# CHAPTER II
LITERATURE REVIEW

2.1 Feedstocks For Biodiesel Production

Biodiesel can be produced from a great variety of feedstocks. These feedstocks include most common vegetable oils (e.g., soybean, palm, peanut, sunflower, and coconut), animal fats and waste oils. Some sample of biodiesel sources are shown in Figure 2.1. The choice of feedstock depends on agricultural, geographical, and climatic conditions. Different nations are looking into different vegetable oils for diesel fuels such as soy bean oil in the United States, rapeseed and sunflower oils in Europe, palm oil in Southeast Asia (mainly Malaysia and Indonesia), and coconut oil in the Philippines (Demirbas, 2006). The different feedstock types are characterized by different properties. In 2008, Ramos and co-workers studied the influence of fatty acid composition of vegetable oils on quality of biodiesel synthesized. Then they found that biodiesel, which have high unsaturated fatty acids (C18:2 and C18:3) produced from soybean, sunflower, and grape seed oils have low cetane numbers but high iodine values. The oxidative stability decrease when increasing the content of polyunsaturated methyl ester. On the other hand, the value of cold filter plugging point is the worst. Therefore, biodiesels derived from almond, olive, corn, rapeseed, and high oleic sunflower oils have good properties because they have greater monounsaturated content.
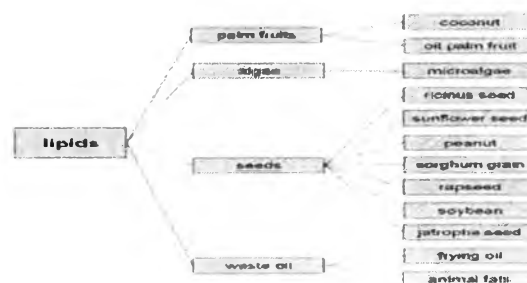
Figure 2.1 Types and classification of lipid feedstock sources (Janssen and Rutz, 2008).

2.1.1 Oilseed Crops

For biodiesel production, oilseed crops provide the primary feedstock, whereas soybean production is the world's largest followed by rapeseed and cottonseed (WWI, 2006). Nearly 85% of biodiesel production is made from rapeseed in Europe, followed by sunflower seed oil, soybean oil, and palm oil (Mittelbach and Remschmidt, 2004).

2.1.1.1 Rapeseed

Rapeseed also known as canola or colza and is closely related to other oilseed crops such as mustard species. China is the largest rapeseed producer in the world. Rapeseed oil is characterized by high levels of erucic acid, high contents of monounsaturated oleic acid and low levels of both saturated and polyunsaturated acids. Therefore, rapeseed oil is an ideal raw material regarding combustion characteristics, oxidative stability, and cold temperature behavior (Mittelbach and Remschmidt, 2004).

2.1.1.2 Soybeans

The main producing countries of soybean oil are the United States, Brazil, and Argentina, where this oil is increasingly being used for biodiesel production. Soybean oil is characterized by iodine values of 121–143 g $I_2/100$ g, which is similar to sunflower oil. Therefore, soybean oil can meet biodiesel standards (Janssen and Rutz, 2008).

2.1.1.3 Palms

Palms are used for oil production mainly in South Asian countries and the two largest producers are Malaysia and Indonesia. While most palm oil is used for food purposes, the demand for palm biodiesel is expected to increase rapidly, particularly in Europe. Palm oil is characterized by high amounts of medium-chain saturated and monounsaturated fatty acids. High contents of saturated fatty acids are leading to unacceptable high values for cold filter plugging point and cloud point which prevents winter operation on neat palm oil methyl esters in

temperate climates. Additionally, high contents of fatty acids in the feedstock cause problems in traditional alkali-catalyzed biodiesel production.

2.1.1.4 Coconut

The coconut is another feedstock source for oil production. Coconut oil is a triglyceride containing high percentages of saturated fatty acids, small amounts of monounsaturated fatty acids, and polyunsaturated fatty acids. Unrefined coconut oil melts at 20–25 °C and smokes at 170 °C, while refined coconut oil has a higher smoke point of 232 °C. In Philippines, the vehicles running on coconut biodiesel can reduce emission levels (WWI, 2006).

2.1.1.5 Sunflower

The oil of sunflower seeds is the world's fifth largest oilseed crop. The yield of sunflower seeds is similar when compared to rapeseed. For fuel production the high contents of linoleic acid limit when use of sunflower seed oil. Additionally pure sunflower oil methyl esters have high iodine values, which is not suitable fuel used as a fuel and the oxidative stability will be poor. To solve the problems, cultivars enriched in oleic acid have been bred (Mittelbach and Remschmidt, 2004).

2.1.1.6 Jatropha

Jatropha has been identified as one of the most feedstock for large-scale biodiesel production in India (Kalbande *et al.*, 2008). The economics of biodiesel from jatropha depends on the seed yields. At present, there has been a substantial amount of variability in yield data for the plant, which can be attributed to differences in germ plasm quality, plantation practices, and climatic. Jatropha oil contains a relatively high percentage of saturated fatty acids, the corresponding methyl esters exhibit relatively poor cold flow properties (Kumartiwari *et al.*, 2007).
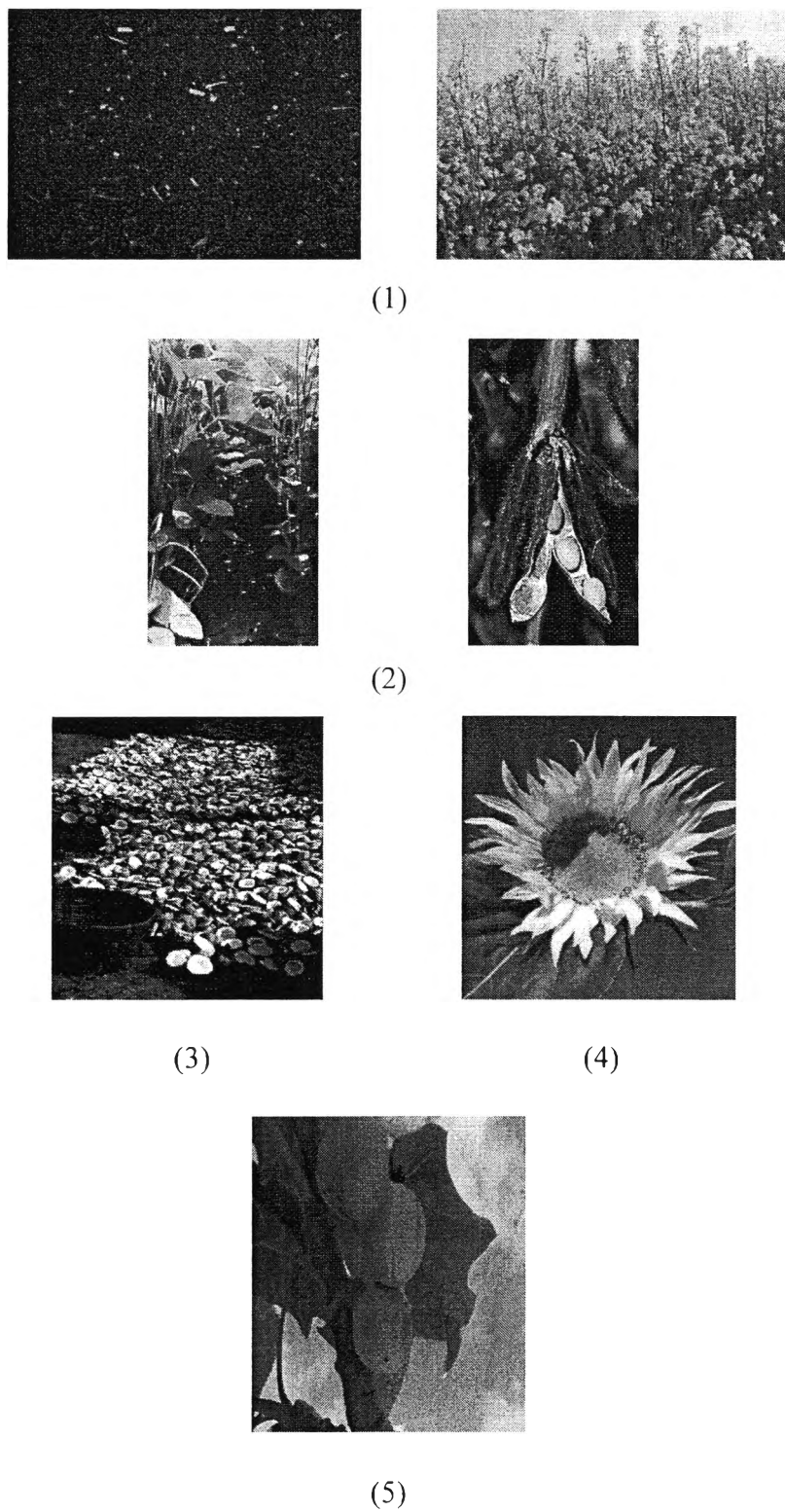
Figure 2.2 Raw materials of biodiesel: (1) Rape seeds and flower, (2) Soy plant and beans, (3) Coconut, (4) Sunflower, and (5) Jatropha (Janssen and Rutz, 2008).

Table 2.1 Fatty acid composition (wt.%) of biodiesel fuels prepared from various alternative oil crop feedstocks (Moser, 2011).

Feedstock	14:00	16:00	16:01	18:00	18:01	18:02	18:03	20:00	20:01	22:00	22:01	other
Jatropha curcas	1.4	11.3		17	12.8	47.3		4.7				5.5
Pongamia pinnata		10.6	6.8	49.4	19			4.1	2.4	5.3		2.4[a]
Madhuca indica	1	17.8		14	46.3	17.9		3				
Melia azedarach		10.1		3.5	21.8	64.1	0.4	0.2	0.3			
Moringa oleifera		6.5		6	72.2	1		4	2	7.1		
Nicotiana tabacum	0.1	11		3.3	14.5	69.5	0.7					0.9
Balanites aegyptiaca		13.7		11	43.7	31.5						
Terminalia catappa		35		5	32	28						
Hevea brasiliensis		10.2		8.7	24.6	39.6	16.3					
Asclepias syiaca		5.9	6.8	2.3	34.8	48.7	1.2	0.2				
Zanthoxylum bungeanum		10.6	5.2	1.4	32.1	25.6	24.1					1
Rice bran		18.8		2.4	43.1	33.2	0.6	0.7				
Raphanus sativus		5.7		2.2	34.5	17.8	12.5	1	10		16.4	
Brassica carinatac		5.3			10	24.6	16.5				43.6	
Calophyllum inophyllum		12		13	34.1	38.3	0.3					

[a] 2.4 wt.% 24:0

Table 2.2 Fatty acid profile (wt.%) of biodiesel fuels prepared from animal fats and waste oil feedstocks (Moser, 2011).

Feedstock	14:00	16:00	16:01	18:00	18:01	18:02	18:03	20:00	20:01	22:00	22:01	other
Salmon	6.8	14.9	6.1	3.2	15.6	2.1	11.5					39.8
Melon bug		30.9	10.7	3.5	46.6	3.9						2.4
Sorghum bug		12.2	1	7.3	40.9	34.5						0.1
Pork lard		26.4		12.1	44.7	12.7	1					3.1
Beef tallow	3.1	23.8	4.7	12.7	47.2	2.6	0.8					5.1[a]
Chicken fat	0.7	20.9	5.4	5.6	40.9	20.5						6.0[b]
Waste frying oil	1	30.7	0.6	5.7	40.5	19.1	0.2	0.6	0.4	0.3	0.4	0.3
Waste cooking oil	16.3	10.6		3.3	8.2	2						59.7[c]
Waste cooking oil		16		5.2	34.3	40.8						
Used frying oil	0.9	20.4	4.6	4.8	52.9	13.5	0.8	0.1	0.8			0.1
Used cooking oil	0.2	11.9	0.2	3.8	31.3	50.8		0.3		0.5	0.2	
Waste frying oil		8.4	0.2	3.7	34.6	50.5	0.6	0.4	0.4	0.8	0.3	
Soybean soapstock		17.2		4.4	15.7	55.6	7.1					
Yellow grease	2.4	23.2	3.8	13	44.3	7	0.7					
Brown grease	1.7	22.8	3.1	12.5	42.4	12.1	0.8					

[a] 1.3 wt.% 14:1; 0.5 wt.% 15:0; 1.1 wt.% 17:0; 2.2 wt.% unknown, [b] 0.1 wt.% 14:1; 3.8 wt.% unknown. [c] 8.8 wt.% 8:0; 6.2 wt.% 10:0; 44.7 wt.% 12:0

2.1.2 Microalgae

Microalgae are microscopic single-cell aquatic plants with the potential to produce large quantities of lipids (plant oils) that are well suited for use in biodiesel production. There are two main systems of cultivating algae: in open-pond systems algae which are vulnerable of being invaded by other algal species and bacteria. There is no control about water temperature and lighting conditions. The growing season is largely dependent on the climatic location and is limited to the warmer months. The advantages of these systems are the low costs and the high production capacity. The second possibility is closed-pond system, a pond system which is covered by a greenhouse. These systems are usually smaller, but they have many advantages. These systems allow the cultivation of more species which are protected from other species from outside. Algae can be also grown in a photobioreactor which incorporates some type of light source. Recently the potential of cultivating algae has been recognized as the algae can be feed by CO_2 emissions. This is possible because carbon dioxide and nitrogen oxides are the primary nutrients for the growth of microalgae (Janssen and Rutz, 2008).

2.1.3 Animal Fats

Animal fats include materials from a variety of domesticated animals, such as cows, chickens, pigs, and other animals such as fish and insects. Due to the low retail prices of these co-products they may be an increasing source for biodiesel production, especially in order to replace fuel for vehicle fleets of companies producing these raw materials. The problem with all of these sources is the discontinuity of supply. It is possible that suddenly a high bulk of material is available followed by a period with no supply. Nevertheless all these animal fats are characterized by high amounts of saturated fatty acids resulting in methyl esters with poor cold temperature properties. This poses problems in the winter. But the high degree of saturation makes animal fat methyl esters excellent fuels regarding to heating value and cetane number (Mittelbach and Remschmidt, 2004).

2.1.4 Waste Oils

Waste oils may include a variety of materials such as used cooking or frying oils, vegetable oil soapstocks, acid oils, tall oil, and other waste materials. There is a large variety of waste oils available for biodiesel production. In general, these waste oils are inexpensive and offer an additional environmental impact by using substances. Waste oils can be divided into three types: waste oil from households and restaurants, food industry, and non-food industry. They are normally characterized by relatively high FFA and water contents and potentially the presence of various solid materials that must be removed by filtration prior to a conversion to biodiesel. In the case of used cooking or frying oils, hydrogenation to increase the useful cooking lifetime of the oil may result in the introduction of relatively high melting trans constituents, which has influence on the physical properties of the resultant biodiesel fuel (Moser, 2011).

2.2 Vegetable Oils

Vegetable oils and animal fats are triacylglycerols (TAG), which are esters of one glycerol with three long-chain fatty acids. The major component of vegetable oils is triglycerides. Vegetable oils comprise most triglycerides and small amounts of mono- and di-glycerides. They contain free fatty acids and traces of water (Srivastava and Prasad, 2000). The general formation of triglyceride is shown in Figure 2.3.
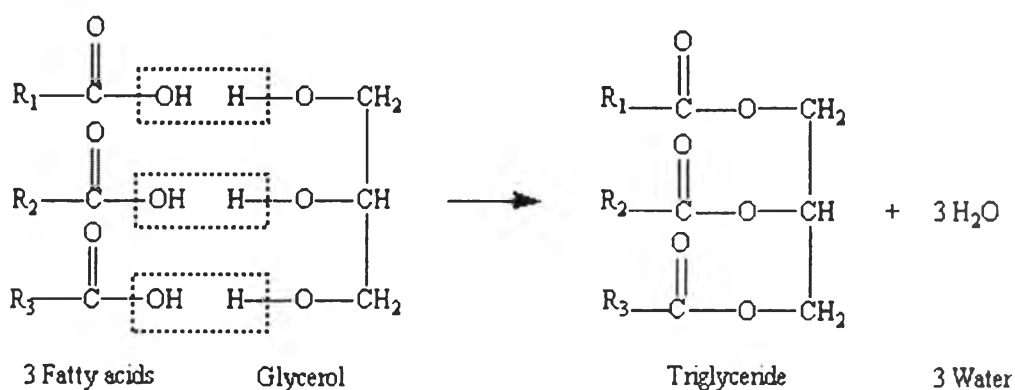
Figure 2.3 General formation of triglyceride (Swern, 1955).

From Figure 2.3 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 different types of fatty acids, which glycerol will be combined. The properties of the triglyceride and the biodiesel fuel are determined by amounts of each fatty acid that show in molecules. Different fatty acids have different carbon chain length and number of double bonds. This reason leads to make different characteristics of vegetable oil (Mittelbach and Remschmidt, 2004). The common fatty acids found in vegetable oils are stearic, palmitic, oleic, linoleic, and linolenic. The name and chemical structure of common fatty acids are shown in Table 2.3 and some properties of the vegetable oils are shown in Table 2.4.

Table 2.3 Chemical structure of common fatty acids (Balat and Balat, 2008)

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 with y double bonds in fatty acid chain

Table 2.4 Properties of the vegetable oils (Marchetti *et al.*, 2007)

Vegetable oil	Kinematics viscosity (mm^2/s)	Cetane number	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)	Lower heating value (MJ/kg)
Peanut	4.9	54	5	-	176	0.883	33.6
Soya bean	4.5	45	1	-7	178	0.885	33.5
Babassu	3.6	63	4	-	127	0.875	31.8
Palm	5.7	62	13	-	164	0.880	33.5
Sunflower	4.6	49	1	-	183	0.860	33.5
Tallow	-	-	12	9	96	-	-
Diesel	3.06	50	-	-16	76	0.855	43.8
20% biodiesel blend	3.2	51	-	-16	128	0.859	43.2

As shown in Table 2.4, the use of vegetable oils directly as diesel fuels leads to a number of problems. The injection, atomization, and combustion characteristics of vegetable oils in diesel engines are significantly different from those of petrodiesel. The high viscosity of vegetable oils which is a main cause of poor fuel atomization resulting in operational problems such as engine deposits was recognized early. Moreover, the high flash point attributes to its low volatility characteristics. This leads to more deposit formation and carbonization. In addition, the combination of high viscosity and low volatility of vegetable oils causes poor cold engine start up and ignition delay. Oxidative and thermal polymerisation of vegetable oils cause a deposition on the injectors and forming a film that will continue to trap fuel and interfere with combustion. The potential biodiesel like sunflower, rapeseed, palm, and jatropha were similar combustion characteristics as diesel (Basha *et al.*, 2009). In the long-term operation, vegetable oils normally develop gumming, injector coking and ring sticking (Srivastava and Prasad, 2000).

Therefore, from these reasons, several methods are attempted to improve characteristics of biodiesel derived from vegetable oils to close to petrodiesel.

2.3 Production of Biodiesel

From the disadvantages of vegetable oils, such as high viscosity, low volatility and polyunsaturated fatty acids, so there are many ways to improve vegetable oils performances to close to petrodiesel. These can be done by four major ways as follows.

2.3.1 Direct Use and Blending

Direct use is the method that vegetable oil or animal fats are used directly as fuel in diesel engine without blending with any substance to change the properties. Blending is the method that diesel oil or kerosene is diluted with vegetable oil or animal oil in difference ratio to decrease a viscosity. Although this route is economically attractive, it brings serious problems of adjustment as the physical and chemical properties of the vegetable oil, such as high viscosity because presence of free fatty acids and bad cold start properties. The main problems associated to the use of the vegetable oils in natural as combustions are incomplete, leading to the accumulation of carbon deposits in the motor, and the thickening of the oil as a result of the polymerization of the unsaturated fatty acids.

2.3.2 Microemulsification

Microemulsification is a dispersion of fluid particles that suspended in oil, water and surfactant. The product exhibits have lower volumetric heating values than diesel fuels, A microemulsion of methanol with vegetable oils can perform nearly diesel fuels and the viscosity was reduced to 11.2 cSt at 258 °C (Srivastava and Prasad, 2000).

2.3.3 Pyrolysis

Pyrolysis or thermal cracking is a process of chemical change by thermal energy, which also known as thermal decomposition. In this process, the

thermal cracking of triglycerides produces a compound of alkanes, alkenes, alkadienes, aromatics, and carboxylic acids shown in Figure 2.4. Mechanisms for the thermal decomposition of triglycerides are complex. Generally, thermal decomposition of these structures proceeds through either a free-radical or carbonium ion mechanism. The pyrolysed soybean oil contains 79% carbon and 11.88% hydrogen (Schwab *et al.*, 1988). It has low viscosity and a high cetane number when compared to pure vegetable oils. The cetane number of pyrolysed soybean oil is increased from 37.9 to 43 and the viscosity is reduced from 32.6 to 10.2 cSt at 388 °C (Bagby, 1988). The pyrolysed vegetable oils possess acceptable amounts of sulphur, water, and sediment and give acceptable copper corrosion values but unacceptable ash, carbon residue amounts, and pour point (Srivastava and Prasad, 2000).
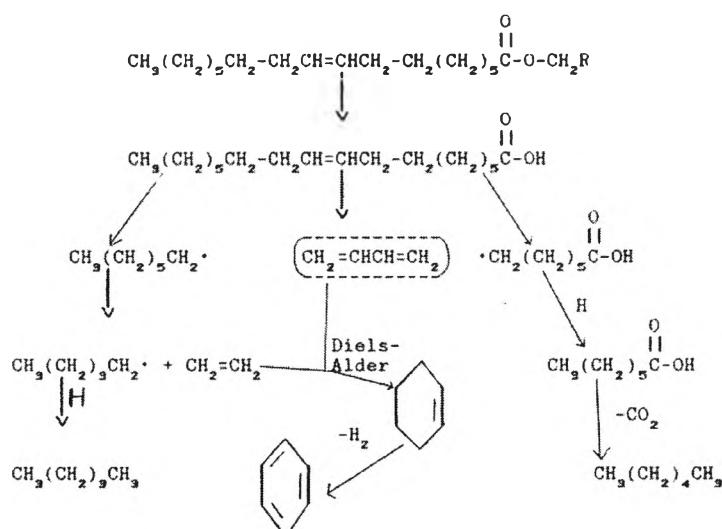
Figure 2.4 Mechanisms for the thermal decomposition triglycerides (Srivastava and Prasad, 2000).

2.3.4 Dilution

Dilution of vegetable oils can perform with diesel fuels or ethanol which are used as a solvent. Ziejewski and co-workers (1983) studied the dilution of sunflower oil with diesel fuels in the ratio of 1:3 by volume and the viscosity of this

blend was 4.88 cSt at 408 °C. The result shows that this blend could not be recommended for long-term use in the direct injection diesel engines because of severe injector nozzle coking and sticking. Moreover, the dilution of sunflower oil with high oleic sunflower oil was also studied and it is suitable for long-term use.

2.3.5 Transesterification

Transesterification or alcoholysis reaction is the process which refined oil molecule is cracked and the glycerol is removed, resulting in glycerin soap and methyl ethyl esters (biodiesel). Transesterification does not alter the fatty acid composition of the feedstocks and this composition plays an important role in some parameters of the biodiesel, as cetane number and cold flow properties (Ramos *et al.*, 2009). One significant advantage of the transesterification is the lower viscosity of biodiesel, which the main reason to transesterification of vegetable oils and animal fats to alkyl esters because increased viscosity affects fuel injection duration, pressure, and atomization of diesel engines. The fuel property that shows this suitability is cetane number. In this reaction, one mole of triglyceride reacts with three moles of alcohol to form one mole of glycerol and three moles of the fatty acid alkyl ester. The bonds are broken by hydrolyzing. The process is revesible reactions, in which that the triglyceride molecule is converted step by step into diglyceride, monoglyceride and glycerol (Mittelbach and Remschmidt, 2004). These transesterification reactions are often addition of an acid or base catalyst and in 2009 Basha and co-workers observed that the base catalysts are more effective than acid catalysts and enzyme.
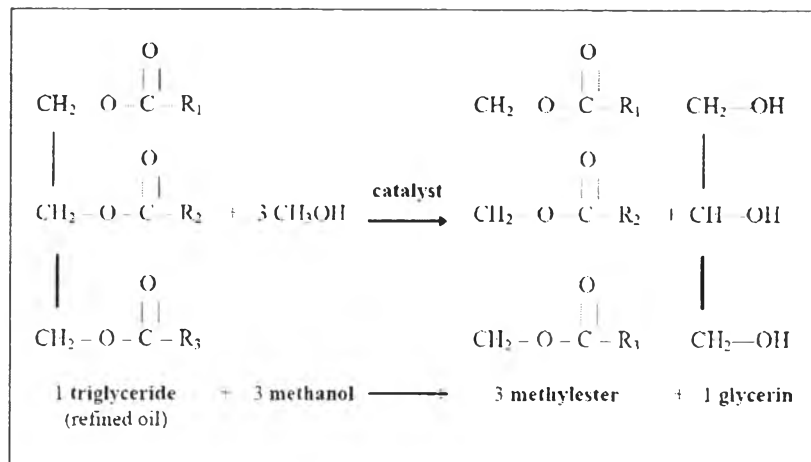
Figure 2.5 The chemical transesterification reaction (Janssen and Rutz, 2008).

The transesterification with methanol, also called methanolysis, is the most commonly method for biodiesel production. Methanol is characterized by its lower prices and its higher reactivity as compared to other alcohols. This reaction can be happened by heating a mixture of 80–90% oil, 10–20% methanol, and small amounts of a catalyst. The received biodiesel after methanolysis is fatty acid methyl ester (FAME) (Janssen and Rutz, 2008).

2.4 Biodiesel

Biodiesel is an alternative energy diesel fuel, is a fuel produced from monoalkyl esters of long-chain fatty acids derived from transesterification of renewable energy sources that are vegetable oils or animal fats meeting the requirements of ASTM D6751 (ASTM 2008a). Biodiesel have been used interchangeably for petrodiesel, which is the diesel fuel derived from petroleum needs to be defined as it is the material the other fuels are compared to. Almost all literature is usually called "diesel" or "diesel fuel". Commonly applied petrodiesel standards are ASTM D975 in the United Stated and EN 590 in Europe (Knothe, 2010) like fuels derived from biological sources. Biodiesel has several advantages compared with petrodiesel. In addition, it is fully competitive with petrodiesel in most technical aspects as follows:

- Derivation from a renewable domestic resources
- Biodegradability
- Reduction of most exhaust emissions. But the emission of oxides of nitrogen (NO_x) from the engine found to be higher on the all fuel blends as compared to diesel (Basha *et al.*, 2009).
- Higher flash point, leading to safer handling and storage.
- Excellent lubricity, adding biodiesel at low levels (1–2%) restores the lubricity (Knothe, *et al.*, 2005).

Some problems associated with biodiesel are stability when exposed to air (oxidative stability) and cold flow properties, that are especially relevant in North America. The oxidative stability depends on the degree of unsaturation of the FAME chain (Wadumesthrige *et al.*, 2009). If the degree of unsaturation is higher, the oxidative stability of FAME will be lower. On the other hand, if the degree of saturation is too high, the cold flow properties will be bad.

The properties of biodiesel and petroleum-based diesel fuels are compared and shown in Table 2.5. From this table, it shows that biodiesel produced from various vegetable oils have viscosities close to those of petrodiesel fuels. Their heating values are a little lower, but they have higher cetane numbers and flash points. Since the characteristics of biodiesel are generally similar to those of petro diesel fuels; therefore, biodiesel is a strong candidate to replace petrodiesel fuels.

Table 2.5 Comparison between properties of biodiesel and diesel fuels
(Srivastava and Prasad, 2000)

Vegetable oil methyl ester	Kinematic viscosity (mm²/s)	Cetane number	Lower heating value (MJ/l)	Cloud point (°C)	Flash point (°C)	Density (g/l)	Sulfur (wt.%)
Peanut	4.9 (37.8 °C)	54	33.6	5	176	0.883	-
Soybean	4.5 (37.8 °C)	45	33.5	1	178	0.885	-
Babassu	3.6 (37.8 °C)	63	31.8	4	127	0.879	-
Palm	5.7 (37.8 °C)	62	33.5	13	164	0.880	-
Sunflower	4.6 (37.8 °C)	49	33.5	1	183	0.860	-
Rapeseed	4.2 (40 °C)	51-59.7	32.8	-	-	0.882	-
Used rapeseed	9.48 (30 °C)	53	36.7	-	192	0.895	0.002
Used corn oil	6.23 (37 °C)	63.9	42.3	-	166	0.884	0.0013
Diesel fuel	12-3.5 (40 °C)	51	35.5	-	-	0.830-0.840	-
JIS-2D (gas oil)	2.8 (30 °C)	58	42.7	-	59	0.833	0.05

2.5 Partial Hydrogenation

Hydrogenation is the chemical reaction that hydrogen atoms are added to double or triple bonds. This process is converted unsaturated fatty acids to saturated fatty acids by add pairs of hydrogen atoms to a molecule. Non-catalytic hydrogenation usually takes place at very high temperature and pressure because it requires high energy to breaking the bonds. Therefore, catalysts are used to reduce the operating temperature and pressure for this reaction and the properties of hydrogenated FAME depend on the hydrogenation time. Furthermore, There are many reaction to improve properties of biodiesel depend on the chemical structure in fatty acid methyl esters (FAME), which was by catalytic hydrogenation, epoxidation, and hydroxylation under different conditions. These reactions can decrease unsaturated fatty acid methyl esters in fraction and increase oxidative stability. In addition, hydrogenation process shows higher cetane number but poorer in cold flow properties. On the other hand, hydroxylation shows the better in cold flow properties and can increase lubricity (Wadumesthrige *et al.*, 2009).

Several reviews dealing with improve oxidative stability by partial hydrogenation of FAME with other catalysts have been published such as in 2008 Nikolaou and co-workers studied the partial hydrogenation of polyunsaturated methyl esters of sunflower oil to monounsaturated compounds using active rhodium sulfonated phosphite (Rh/STPP) under mild condition and high catalytic activities. In 2009, Sonthisawate and co-workers studied the upgrading of biodiesel fuel quality by partial hydrogenation process by using Pd-Pt/Yb-USY under atmospheric pressure and reaction temperature of 100 °C. Not only to improve oxidative stability but also prevent acid formation and decrease sludge formation after polymerization without adding the antioxidant and in the same year Papadopoulos and co-workers reported the homogeneous hydrogenation of FAMEs of cotton seed biodiesel catalyzed by $RhCl_3.3H_2O$ and STPP-TiOA catalyst precursor. The reaction was taken place at mild condition and high catalyst activity was obtained. There are four effects which were concerned: pressure, temperature, reaction time, and molecular ratio C=C/Rh. The result shows that the partial hydrogenation of FAMEs of cotton seed biodiesel can improve the oxidative stability and cetane number.

Moreover, the decarbonylation, decarboxylation, and deoxygenation of FAME processes can transform the biodiesel in to hydrocarbon base fuel. The decarbonylation and decarboxylation have advantages over hydrogenolysis because, while the hydrocarbons thus produced may contain less carbon than its fatty acid (Maier *et al.*, 2003). The properties of the fuel obtained by decarbonylation and decarboxylation are not different from those obtained from hydrogenolysis. Typically, decarbonylation takes place over supported metal catalysts at high temperatures (>350 °C). For example, Pd/C has been found to be an effective catalyst for decarbonylation and decarboxylation (Maki-Arvela *et al.*, 2007). In 2007, Snare and co-workers studied deoxygenation of unsaturated renewables, such as oleic acid, methyl oleate, and linoleic acid with high selectivity to saturated diesel fuel range hydrocarbons. The reactions were carried out over a Pd/C catalyst under constant pressure and temperature. The deoxygenation catalyst was characterized by physisorption, temperature–programmed desorption (TPD), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). They studied parameters through initial hydrogenation of double bonds and subsequent deoxygenation of corresponding saturated feeds. The hydrogenation formation of diunsaturated acids occurred. Under a hydrogen rich atmosphere the hydrogenation was enhanced and the deoxygenation reaction became predominant. Additionally, isomerisation of oleic acid occurred prior to hydrogenation and deoxygenation. The deoxygenation of unsaturated feeds was performed in continuous mode under conditions of strong mass transfer influence.

2.6 Palladium on Silica Support

Supported Pd catalysts are widely used in liquid phase hydrogenation. Common catalyst supports include activated carbon, silica, alumina, polymers, and zeolite. A support has an important effect on the catalytic activity, selectivity, recycling, refining, materials handling, and reproducibility (Panpranot *et al.*, 2004). For examples, Tamai and co-workers (2009) prepared Pd supported on microporous and mesoporous activated carbons by immersing the activated carbons in a Pd solution. The catalytic activities of the prepared catalysts for the hydrogenation of

methyl linoleate were investigated. As a result, they found that Pd particles were mainly supported on mesopores. Moreover, the Pd supported on mesoporous activated carbons exhibited higher catalytic activities when compared with Pd supported on microporous activated carbons. It indicated that Pd particles supported on mesopores play an important role in the catalytic activity.

Furthermore, the different types, structures and particle sizes of support can also affect catalyst performance in hydrogenation process. Shen and co-workers (2001) discussed the effects of Pd supports on Al_4O_3, SiO_2, TiO_2, and ZrO_2 in catalytic hydrogenation of CO. The result shows that the highest activity and selectivity of methanol was obtained over Pd/ZrO_2, while Pd/SiO_2 exhibited high selectivity of methanol but has less CO conversions. The Pd/TiO_2 favor methane formation at higher temperatures and Pd/Al_2O_3 was observed to show specific selectivity for dimethyl ether. In addition, Pinna and co-workers (2001) compared Pd on different supports: activated carbon, silica, and alumina, in the selective hydrogenation of benzaldehyde to benzyl alcohol. They found that Pd/Al_2O_3 showed strong metal–support interaction, while Pd/C showed the good selectivity for benzaldehyde hydrogenation and they also observed that small Pd particles are sensitive with benzaldehyde hydrogenation.

Perez-Cadenas and co-workers (2008) studied the partial hydrogenation of polyunsaturated methyl esters of sunflower oil but they discussed the performance of three different carbon-based monoliths as Pd catalyst supports. First, the high performance monolith (HPM) was a classical square channel modified with $\alpha\text{-}Al_2O_3$. The other two monolithic supports were composite carbon and ceramic monoliths, a microporous (WA) and a mesoporous (WB), respectively. This work demonstrates that the type of porosity of carbon materials strongly affect the activity and selectivity in selective hydrogenation. The Pd/HPM is the best catalyst when compared to the other two samples in term of much lower formation of trans double bonds at the same level of double conversion because it has shorter diffusion distance of the reactants and products so Pd particles are placed at the external nonporous surface of the carbon layer.

Palladium supported on silica (Pd/SiO_2) will be used as a catalyst in this work. Because of the high activity and selectivity of Pd metal in hydrogenation

reaction. In addition, the macroporosity of SiO_2 support where Pd can be located inside and big FAME molecule can be easily access. Joongjai and co-workers (2004) studied the characteristics and catalytic properties of Pd/MCM-41 and Pd/SiO_2 compared in terms of Pd dispersion, catalyst particle size, catalytic activities for liquid-phase hydrogenation of 1-hexene, and deactivation of the catalysts. The catalysts were prepared by impregnation method and were characterized by BET surface area, X-ray diffraction, SEM and TEM micrographs, and the CO chemisorption. The result shows that the characteristics and catalytic properties of the silica supported Pd catalysts in liquid-phase hydrogenation depend on type of silica, pore size, and pore structure. From the four types of the supported Pd catalysts: (small pore and large pore of Pd/MCM-41 and Pd/SiO_2). Pd/MCM-41-large pore showed the highest Pd dispersion and the highest hydrogenation rate with the lowest amount of metal loss.

2.7 Properties of Biodiesel

Biodiesel produced from different feedstocks will exhibit different fuel properties because each feedstock has a unique chemical composition. The important properties of biodiesel that influenced by fatty acid methyl ester composition are:

2.7.1 Cetane Number

Cetane Number is one of the primary indicators of the fuel quality. It is related to the ignition delay time a fuel experiences that it has been injected into a diesel engine's combustion chamber (Moser, 2011). Diesel engine relies on the high pressures and temperatures generated during the compression stroke to bring about auto-ignition of the air-fuel mixture. Auto-ignition is defined as the condition when the air-fuel mixture spontaneously ignites without an external source of ignition, such as flame or spark. The tendency of the diesel fuel to ignite under these conditions is known as its ignition quality, which is conveniently expressed in terms of cetane number. The higher the cetane number, the better the ignition quality. Higher cetane number shortens the ignition delay period, which translates to

smoother combustion and thereby optimizing the power generated. Cetane number also influences cold start performance, white smoke, engine noise, and emission.

2.7.2 Sulphur Content

Most biodiesel fuels have low sulfur content meeting specsification in biodiesel standards (0.05 mass% in ASTM D6751) (Knothe, 2010). These ultra-low sulphur levels are mandated by Federal legislation and required for all 2007 model year vehicles that will be equipped with advanced emission control systems utilizing diesel particulate filters (DPFs) in exhaust systems. High sulphur fuel will be potentially harmful because it will result in premature filter plugging with sulphates.

2.7.3 Lubricity

Lubricity is the ability to reduce friction between two surfaces in relative motion. It is a measure of fuel's effectiveness as a lubricant. Biodiesel possesses inherently good lubricity, especially when compared to petrodiesel. Diesel fuel also functions as lubricant in fuel injection equipment such as rotary or distributor type injection pumps, and injectors. The severe hydrotreatment process involved to lower the sulphur content of the diesel fuel to where it is now tends to reduce its natural lubricating properties. Lubricity additives are used to enhance the lubricating property of this severely hydrotreated diesel fuel. Industry standards require diesel fuel to provide acceptable performance in accordance with prescribed test methods. Increased wear in the fuel injection system will cause insufficient fuel delivery and will lead to poor engine driveability. In the long term and in extreme cases, fuel pumps and injectors will seize and breakdown.

2.7.4 Cloud Point

Cloud point is the temperature at which wax crystals begin to form in the fuel. The cloud point temperature of the diesel fuel indicates how well it performs at low temperatures. This property is important because wax crystals can block fuel filters, thus starving the engine of fuel. The industry standard for supplying diesel fuel is to ensure that the cloud point does not exceed a prescribed temperature for a given half-month period.

2.7.5 Flash Point

Flash point is the lowest temperature at which the diesel fuel will start to emit vapor that can be ignited by an external source. Flash point has no direct influence on engine performance, but it is important for safe storage, handling, and transport of diesel fuel. A low flash point fuel can be a fire hazard. In addition, low flash point may provide an indication of contamination with more volatile fuels such as gasoline.

2.7.6 Viscosity

Viscosity is a measure of a liquid's resistance to flow under pressure and is dependent upon temperature. At higher temperature, the viscosity of the fuel decreases and at lower temperature its viscosity increases. Viscosity of diesel fuel influences engine performance in two ways: injection pump and injector performance, and injected fuel spray pattern and atomization. A very low viscosity fuel can cause internal leakages in the injection pump causing low pressure build up resulting to fuel starvation in the combustion chamber of the engine. This could also lead to undesirable spray pattern that promotes incomplete combustion. Fuel starvation and incomplete combustion will both contribute to reduced power and excessive emission. A very low viscosity fuel also causes excessive wear in the injection system and poor hot re-start. On the other hand, a very high viscosity fuel will cause poor atomization during injection. As a result, the fuel is not evenly distributed in the combustion chamber to mix well with the air a requisite for good combustion.

2.7.7 Volatility (Distillation)

The distillation characteristics of a diesel fuel impart an important influence on diesel engine performance. Volatility of the diesel fuel tends to affect power output and fuel economy. A less volatile fuel tends to reduce power output and fuel economy due to poor atomization. A diesel fuel with too high volatility tends to promote vapor lock in the fuel system and unfavorable spray penetration from the injector thereby reducing power output and fuel economy. Distillation characteristics of diesel fuel also influence cold start exhaust smoke and odors.

2.7.8 Oxidation Stability

Oxidative stability of biodiesel is determined through measurement of the oil stability index (OSI) by the Rancimat method (EN 14112). The Rancimat method indirectly measures oxidation by monitoring the gradual change in conductivity of a solution of water caused by volatile oxidative degradation products that have been transported via a stream of air (10 L/h) from the vessel (at 110 °C) containing the biodiesel sample. The OSI is mathematically determined as the inflection point of a computer-generated plot of conductivity (μS/cm) of distilled water versus time (h). One important problem associated with renewable fuel derived from vegetable oil and animal fats (i.e., biodiesel) is poor oxidative stability. This is especially true for soy-based biodiesel which has significantly higher levels of polyunsaturation (Moser, 2011).