CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is a renewable fuel that derived from either the transesterification of triglycerides (TGs) or the esterification of free fatty acids (FFAs) with alcohols. Biodiesel is liquid fuel often referred to as B100 for its pure, unblended form. It is used in fuel compression-ignition engines, the diesel engines, because its flow and combustion properties are similar to petroleum diesel. It can be used alone, or mixed with petroleum diesel. This fuel is nontoxic and biodegradable, as well as cleaner and safer to handle, and has higher flash point and higher oxygen content than petroleum diesel. As clean combustion of biodiesel, there will be a major reduction of emission of all types of pollutants adding to global warming (Berkeley Biodiesel, 2014). The typical physical properties of biodiesel are shown in Table 2.1 (Alternative Fuel Data Center, U.S. Department of Energy, 2014).

It refers to nonpetroleum-based fuel which comprises of long-chain alkyl esters, C12-C22 (ASTM D675), which composes of a long chain of carbon atoms attached by hydrogen atoms and an ester functional group at one end, an example of biodiesel structure is shown in Figure 2.1.

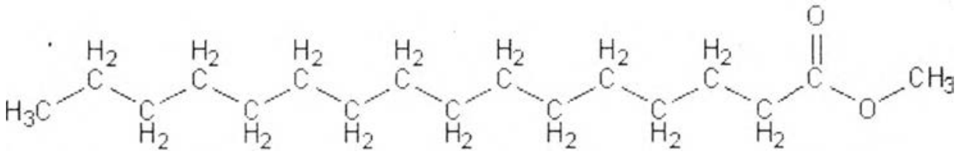


Figure 2.1 Molecular structure of biodiesel (Methyl Palmitic).

Table 2.1 Typical physical properties of biodiesel

Biodiesel's Properties	
Specific gravity	0.88
Kinematic viscosity at 40 °C	4.0 to 6.0
Cetane number	48 to 65
Higher heating value, Btu/gal	127,042
Lower heating value, Btu/gal	118,170
Density, lb/gal at 15.5 °C	7.3
Carbon, wt %	77
Hydrogen, wt %	12
Oxygen, by dif. wt %	11
Boiling point, °C	315-350
Flash point, °C	100-170
Sulfur, wt%	0.0 to 0.0024
Cloud point, °C	-3 to 15
Pour point, °C	-5 to 10

It is typically made through a chemical process, which converts oils and fats of natural origin into fatty acid methyl esters (FAMEs) by reacting with an alcohol chemically, chemical composition of common FAMEs are shown in Table 2.2 (Lam *et al.*, 2010). Its quality is governed by ASTM D 6751 quality parameters (Pacific Biodiesel, 2014). A brief comparison of American Society for Testing and Materials (ASTM) standard for diesel and biodiesel is shown in Table 2.3.

Table 2.2 Chemical compositions of common FAMEs

FAME	Formula	Common acronym	Molecular weight
Methy palmitic	$C_{17}H_{34}O_2$	C16:0	270.46
Methy stearate	$C_{19}H_{38}O_2$	C18:0	298.51
Methy oleate	$C_{19}H_{36}O_2$	C18:1	296.50
Methy linoleate	$C_{19}H_{34}O_2$	C18:2	294.48
Methy linolenate	$C_{19}H_{24}O_2$	C18:3	292.46

Today, biodiesel is a globally produced and traded fuel. It is commercial use in USA and many other countries. Rising fossil fuel prices make biodiesel investment more attractive (Kotrba, R., Biodiesel Magazine, 2011). Lam *et al.* (2010) reported that the biodiesel industries are worldwide growing very fast. Several countries are actively supporting the production of biodiesel from an agriculture sector. Continued feedstock research intends to find the feedstock that can be used on a commercial level. The driving forces for development are economic, energy and environmental security, improving trade balances and expansion of agriculture sector (Zhou and Thomson, 2009). Currently, the major concern of biodiesel production is economic feasibility. The biodiesel production will not be favored if the production cost is higher than diesel-fossil fuel (Demirbas and Balat, 2006). In order to ensure economic viability in biodiesel production, biodiesel manufacturer are focusing their attention on using low-cost feedstock such as waste cooking oil, with the intent to increase supply and lower price. The advantages and disadvantages of biodiesel compared to diesel are shown in Table 2.4 (Alternative Fuel Data Center, U.S. Department of Energy, 2014).

Table 2.3 Values for ASTM standard of maximum allowed quantities in diesel and biodiesel

Property	**Diesel**	**Biodiesel**
Standard	ASTM D975	ASTM D6751
Composition	HC(C10-C21)	FAME(C12-C22)
Kinetic viscosity (mm^2/s) at 40°C	1.9-4.1	1.9-6.0
Specific gravity (g/mL)	0.85	0.88
Flash point (°C)	60-80	100-170
Cloud point (°C)	-15to5	-3to12
Pour point (°C)	-35 to -15	-15 to 16
Water (vol %)	0.05	0.05
Carbon (wt %)	87	77
Hydrogen (wt %)	13	12
Oxygen (wt %)	0	11
Sulfur (wt %)	0.05	0.05
Cetane number HFRR* (μm)	40-55	48-60
HFRR (μm)	685	314
BOCLE** scuff (g)	3600	>7000

*High Frequency Reciprocating Test Rig, **Ball-on-Cylinder Lubricity Evaluator

Table 2.4 Advantages and disadvantages of biodiesel compared to diesel

Advantage	Disadvantage
• Domestically produced from non-petroleum, renewable resources • Can be used in most diesel engines, especially newer ones • Less air pollutants (other than nitrogen oxides) • Less greenhouse gas emissions (e.g., B20 reduces CO_2 by 15%) • Biodegradable • Non-toxic • Safer to handle	• Use of blends above B5 not yet approved by many auto makers • Lower fuel economy and power (10% lower for B100, 2% for B20) • Currently more expensive • B100 generally not suitable for use in low temperatures • Concerns about B100's impact on engine durability • Slight increase in nitrogen oxide emissions possible in some circumstances

2.2 Diesel and Diesel Engine

Diesel engines can burn biodiesel fuel with no modifications (except for replacing some rubber tubing that may soften with biodiesel). This is possible because biodiesel is chemically very similar to regular diesel, as shown in Figure 2.2. It can be noticed that regular diesel also has the long chain of carbon and hydrogen atoms, but doesn't have the ester group.

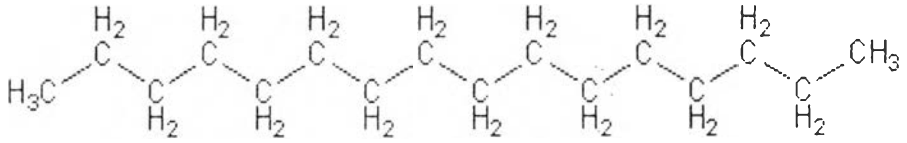


Figure 2.2 Molecular structure of diesel.

2.3 Lipid Feedstock for Biodiesel Production

Lotero *et al.*, (2005) inferred that commonly, biodiesel is prepared from TG sources such as vegetable oils, animal fats, and waste greases such as yellow and brown greases from used cooking oil. Oils and fats belong to an ample family of chemicals called lipids. In general, lipids are found in animals and plants. Typically, fats come from an animal sources and oils from a plant sources. Fats and oils are primarily formed of TG molecules. A TG molecule is basically a triester of glycerol (a triol) and three fatty acids (long alkyl chain carboxylic acids).

There are characteristics of biodiesel that strongly depend on feedstock composition, even though biodiesel can be derived from animal, the biodiesel and its blends in cold climates have significant problems of high pour points, cloud points, and cold filter plugging points, because of more saturated character of the fatty acid compositions of animal fats, as shown in Table 2.5 (Lotero *et al.*, 2005). In contrast, biodiesel prepared from vegetable oils mainly contains esters of oleic and linoleic acids, which have unsaturated alkyl chains. In general, the unsaturation degree of the alkyl chains correlates well with the cold flow performance of biodiesel. This means that the more double bonds on the alkyl chain, the lower the melting point of the esters obtained. Therefore, the colder it doesn't exhibit undesirable high viscosity or solidifying. So that is why animal fats are less attractive than vegetable oils for biodiesel productions.

2.3.1 Vegetable Oil

Actually, the first diesel engine runs on vegetable oil or TG, a sample molecule of which is shown in Figure 2.3. It has the long rows of carbon and hydrogen atoms, but is about three times larger than normal diesel molecules. It also has ester functional groups, like biodiesel. Examples of the vegetable oils are soybean, cottonseed, groundnut, sunflower, rapeseed, sesame, corn, olive, palm, palm kernel, coconut, linseed, and castor.

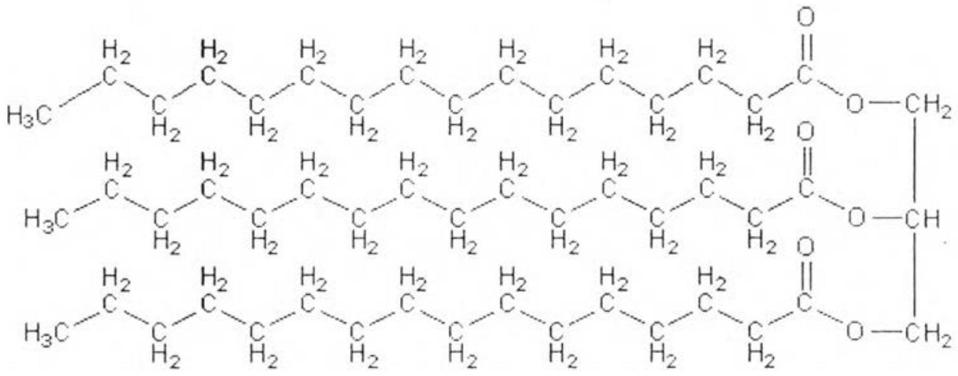


Figure 2.3 Molecular structure of triglyceride.

Larger sizes of vegetable oils mean that in cold weather it gels, making it hard to use in an engine. Converting it into biodiesel makes it a smaller molecule, closer to the size of regular diesel, so that it has to get colder than vegetable oil before it starts to gel.

2.3.2 Waste Cooking Oil

Due to high cost of refined vegetable oils, waste cooking oil has become an alternative feedstock to produce biodiesel. Generation of waste cooking oil of many countries in the world is huge and will result to environmental contamination if no proper disposal method is implemented. Table 2.5 shows the estimate waste cooking oils produced in selected countries (Gui *et al.*, 2008).

Table 2.5 Quantity of waste cooking oil produced in selected countries

Country	Quantity (million ton/year)
China	4.5
European	0.7–1.0
United States	10.0
Japan	0.45–0.57
Malaysia	0.5
Canada	0.12
Taiwan	0.07

Most of the vegetable oils is used for deep-flying processes, which could cause disposal problem. This scenario does not only contribute to pollution problems but is also harmful to human being. During frying, various physical and chemical properties in oil are changed. Some physical change in oil, depend on types of oil and oil compositions, are (i) an increase in viscosity, (ii) an increase in specific heat, (iii) a change in surface tension, and (iv) a change in color (Cvengros and Cvengrosova, 2004). The oil are also subjected to three types of reactions, (i) mainly thermolytic, (ii) oxidative and (iii) hydrolytic (Mittelbach and Enzelsberger, 1999; Nawar, 1984). These three reactions will continuously cause the formation of many undesired and harmful compounds if the oil is used repeatedly. The toxicological effects of these compounds upon human consumption are still not completely known. However, if waste cooking oil is to be made feedstock for biodiesel production, the amount of polar compound in the waste cooking oil, especially free fatty acids (FFAs), must be taken into consideration as it will greatly affect the transesterification reaction.

2.3.3 Free Fatty Acid

Free fatty acids are the free molecules of fatty acids that derived fromsome chemical processes of TGs and then contaminate in them. The fatty acid is a carboxylic acid with a long aliphatic tail (chain), which is either saturated or unsaturated. Most naturally occurring fatty acids have a chain of an even number of carbon atoms, from 4 to 28. Refined oil usually contains less than 0.5 wt % FFAs whereas for waste cooking oil, FFAs contents range between 0.5 and 15 wt % (Knothe*et al.*, 2004).

Table 2.6 Fatty acid in TGs composition of some common vegetable oil, animal fat, and grease (Lotero *et al.*, 2005)

Vegetable Oil/Animal Fat/Grease	**Fatty Acid Composition (wt %)**							
	myristic 14:00*	palmitic 16:00	palmitoleic 16:01	stearic 18:00	oleic 18:01	linoleic 18:02	inolenic 18:03	Sat. (%)
Rapeseed Oil (Aranda *et al.*, 2004)	-	3.5	-	0.9	64.4	22.3	8.2	4.4
Virgin Olive Oil (Engel*et al.*, 2001)	-	9.2	0.8	3.4	80.4	4.5	0.6	12.6
Sunflower Oil (Graboski*et al.*, 1998)	-	6.0	-	4.2	18.7	69.3	-	10.2
Soybean Oil (Canakci *et al.*, 1999)	0.1	10.6	-	4.8	22.5	52.3	8.2	15.5
Palm Oil (Aranda *et al.*, 2004)	1.2	47.9	-	4.2	37	9.1	0.3	53.3
Poultry Fat (Paleari *et al.*, 2004)	-	22.2	8.4	5.1	42.3	19.3	1.0	35.7
Lard (Zheng *et al.*,1996)	1.7	17.3	1.9	15.6	42.5	9.2	0.4	34.6
Edible Tallow (Zheng *et al.*,1996)	4.8	28.4	-	14.8	44.6	2.7	-	52.0
Yellow Grease (Canakci *et al.*, 1999)	2.4	23.2	3.8	13.0	44.3	7.0	0.7	38.6
Brown Grease (Canakci *et al.*, 1999)	1.7	22.8	3.1	12.5	42.4	12.1	0.8	37.0

*14:00: the alkyl chain contains 14 carbons and zero double bond

2.3.4 Oleic Acid

Oleic Acid (also called *cis*-9-octadecenoic acid) is an example of a fatty acid found in animal and vegetable oils. It is a *mono-unsaturated* fatty acid, due to the presence of a single double bond. The physical properties of fatty acids like oleic acid are determined by the number, geometry, and position of the double bonds in the chain, along with the degree of unsaturation (*i.e.* number of double bonds). In naturally occurring fatty acids, such as those found in vegetable oils, the double bonds are all in *cis* configuration, making the molecules bent or curved. This also makes the molecules much less flexible than those of fully saturated fatty acids (*e.g.* stearic acid). Their bent shape also hinders crystallization, and explains why these acids are oils at room temperature. (Saturated acids in *trans* configuration have straight chains and can pack easily into a crystal lattice, and so are solid at room temperature, *e.g.* butter).

The oleic acid is odorless and colorless oil, although commercial samples may be yellowish. In chemical terms, oleic acid is classified as a monounsaturated omega-9 fatty acid, abbreviated with a lipid number of 18:1 cis-9. It has the formula $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ (Thomas, 2000). The term "oleic" means related to, or derived from, oil or olive, the oil that is predominantly composed of oleic acid. Its molecular structure is shown in Figure 2.4 and its physical and chemical properties are shown in Table 2.7 (Oleic acid MSDS, Science Lab, 2012).

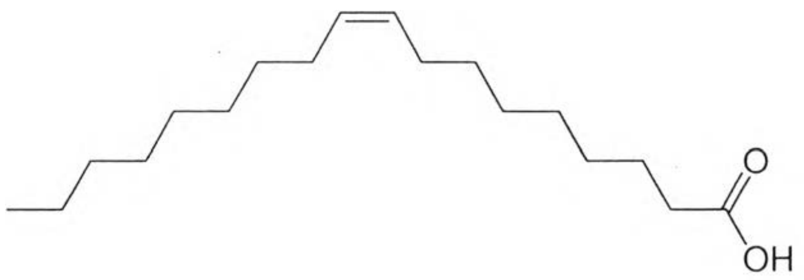


Figure 2.4 Molecular structure of oleic acid.

Table 2.7 Physical and chemical properties of oleic acid

Property of Oleic Acid	
Chemical Formula	$C_{18}H_{34}O_2$
Molecular Weight (g/mole)	282.47
Density (g/ml)	0.895
Boiling Point (°C)	286.11 (547°F)
Melting Point (°C)	16.3 (61.3°F)
Flash Point (°C)	189
Solubility	Soluble in water

Methyl oleate (also called methyl *cis*-9-octadecanoate) will be derived when oleic acid is used in biodiesel production. Its molecular structure and property are shown in Figure 2.5 and Table 2.8, respectively. (Methyl oleate, chemBlink, 2014)

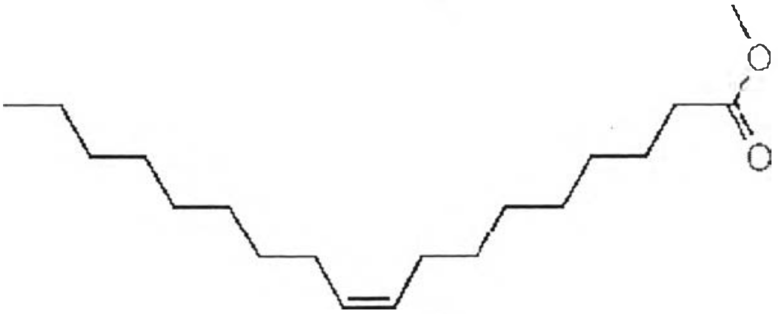


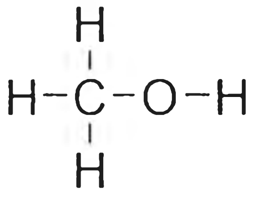
Figure 2.5 Molecular structure of methyl oleate.

Table 2.8 Physical and chemical properties of methyl oleate

Property of Methyl Oleate	
Chemical Formula	$C_{19}H_{36}O_2$
Molecular Weight (g/mole)	296.49
Density (g/ml)	0.876
Boiling Point (°C)	407.88-410.87 at 760 mmHg
Melting Point (°C)	-20
Flash Point (°C)	180
Refractive Index	1.451-1.458

2.4 Short Chain Alcohol for Biodiesel Production

Methyl alcohol (also called methanol) is the most widely used alcohol for biodiesel production. Its molecular structure and properties are shown in Figure 2.6 and Table 2.9, respectively. (Methyl alcohol MSDS, Science Lab, 2013)



$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & O & - & H \\ & & | & & & & \\ & & H & & & & \end{array}$$

Figure 2.6 Molecular structure of methyl alcohol.

Table 2.9 Physical and chemical properties of methyl alcohol

Property of Methyl Alcohol	
Chemical Formula	CH_3OH
Molecular Weight (g/mole)	32.04
Density (g/ml)	0.792
Boiling Point (°C)	64.5
Melting Point (°C)	-97.8
Flash Point (°C)	12
Solubility	Soluble in water

2.5 Chemical Conversion of Biodiesel Production

Vegetable oil belongs to a category of compounds called *esters* like biodiesel. Therefore, converting vegetable oil into biodiesel is called a transesterification reaction, as shown in Figure 2.7. This reaction requires short chain alcohol and catalyst. Glyceral, Mono-, and di-glyceride can be obtained from TGs by substituting three, two, and one fatty acid moieties with hydroxyl group.

An effective producing of biodiesel requires several other steps besides the transesterification reaction. The first is to remove any traces of water in the vegetable oil. unless the water can react with the vegetable oil in the reaction and produce free fatty acid. as shown in Figure 2.8. Furthermore, basic catalyst, such as NaOH or KOH. can react with TGs and produce soap and water. and this water can react with FAMEs backward to the reactant of TGs and short chain alcohol. as shown in Figure 2.8(a) and 2.8(b). respectively. These reactions affect to decrease the production yield. and when soap formation occurs. then later it interferes the steps after the transestcrication reaction that are needed to separate the biodiesel from left over methanol. the catalyst. and the glycerol byproduct (Department of Chemistry, Goshen College, 2014).

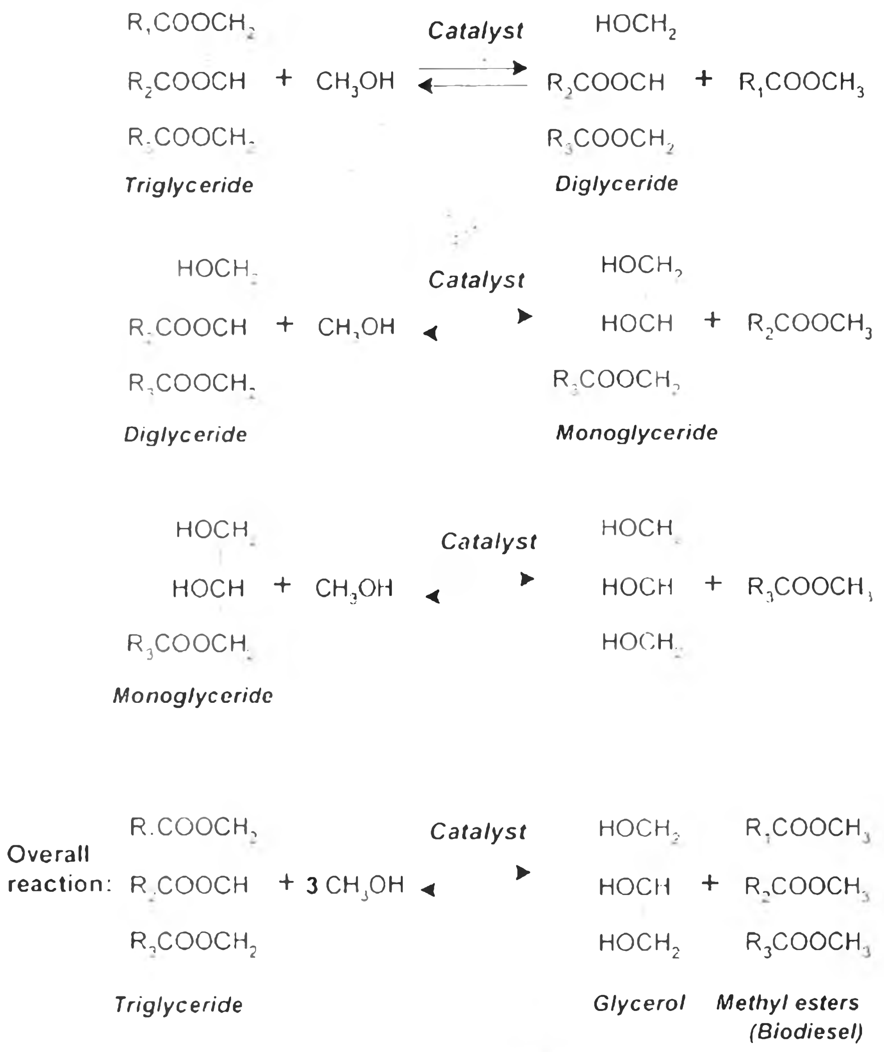


Figure 2.7 Transesterification reaction of triglyceride (Lotero *et al*, 2005).

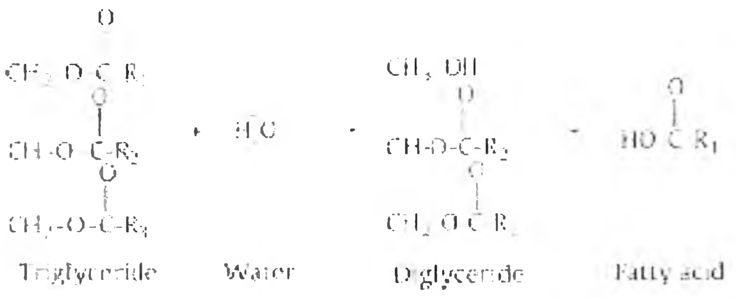


Figure 2.8 Production reaction of fatty acid from triglyceride and water (Lam *et al*, 2010).

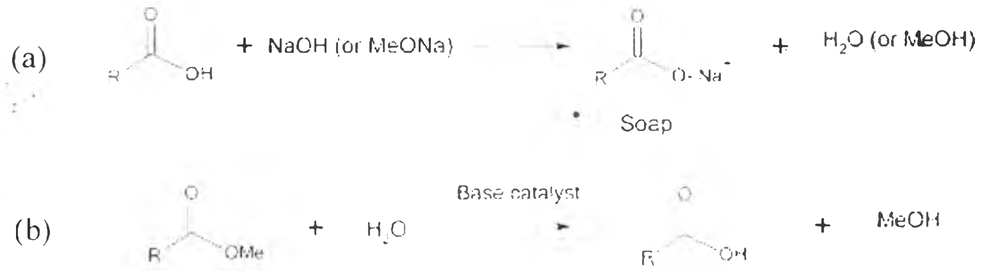


Figure 2.9 (a) Saponification reaction of free fatty acid and (b) Hydrolysis reaction of methyl ester. (Lotero *et al*, 2005)

However, fatty acid methyl ester can be also produced from free fatty acid with the short chain alcohol with the presence of an acid catalyst by esterification reaction, as shown in Figure 2.10.

$$\text{R-COOH} \quad + \quad \text{MeOH} \quad \longrightarrow \quad \text{RCOOMe} \quad + \quad H_2O$$

Free Fatty Acid	Short Chain Alcohol (Methanol)	Fatty Acid Methyl Ester	Water

Figure 2.10 Esterification reaction of free fatty acid.

2.6 Catalyst for Biodiesel Productions

Transesterification and esterification reaction needs a catalyst to increase the rate of reaction and yield of FAMEs. Sodium hydroxide and potassium hydroxide are used most frequently as basic catalysts. Sulfuric acid and hydrochloric acid are usually used as acid catalysts. Phases of the catalysts are divided into homogeneous and heterogeneous catalyst. Reaction conditions and post-separation steps are determined by the nature of catalyst used.

Homogeneous basic catalysts are commonly used in the industries due to its ability to catalyze reaction at low reaction temperature and pressure (Lotero *et al.*, 2005). High conversions can be achieved in a minimal time with moderate conditions. They are widely available and economical. Tomasevic and Siler-Marinkovic (2003) 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. However, the base-catalyzed are commonly used, they have many limit conditions such as it is very sensitive to water and free fatty acids, as explained in the previous section. Undesirable reactions reduces the biodiesel yields and considerably difficult to recover of the glycerol. The problems can proved by using acid catalyst instead. 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 for a monoglyceride, as shown in Figure 2.11. However, it can be extended to di- and tri-glycerides. The protonation of the carbonyl group of the ester leads to the carbocation, after nucleophilic attack of alcohol, produces the tetrahedral intermediate, which eliminates glycerol to form the new ester, and to regenerate the catalyst H$^+$.

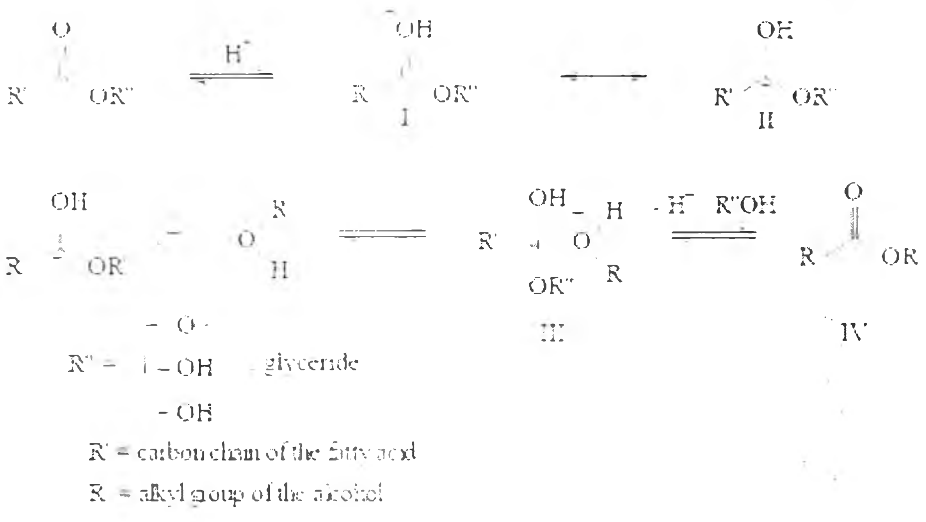


Figure 2.11 Mechanism of acid-catalyzed transesterification of monoglyceride.

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. However, in a study of acid-catalyzed transesterification of waste cooking oil using H_2SO_4, Wang *et al.* (2006) reported that the yield of FAMEs 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). Because of that slow reaction rate, it requires high reaction temperature and high molar ratio of alcohol to oil, separation of the catalyst from the mixture, and it cause serious environmental and corrosion related problem, this system is not a popular choice for commercial applications (Jacobson *et al.*, 2008, Wang *et al.*, 2006).

Heterogeneous acid catalyst is an interesting alternative and widely studied today. The first advantage is easier to separate the catalyst from the process than the homogeneous catalyst; however, utilized condition is needed to be optimized in the biodiesel production. Fu *et al.* (2009) studied transesterification of waste cooking oil using SO_4^{2-}/ZrO_2 prepared by an impregnation method. A yield of biodiesel of 93.6% was achieved under the reaction conditions: 3 wt% catalyst, 1:9 molar ratio of oil to methanol and temperature of 120°C. Muthu *et al.* (2010) synthesized sulfated zirconia (SZ) by in a solvent free method which was used to prepare Neem Methyl Ester (Biodiesel) by a two-step process of esterification and transesterification from Neem oil. Acid catalyst was used for the esterification and KOH catalyst for the transesterification reaction. Optimal Free Fatty Acid (FFA) conversion was achieved using 1 wt% SZ as an acid catalyst with a methanol-to-oil molar ratio of 9:1, temperature of 65 °C and reaction time of 2 h. The acid value was reduced to 94% of the raw oil (24.76 mg KOH/g), which confirmed the conversion. Consequently, this pretreatment reduces the overall complexity of the process and a conversion efficiency of 95% was reported when pretreated oil reacts with methanol in the presence of KOH. Furthermore, Jitputti *et al.* (2006) reported that SO_4^{2-}/ZrO_2 could produce the 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 ZrO_2 was used as a catalyst instead of SO_4^{2-}/ZrO_2, only 64.5% (palm kernel oil) and 49.3% (crude coconut oil) of methyl ester yield were reported. Corro *et al.* (2010) carried out transesterification from waste frying oil (WFO) in two steps catalyzed process. The free fatty acids (FFA) were first esterified with methanol catalyzed by SiO_2 pretreated with HF. After 10 esterification runs, the catalyst activity remained unchanged. During the second step, the triglycerides WFO were transesterified with methanol catalyzed by NaOH. Gas chromatography and mass spectrometry analysis revealed that the process proposed in this investigation led to a biodiesel containing 96% methyl esters. The process may thus be regarded as heteroageneous–homogeneous catalytic process. Mittelbach *et al.* (1996) compared the activities of a series of layered aluminosilicates loaded with sulfuric acid for the transesterification of rapeseed oil. They used an initial oil/methanol molar ratio of 1:30 and 5 wt% catalyst. The solid catalysts showed a wide range of activities dependingon the reaction conditions. The most active catalysts were those activated by sulfuric acid impregnation. The 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. It is also likely that some degree of homogeneous catalysis was taking place due to sulfuric acid leaching.

Activating reagent is an important factor that affects to an efficiency of the solid acid catalyst. Even though H_2SO_4 is the common activating reagent, other acids are also studied. Aldana-Pérez *et al.* (2012) studied sulfonation method for preparation of solid acid catalyst. Acids solids sulfonated carbons Starbons-300 were prepared by using a mixture of $ClSO_3H/H_2SO_4$ and H_2SO_4 (98%) as sulfonating agents. They studied the sulfonation of Starbons-300-H_2SO_4-15, Starbons-300-2-$ClSO_3H$-H_2SO_4-5 and Starbons-300-3-$ClSO_3H$-H_2SO_4-5 (For identification the solids were labeled as Starbons-300-V–S–T, where V indicates volume of the sulfonated agent (v/v), S is the sulfonated agent and T is the time reaction. The sulfonation affects textural properties and acidity of the catalyst. The sulfonated Starbons-300 showed very high activity for the esterification of free fatty acids with ethanol. Conversions up to

60% of oleic acid and selectivity to the ester of 100% were reached after 3 h of reaction at 80 °C. The results showed that the sulfonated carbon Starbons-300 catalysts are promising acids catalysts to be used in the esterification of free fatty acids with ethanol. It is shown that the sulfonation by aromatic electrophilic substitution of Starbons-300 produced solid acids with important acid strength. The sulfonate agent and reaction conditions used for the sulfonation are crucial to develop acid strength in the sufonated carbons. The $ClSO_3H/H_2SO_4$ mixture is a suitable agent for the sulfonation of Starbons-300. The sulfonated carbons Starbons-300 catalysts showed a high selectivity (100%) to the esterification of free fatty acids. Starbons-300-2-$ClSO_3H$-H_2SO_4-5 was the catalyst with the highest turnover frequency. However, the active sites bounded to aromatic ring polycyclics are leaching, resulting in a decrease of 30% in the used catalyst. The applications of sulfonated carbons Starbons-300 can also be extended to other acid-catalyzed reactions. Zhang *et al.* (2010) studied the preparation of solid acid catalyst. They simply prepared a novel carbon-based solid-acid catalyst by the thermal treatment of p-toluenesulfonic acid (TsOH) with D-glucose at 180 °C in a sealed autoclave. In this method, TsOH was used in the synthesis instead of concentrated/fuming sulfur acid and it makes the preparation safer by avoiding usage of dangerous chemicals. The prepared catalyst exhibits much higher acidity and then catalytic activity than sulfonated active carbon in the reaction of esterification of succinic acid with ethanol. The cycle usage test indicated that the catalyst prepared by this method was relative stable. It would be noted that the method described here can be further extended to one-step synthesis of various functionalized carbon materials from saccharide and aromatic compounds with target functional groups, such as glucose/salicylic acid system. Furthermore, mixture of 0.8 g of TsOH, 0.36 g of p-formaldehyde, and 0.8 ml of H_2SO_4 was used as activating reagent by Shokrolahi *et al.* (2012). They prepared the solid acid catalyst from SBA-15 and MCM-48 and reported that the novel solid acid catalysts had higher pore diameter and specific area, respectively. They concluded that the starting solid and acid activating reagent played a crucial role in surface area and pore structure of the solid acid catalyst. They are many important parameters that affected to an efficiency of catalytic activity in esterification reaction of fatty acid. The highest conversion of biodiesel production from oleic acid and methanol (62.4%) was derived from the reaction with the presence of the catalyst that had specific surface area, pore volume, and pore diameter of 920 m^2/g, 0.8 cm^3/g, and 2.6 nm, respectively, with 4.95 mmol/g of acid density.

2.7 Solid Acid Catalyst from Lignocellulosic Biomass

From many research works of solid acid catalysts, researchers tried to load sulfonated group ($-SO_3H$) into various type of solid materials. Many carbon-based materials were studied to produce the solid acid catalysts, such as naphthalene, glucose, starch, cellulose, sucrose, vegetable oil asphalt, etc., since the advantages of materials source obtaining from recycling waste, economical and available materials, etc. 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. A 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 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. 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 taking 5 h. In addition to the biodiesel production, a lignin derived solid acid catalyst may find other applications as a heterogeneous green catalyst.

Lignin, waste from bio-butanol production process (Nantapipat, 2012), that used corncobs as starting material, was an interesting alternative. It is an amorphous carbon-based structure likely to the previously studied carbon-based material. Generally, corncob contains 38–50 % cellulose, 23–32% % hemicelluloses, and 15–30 % lignin. Cellulose is a polysaccharide of glucose units that serve as the main structural component of the cob's cell walls, consisting of d-glucose molecules bound together by ß-1, 4-glycoside linkages. Hemicellulose is a less complex polysaccharide that can more easily be broken down to simpler monosaccharides, simple sugars. It is an amorphous and heterogeneous group of branched polysaccharides (copolymer of any of the monomers glucose, galactose, mannose, xylose, arabinose, and glucuronic acid); hemicellulose surrounds the cellulose fibers and is a linkage between cellulose and lignin. Lignin is a complex, non-carbohydrate, structural component, which binds to cellulose and stiffens plant cell walls. It is a highly complex three-dimensional polymer of different phenyl propane units bound together by ether and carbon–carbon bounds. Lignin is concentrated between the outer layers of the fibers, leading to structural rigidity and holding the fibers of polysaccharides together. In addition, small amounts of extraneous organic compounds are found in lignocellulosic materials, about 4 % (Zych, 2008 and Stöcker, 2008). Molecular structure of cellulose, hemicellulose and lignin are shown in Figures 2.12-2.14, respectively.

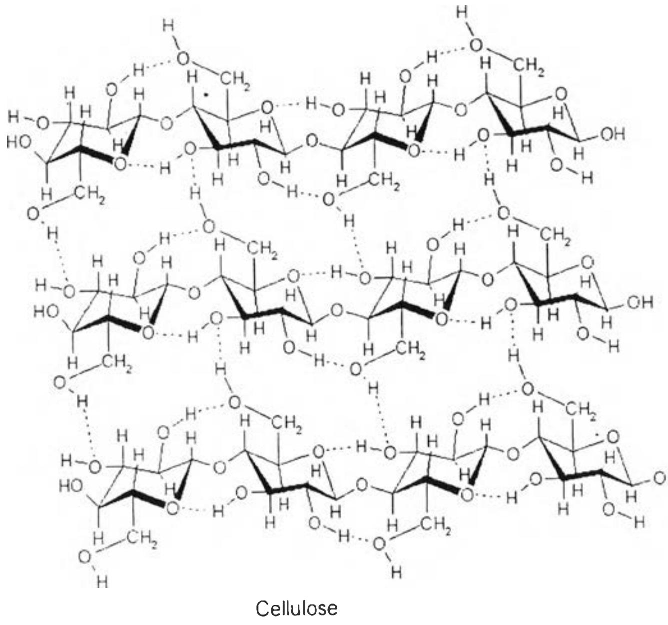


Figure 2.12 Molecular structure of cellulose.

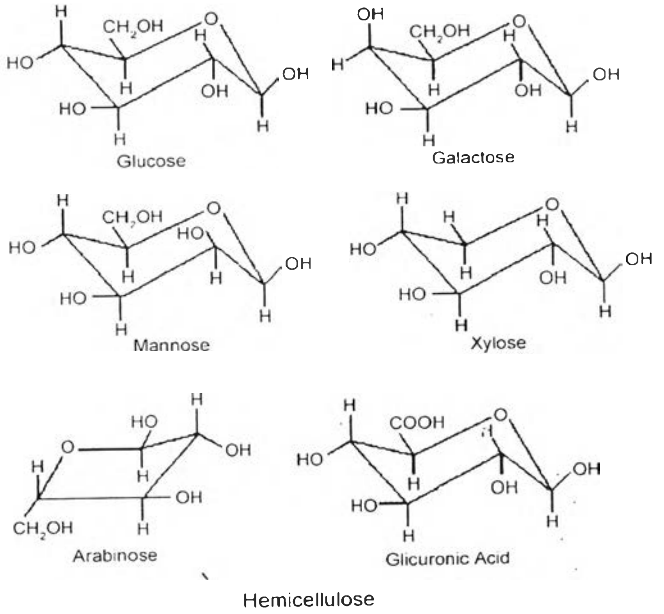


Figure 2.13 Molecular structure of hemicellulose.

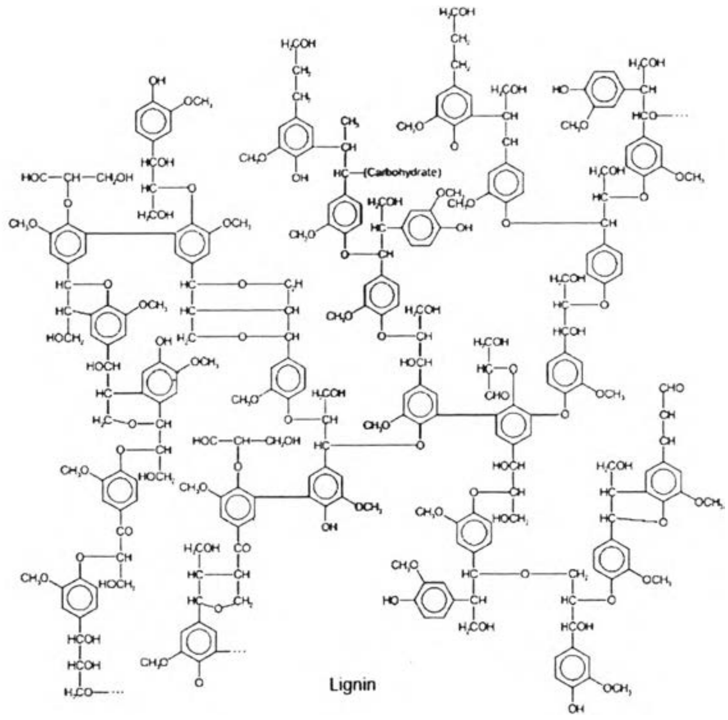


Figure 2.14 Molecular structure of lignin.

In the present study, biodiesel production using the prepared solid acid catalyst from the waste of lignocellulosic biomass from biobutanol production process was studied. The residue from biobutanol production was employed as a solid base catalyst for esterification of oleic acid due to its availability and cheap. P-Toluenesulfonic acid is utilized as the sulfonation agent and compared with the common sulfuric acid in sulfonation method. Furthermore, the catalyst was used in many cycles of biodiesel production to study its reusability.