, high molar ratio of methanol to oil and acid catalyst is more corrosive than base catalyst.

2.3.3 Homogeneous Base Catalyst

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Moreover, the alkaline catalysts are less corrosive than acidic compounds. So the industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Figure 2.5 (Schuchardt *et al.*, 1998). 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) from 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.

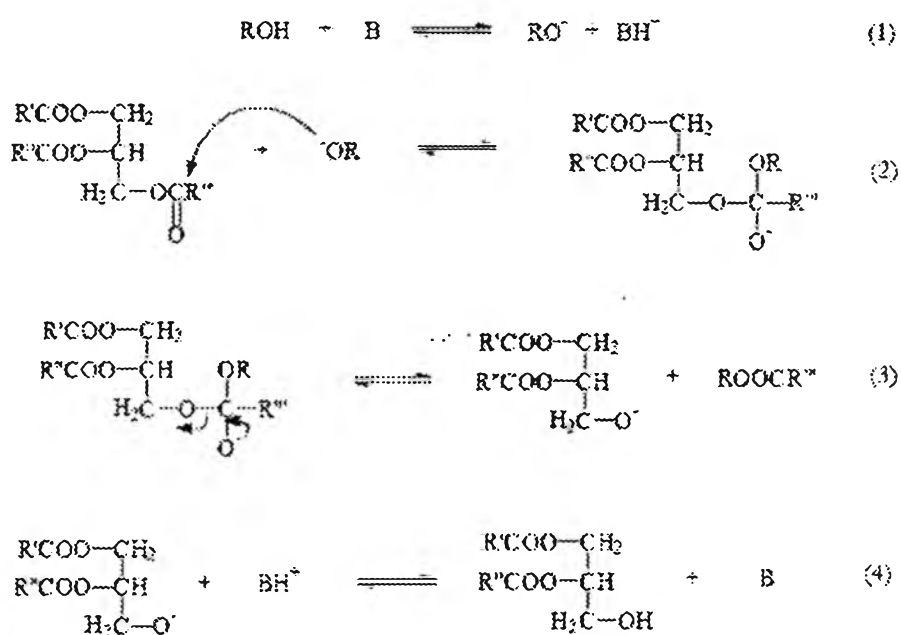


Figure 2.5 Mechanism of the base-catalyzed transesterification of vegetable oils.

Although the base-catalyzed are widely used, they have many limitations, such as high sensitivity to water and free fatty acids. Water can react with alcohol lead to produce soap formation as shown in Figure 2.6 (Schuchardt *et al.*, 1998). This undesirable saponification reaction reduce the ester yields and considerably difficult to recover of the glycerol.



Figure 2.6 Saponification of fatty acid alkyl ester.

Darnoko *et al.* (2000) studied the kinetic transesterification of palm oil using potassium hydroxide as a catalyst. They found that the optimum amount of KOH should be 1% based on the weight of oil at a 6:1 methanol to oil molar ratio. The conversion of glycerides to methyl esters fell out to be second order up to 30 minutes. Though the results were convincing, they reported the reaction rate constants based on the glyceride hydrolysis reaction, which is not the usual method applied in studying the kinetics.

In addition, Vicente *et al.* (2003) compared the activity of different basic catalysts (sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide) for methanolysis of sunflower oil. They found that biodiesel purity was near 100 %wt. for all catalysts. However, almost 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.

Moreover, Karmee *et al.* (2005) used KOH as a catalyst for transesterification of the non-edible oil of *Pongamia pinnata*. They found that the maximum conversion of 92% (oil to ester) was achieved using a 1:10 molar ratio of oil to methanol at 60°C. Furthermore, when tetrahydrofuran (THF) was used as a co-solvent, the conversion was increased to 95%.

However, in the conversional homogeneous manner, the removal of the base catalysts after reaction is the major problem, since aqueous quenching resulting in the formation of stable emulsion and saponification, making separation of methyl ester difficult and a large amount of wastewater was produced to separate and clean the catalyst and product.

2.3.4 Heterogeneous Catalyst

In the present day heterogeneous catalyst is widely used as a catalyst for transesterification because it is easily separated the catalyst from the products, leading to high yield of biodiesel and no waste from washing step. Peterson *et al.* (1984) was the first group to discover that CaO.MgO catalyst had activity comparable to sodium methoxide catalyzed transesterification with 95% methyl ester yield. However, this catalyst produces substantial amount of soap product thereby rendering the effectiveness of this heterogeneous catalyst.

Xie *et al.* (2006) investigated the calcined Mg-Al hydrotalcites as a solid base catalyst for methanolysis of soybean oil. They found that at 15:1 molar ratio of methanol to oil soybean, 9 hours and 7.5% amount of catalyst, soybean oil can be converted to biodiesel in 67 % conversion. Moreover, in the same year they tried to change the type of metal that loaded on alumina support. They found that when they loaded KNO₃ on alumina support, the conversion reached 87%. The maximum conversion was obtained when the molar ratio was very close to 15:1, 35% KNO₃ loaded on alumina support, 6.5% amount of catalyst in 7 hours.

Furthermore, Ebiura *et al.* (2005) used K₂CO₃, KF, LiNO₃ and NaOH loaded on the alumina support. They found that K₂CO₃ loaded alumina catalyst gave the highest yield of 94%. They used a small amount of catalyst (0.3g), the short reaction (1 hour) and high molar ratio of methanol to oil (25:1).

On the other hand, Xie *et al.* (2006) varied the type of catalyst (KF, KCl, KBr, KI, K₂CO₃, KNO₃, KOH on Al₂O₃). They indicated that KI was the best catalyst, they obtained 96% conversion of soybean oil. Besides, they varied the type of support ZrO₂, ZnO, NaX zeolite, KL zeolite and Al₂O₃ support. They discovered that the basic strength of the support affect to the conversion, the more basic strength the more conversion. Moreover, they suggested that the activity of catalyst was strongly affected not only by the strength of basic site but also by the amount of basis sites.

Di Serio *et al.* (2006) confirmed that not only the basic strength affect to the conversion of methyl ester but also the morphology of catalyst. In this work they prepared the catalyst by varying calcined temperature and ratio of Al/(Mg+Al).

They discovered that MgO (type3) gave 93 % yield of FAME because of high basicity. But calcined hydritalcite (CHT), which have low basicity, gave high yield of FAME. They suggested that because CHT had large pore radius (20 Angstrom). The presence of large pore size in CHT favored the reaction by rendering the active sites more accessible to bulky triglyceride molecules.

Suppes *et al.* (2003) used porous material which is zeolite. In this work they studied the ion exchange with electropositive metal. The NaX zeolite was exchanged to potassium and cesium and was carried out at a 1:6 molar ratio of soybean oil to methanol, 150 °C and 24 hours. of reaction time. They found that cesium gave the conversion of methyl ester (24.2 wt.%) lower than potassium (31.5 wt.%) because the large size of cesium cation limited the exchanged capacity lower than smaller potassium which affect to the basicity. Moreover, they impregnated 1M of sodium azide on the porous material. They found that the conversion of methyl ester (79.1 wt.%) increase more than the parent zeolite (23.9 wt.%) and when they increase concentration of sodium azide from 3 and 4 M. The conversion of methyl ester was 94 and 96.5 wt.%, respectively.

In recent study, Yang *et al.* (2007) used alkalined earth metal over zinc oxide. They found that when they used THF as co-solvent, the maximum conversion was 94.7% at 5 wt.% of amount catalyst, 12:1 of molar ratio of methanol to oil in 5 hours.

2.3.5 Transesterification Using Enzymatic Catalyst

Biocatalytic routes permit one to carry out the transesterification of a wide variety of oil feedstock in the presence of acidic impurities, such as free fatty acids. The enzymatic processes are very promising because of their high selectivity and mild operative conditions. Lipase is one type of enzymes that can be used in transesterification process.

Fermandes *et al.* (2007) obtained 94% of conversion of biodiesel by using the Burkholderia capacis as a catalyst. Although they obtained high conversion, the reaction time was very long (18 hours) and it required high molar ratio of alcohol (5:1).

On the other hand, Hernandez *et al.* (2006) studied immobilized lipase preparation for synthesis of biodiesel by using Novozym 435 and LipozymenTL IM as a enzyme catalyst. They found that Lipozyme TL IM produced a rapid reaction rate

(7 hours), required minimum volume of alcohol (ratio 2:1) but the conversion to the FAME was not greater than 84%. While Watanabe *et al.* (2006) found that *Candida Antarctica* lipase can convert acid oil by-product in vegetable oil refinery to biodiesel fuel in 91.1%. But *Candida antractica* lipase was unstable and was not durable for repeated use.

Moreover, Salis *et al.* (2006) obtained the high conversion, short reaction and small volume of alcohol by using *Candida antarctica* B, *Rizhomucor miehei*, and *Pseudomonas cepacia* lipaser in transesterification from pure triolein. They found that *Pseudomonas cepacia* lipase is the most active enzyme, reaching 100 % of conversion after 6 hours and the molar ratio of butanol:triolein of 3:1.

The advantage of using biocatalyst as a catalyst is separation and purification of the biodiesel fuels because of the absence of soap by-products. Biocatalysts are more expensive than traditional chemical catalysts; however, their recycle is compulsory to overcome economical costs.

2.3.6 Transesterification Using Supercritical Method

Supercritical transesterification is the process that uses high temperatures and high pressures to convert oil to biodiesel. Supercritical transesterification has 2 major steps for converting the vegetable oil to biodiesel which are transesterification of triglyceride and esterification of free fatty acid. These two reactions occur in the same time. Supercritical technique is the process to solve the problem such as recovery of the unreacted reactants, purification of the esters, separation of glycerol and the separation of the catalyst from the reactants and products. The advantages in supercritical are short reaction time, high yield of biodiesel, easy to separate the biodiesel form glycerol and no effect with water and free fatty acid in starting vegetable oil.

Kusdiana *et.al.* (2001) studied the condition of biodiesel production from rapeseed oil by supercritical methanol. The condition of conversion of rapeseed

oil was 300 °C, 30 MPa in 240 second with molar ratio 42:1 and the maximum was achieved the conversion is 98.5%.

Besides, Wang *et.al.* (2007) added liquid organic amine, Ethylenediamine (EDA), Diethylamine (DEA) or Triethylamine (TEA), to speed up the production of methyl ester from crude rapeseed oil in supercritical method. They found that the order of catalytic activity was EDA > DEA > TEA, respectively, in 10 minutes. They used the molar ratio of methanol to oil is 24:1 at 290 °C. But the yield of methyl ester could reach 89.5% which is much lower than Kusdiana *et.al.* work.

Moreover, Rathore and Madras (2007) tried to combine enzymatic system and supercritical alcohol. They used Novdzym 435 lipase as enzyme, and found that edible and non edible oil can covert biodiesel more than 80% within 10 minutes. When they compared between combine system with enzymatic system and supercritical system, they found that at the same conversion, supercritical system can be achieved in 40 minutes. For the enzymatic system, obtain the conversion of 60-70% can be obtained within 8 hours. Furthermore, they suggested that in combined system, high temperature should be avoided since the enzyme can be died.

Although supercritical process has short reaction time and has no soap formation, it has many drawbacks such as high operating cost because the process is operated in high temperatures and pressures.

2.4 Alcohol in Transesterification

An alcohol is a molecule in which any carbon atoms have the maximum number of hydrogen atoms attached, except for one atom which has an OH group attached. The simplest alcohol, and the one used often in biodiesel production, is methanol. Methanol consists of only one carbon atom, with three hydrogen atom attached, and one oxygen attached. The oxygen atom also has a hydrogen atom attached. Thus, methanol is often written as CH₃OH. Use methanol in transesterification can improve the property of biodiesel such as viscosity. Moreover methanol has low price. The next simplest alcohol is ethanol, which has one more carbon atom, with two hydrogen atom attached, in between the CH₃ group and the OH group. Ethanol is written as either CH₃CH₂OH or C₂H₅OH. The former method

is often used to give more of a description of structure. The use of higher alcohol can improve the property of biodiesel such as cold point and pour point because it produces longer and branch of ester but it provides higher energy input and cannot be synthesized with alkaline catalyst.