CHAPTER II

LITERATURE REVIEW

2.1 Vegetable Oils

One hundred years ago, Rudolf Diesel tested vegetable oil as a fuel for his engine (Shay, 1993). With the advent of cheap petroleum, appropriate crude oil fractions were refined to serve as fuels and diesel fuels and diesel engines evolved together. In the 1930s and 1940s, vegetable oils were used as diesel fuels from time to time, but usually only in emergency situations (Ma and Hanna, 1999). Recently, due to the concern about the depletion of the world's non-renewable resources and degradation of environment, the use of vegetable oils as fuels for diesel engines are recalled to use worldwide. For biodiesel production, oilseed crops are used as the primary feedstock. There are more than 350 oil bearing crops identified; however, among which only sunflower, safflower, soybean, cottonseed, rapeseed, and peanut oils are considered as potential alternative fuels for diesel engines (Demirbas, 2005). Furthermore, the interest in vegetable oils is different from country to country depending on the abundance of feedstock. For example, soybean oil in the US, rapeseed and sunflower oils in Europe, palm oil in South-east Asia (mainly Malaysia and Indonesia) and coconut oil in the Philippines are used as biodiesel feedstocks (Barnwal and Sharma, 2005).

Vegetable oils, also known as triglycerides, have the chemical structure, as shown in Figure 2.1. They comprise of 98 % triglycerides and small amount of mono- and diglycerides (Barnwal and Sharma, 2005). In addition, there are also traces of water. Triglycerides are principally composed of triacylglycerols (TAG) consisting of long-chain fatty acids (which can be different types) chemically bound to a glycerol (1,2,3-propanetriol) backbone (Moser, 2009). There are many triglycerides; depending on the oil source, some are highly unsaturated, some less so.
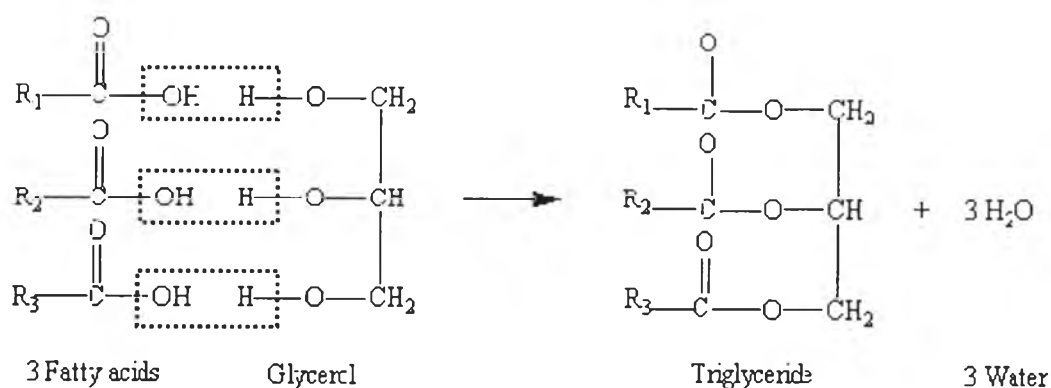
Figure 2.1 General formation of triglyceride (Swern, 1979).

From Figure 2.1, R_1, R_2, and R_3 represent a chain of carbon atoms with hydrogen atoms attached. The differences of R_1, R_2, and R_3 result in different types of fatty acids which glycerol will be combined. The three fatty acids may or may not be identical. In fact, three different fatty acids may be present. Since fatty acids vary in their carbon chain length and in the number of double bonds (Barnwal and Sharma, 2005); therefore, the properties and characteristics of each vegetable oil are also different. Naturally, most occurring fatty acids have chain lengths between C_{16} and C_{22}, with C_{18} fatty acids dominating in most plant oils. Amongst enormous types of fatty acids, there are common types found in vegetable oils: they are stearic, palmitic, oleic, linoleic, and linolenic. The name and chemical structure of common fatty acids are shown in Table 2.1. The fatty acid compositions of some vegetable oils are given in Table 2.2. In addition, the properties of vegetable oils and biodiesel from different oil are represented in Tables 2.3 and 2.4, respectively. Moreover, the comparisons of some fuel properties of vegetable oils and their esters with diesel fuel are exhibited in Table 2.5.

Table 2.1 Chemical structure of common fatty acids (Balat and Balat, 2008)

Name of fatty acid	Chemical name of fatty acids	Structure *(xx:y)* *	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	$C_{22}H_{42}O_2$

*xx:y indicates x carbons with y double bonds in fatty acid chain

Table 2.2 Fatty acid composition of some vegetable oils (%) (Balat and Balat, 2008)

Vegetable oil	Fatty acid composition, wt.%						
	Palmitic 16:0	Stearic 18:0	Palmitoleic 16:1	Oleic 18:1	Linoleic 18:2	Ricinic 12-OH-oleic	Others
Tallow	29.0	24.5	-	44.5	-	-	-
Coconut oil	5.0	3.0	-	6.0	-	-	65.0
Olive oil	14.6	-	-	75.4	10.0	-	-
Groundnut oil	8.5	6.0	-	51.6	26.0	-	-
Cotton oil	28.6	0.9	0.1	13.0	57.2	-	0.2
Corn oil	6.0	2.0	-	44.0	48.0	-	-
Soybean oil	11.0	2.0	-	20.0	64.0	-	3.0
Hazelnut kernel	4.9	2.6	0.2	81.4	10.5	-	0.3
Poppy seed	12.6	4.0	0.1	22.3	60.2	-	0.8
Rapeseed	3.5	0.9	0.1	54.1	22.3	-	9.1
Safflower seed	7.3	1.9	0.1	13.5	77.0	-	0.2
Sunflower seed	6.4	2.9	0.1	17.7	72.8	-	0.1
Castor oil	-	3.0	3.0	3.0	1.2	89.5	0.3

Table 2.3 Properties of vegetable oils (Barnwal and Sharma, 2005)

Vegetable oil	Kinematic viscosity at 38°C (mm²/s)	Cetane number[a]	Heating value (MJ/kg)	Cloud Point (°C)	Pour Point (°C)	Flash Point (°C)	Density (kg/l)
Corn	34.9	37.6	39.5	-1.1	-40.0	277	0.9095
Cottonseed	33.5	41.8	39.5	1.7	-15.0	234	0.9148
Crambe	53.6	44.6	40.5	10.0	-12.2	274	0.9048
Linseed	27.2	34.6	39.3	1.7	-15.0	241	0.9236
Peanut	39.6	41.8	39.8	12.8	-6.7	271	0.9026
Rapeseed	37.0	37.6	39.7	-3.9	-31.7	246	0.9115
Safflower	31.3	41.3	39.5	18.3	-6.7	260	0.9144
Sesame	35.5	40.2	39.3	-3.9	-9.4	260	0.9133
Soya bean	32.6	37.9	39.6	-3.9	-12.2	254	0.9138
Sunflower	33.9	37.1	39.6	7.2	-15.0	274	0.9161
Palm	39.6	42.0	-	31.0	-	267	0.9180
Babassu	30.3	38.0	-	20.0	-	150	0.9460
Diesel	3.06	50	43.8	-	-16.0	76	0.855

[a] Cetane number (CN) is a measure of ignition quality of diesel fuel.

As shown in Table 2.3, the properties of vegetable oils such as the cetane number and heating value of vegetable oils are relatively similar to that of fossil diesel. Therefore, vegetable oils are attractive alternative energy source. However, the value of viscosity and flash point are much greater than diesel fuels and the use of pure vegetable oils directly as diesel fuels leads to a number of problems. The extremely high viscosity of vegetable oils is the main cause of severe operation problems which are poor fuel atomization, incomplete combustion, carbon deposition on the injectors, and fuel build-up in the lubricant oils (Encinar *et al.*, 2002). For the high flash point value, it provides low volatility characteristics that lead to more deposit formation and carbonization. In addition, the combination of high viscosity and flash point of vegetable oils causes poor cold engine start up and ignition delay. Thus, although short-term use of neat vegetable oils shows promising results, problems appear after the engine has been operated for longer periods. These include injector coking with trumpet formation, more carbon deposits and piston oil ring sticking, as well as thickening and gelling of the engine lubricating oil (Rakopoulos *et al.*, 2006). There are a number of ways to reduce the viscosity of vegetable oil. Dilution, micro-emulsification, pyrolysis, and transesterification are the four techniques applied to solve the problems encountered with the high fuel viscosity. One of the most common methods used to reduced oil viscosity in biodiesel industry is called transesterification (Demirbas, 2008).

Table 2.4 Properties of biodiesel from different oils (Barnwal and Sharma, 2005)

Vegetable oil methyl esters (biodiesel)	Kinematic viscosity (mm²/s)	Cetane number	Lower heating value (MJ/kg)	Cloud Point (°C)	Pour Point (°C)	Flash Point (°C)	Density (kg/l)
Peanut	4.9	54	33.6	5	-	176	0.883
Soya bean	4.5	45	33.5	1	-7	178	0.885
Babassu	3.6	63	31.8	4	-	127	0.875
Palm	5.7	62	33.5	13	-	164	0.880
Sunflower	4.6	49	33.5	1	-	183	0.860
Tallow	-	-	-	12	9	96	-
Diesel	3.06	50	43.8	-	-16	76	0.855
20 % biodiesel blend	3.2	51	43.2	-	-16	128	0.859

Table 2.5 Comparison of some fuel properties of vegetable oils and their esters with diesel fuel (Demirbas, 2005)

Fuel type	Calorific value (MJ/kg)	Density (kg/m$^{3)}$	Viscosity at 300 K (mm^2/s)	Cetane number
No. 2 diesel fuel[a]	43.4	815	4.3	47.0
Sunflower oil	39.5	918	58.5	37.1
Sunflower methyl ester	40.6	878	10.3	45.5
Cottonseed oil	39.6	912	50.1	48.1
Cottonseed methyl ester	40.6	874	11.1	45.5
Soybean oil	39.6	914	65.4	38.0
Soybean methyl ester	39.8	872	11.1	37.0
Corn oil	37.8	915	46.3	37.6
Opium poppy oil	38.9	921	56.1	-
Rapeseed oil	37.6	914	39.2	37.6

[a] No. 2 diesel fuel is the primary fuel for mobile diesel engine applications.

The properties of vegetable oils after they are transesterificated are shown in Table 2.4. It shows that both the viscosity and flash point values are reduced, particularly the viscosity which gets close to the value of diesel fuels. In the same way, the comparisons of some fuel properties of vegetable oils and their esters with diesel fuel are summarized and represented in Table 2.5. This table obviously shows that the viscosity of biodiesel becomes lower as compared to its raw oil. However, the viscosity of biodiesel is still more than that of diesel fuel.

2.2 Transesterification of Vegetable Oils

For solving the problems related with high fuel viscosity, several methods can be applied. There are four possible treatments: dilution, micro-emulsification, pyrolysis, and transesterification. The last method has doubtlessly been the most common method employed.

Transesterification is, otherwise, known as alcoholysis. It is the reaction processes by means of which triglyceride molecules present in vegetable oils or animal fats react with an alcohol in the presence of a catalyst to form esters and glycerols, as shown in Figure 2.2. Since, this figure shows the transesterification reaction by using methanol, it is also called methanolysis.

$$
\begin{array}{lll}
CH_2-O-CO-R_1 & & CH_3-O-CO-R_1 \quad CH_2-OH \\
| & \textit{Catalyst} & | \\
CH-O-CO-R_2 \;+\; 3\,CH_3-OH \;\;\rightleftharpoons\;\; & CH_3-O-CO-R_2 \;+\; CH-OH \\
| & & | \\
CH_2-O-CO-R_3 & & CH_3-O-CO-R_3 \quad CH_2-OH \\
\textit{Triglycerides} \qquad \textit{Methanol} & & \textit{Methyl Esters} \qquad \textit{Glycerol}
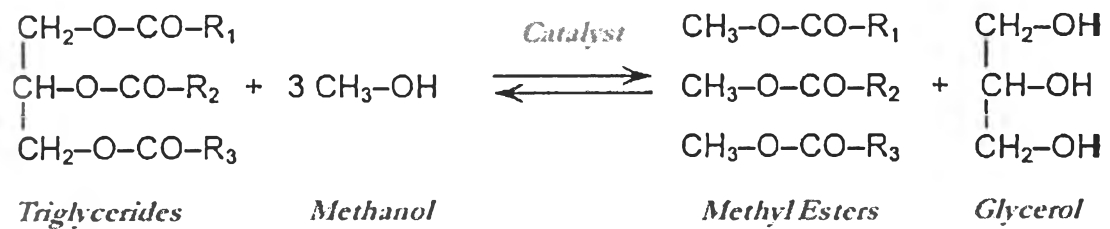\end{array}
$$

Figure 2.2 Triglycerides transesterification reaction with methanol (Borges and Díaz, 2012).

When the transesterification reaction with alcohol proceeds, the first step is the triglycerides to diglycerides conversion, which is followed by the subsequent higher glycerides to lower glyceride conversion and then to the glycerol, yielding one methyl ester molecule from each glyceride at each step. These conversion steps are presented in Figure 2.3.
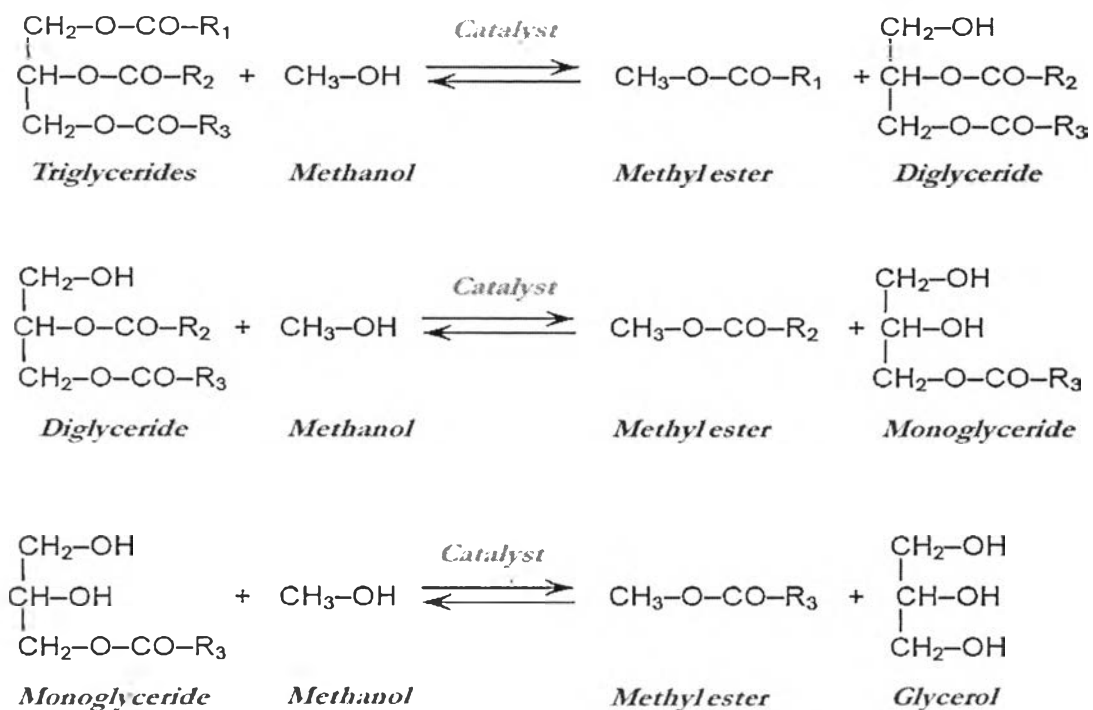
$$CH_2-O-CO-R_1$$
$$CH-O-CO-R_2 \; + \; CH_3-OH \; \underset{\longleftarrow}{\overset{Catalyst}{\longrightarrow}} \; CH_3-O-CO-R_1 \; + \; CH-O-CO-R_2$$
$$CH_2-O-CO-R_3 \qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2-O-CO-R_3$$

Triglycerides   *Methanol*   *Methyl ester*   *Diglyceride*

$$CH_2-OH$$
$$CH-O-CO-R_2 \; + \; CH_3-OH \; \underset{\longleftarrow}{\overset{Catalyst}{\longrightarrow}} \; CH_3-O-CO-R_2 \; + \; CH-OH$$
$$CH_2-O-CO-R_3 \qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2-O-CO-R_3$$

Diglyceride   *Methanol*   *Methyl ester*   *Monoglyceride*

$$CH_2-OH$$
$$CH-OH \; + \; CH_3-OH \; \underset{\longleftarrow}{\overset{Catalyst}{\longrightarrow}} \; CH_3-O-CO-R_3 \; + \; CH-OH$$
$$CH_2-O-CO-R_3 \qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2-OH$$

Monoglyceride   *Methanol*   *Methyl ester*   *Glycerol*

Figure 2.3 Transesterification reaction steps (Borges and Díaz, 2012).

Amongst various types of alcohol such as methanol, ethanol, propanol, and butanol, methanol and ethanol are used commercially. When methanol is applied as reactant, reaction product will be a fatty acid methyl esters mixture (FAME). If ethanol were used instead of methanol, a fatty acid ethyl esters mixture (FAEE) will be produced (Borges and Díaz, 2012). Nevertheless, methanol is widely used in biodiesel production due to its low cost and its physical and chemical advantages (Ramadhas *et al.*, 2004).

In general, there are three common kinds of catalysts which can be used in transesterification reaction in order to enhance the reaction rate. There are strong alkalis, strong acids, and enzymes. Since, the main advantages of using a strong alkali as a catalyst are shorter reaction time, low cost, well-dissolve in methanol, and less of amount catalyst required in the manufacturing process of transesterification reaction. Therefore, strong alkaline catalysts including sodium hydroxide (NaOH) and potassium hydroxide (KOH), are widely used in the industry for mass biodiesel production (Shahbazi *et al.*, 2012). In addition, the use of alkaline catalyst was supported in Velasquez-Orta *et al.*, 2012's work. The experiment was designed in

order to understand the impact of process variables (catalyst ratio, solvent ratio, and reaction time) in the production of Fatty Acid Methyl Ester (FAME) from *Chlorella vulgaris* microalgae. The result showed that the alkaline catalyst (sodium hydroxide) outperformed the acid catalyst (sulphuric acid) obtaining higher conversions at lower reaction times. In addition, Leevijit *et al.* (2004) studied the product concentrations by using a second-order reaction mechanism and the result showed that the yield of the reaction which was carried out with KOH as a catalyst has a higher value than the reaction when NaOH was used as a catalyst.

According to Figure 2.2, it shows that the transesterification is one of the reversible reactions and proceeds substantially by mixing the reactants. Therefore, the excess methanol is required for shifting the equilibrium to the products side and allowing its phase separation from the glycerol formed. To complete transesterification process, a 3:1 molar ratio of methanol to triglycerides is needed (Ramadhas *et al.*, 2004). In practice, this ratio needs to be greater in order to impulse the equilibrium to a maximum methyl ester yield. The methyl ester products, also known as biodiesel, are really attractive as alternative energy.

Furthermore, Agarwal and co-workers (2012) synthesized biodiesel by using KOH as homogeneous and heterogeneous (KOH/Al_2O_3) catalyst. The objective of their work was to study the catalytic behavior for biodiesel synthesis by methanolysis of waste cooking oils. They reported that heterogeneous catalyst should be preferred due to easy separation of glycerol, no water washing, and reusability of catalyst. In addition, it can be used efficiently for continuous process because of reusability of the catalyst. However, there is no reuse of the catalyst in case of homogenous one. Apart from that, the optimum conditions for maximum yield for heterogeneous catalyzed reaction were obtained at 70 °C, 2 hours reaction time, 5 % catalyst concentration, 15 wt% catalyst loading, and 9:1 methanol to oil molar ratio. Whereas for homogeneous catalyzed reaction the optimum reaction conditions were 70 °C reaction temperature, 1 hour reaction time, 1 % catalyst concentration, and 6:1 methanol to oil molar ratio.

2.3 Biodiesel

Biodiesel is defined as the monoalkyl ester of long chain fatty acids derived from renewable lipid feedstock such as vegetable oils or animal fats, for use in compression-ignition engines with little or no modification. Biodiesel is the name for a variety of ester based oxygenated fuel from renewable biological resources. The main reaction to produce this fuel is transesterification reaction, where triglycerides interact with alcohol, in the presence of a catalyst, to produce ester and glycerin. By this means, three smaller molecules of ester and one molecule of glycerin are obtained from one molecule of fat/oil. Glycerin, also known as glycerol, is removed as byproduct and esters are known as biodiesel (Fazal *et al.*, 2011). Biodiesel is an environmentally friendly liquid biofuel similar to conventional petro-diesel in term of fuel quality and combustion characteristics (Jain and Sharma, 2011). From this point of view, it is considered as a promising alternative fuel.

As shown in Table 2.6, the properties of biodiesel and petroleum-based diesel fuels are compared. This table shows that biodiesel produced from various vegetable oils give the viscosity values closer to those of petroleum-based diesel fuels. In addition, cetane numbers and flash points of biodiesel are higher than diesel fuel; while their heating values are slightly lower. Since, the characteristics of biodiesel are rather similar to those of diesel fuel therefore, biodiesel is evaluated as a strong candidate as an alternative to diesel fuel.

Table 2.6 Comparison between properties of biodiesel and petroleum-based diesel fuel (Fukuda *et al.*, 2001)

Vegetable oil methyl ester	Kinetic 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

Apart from the similar characteristics between biodiesel and petroleum- based diesel, biodiesel has lot of advantages over petroleum-based diesel which makes it more applicable and more compatible to work with petroleum-based. Among the advantages of biodiesel fuel, some of them include the followings: safe to use in all conventional diesel engines, offers the same performance and engine durability as the petroleum-based diesel fuel, non-flammable and nontoxic, reduces tailpipe emissions, visible smoke and noxious fumes and odors (Bozbas *et al.*, 2008). In addition, the main advantages that have attracted many views are biodegradability, renewability, and nontoxicity; particularly free of sulfur and aromatic compounds. That causes biodiesel to have lower emissions of SO_x, CO, unburnt hydrocarbon and particulate matter as compared to petroleum-based diesel fuel (Chen and Luo, 2011).

However, using biodiesel can lead to several problems such as emissions of nitrogen oxides from combustion, decrease in horsepower, and degradation and softening of the rubber and plastics in engine. The main disadvantages of biodiesel when compared to diesel oil are: high viscosity, high density, and low volatilization (high flash point) (Freire *et al.*, 2012). Besides, there are some specific problems related to its properties especially oxidative stability and cold flow properties.

2.4 Properties and Stability of Biodiesel

There are many properties which are important and influenced by fatty acid methyl ester (FAME) composition. For example, cetane number, viscosity, lubricity, cloud point, pour point, flash point, and etc. In general, sulfur content, iodine value (IV), and cold flow properties are mostly focused on as compared to others. For stability, oxidative stability and thermal stability are the most concerns in many researches.

2.4.1 Sulfur Content

Generally, most biodiesel fuels have very low sulfur content in their compound, with no significant differences among them. All biodiesels are well below the sulfur specification maximum in ASTM D6751 (15 ppm) and EN 14214 (10 ppm) (Hoekman *et al.*, 2012). Because of low sulfur content in its compound, the

emission of SO_x after biodiesel combustion is also small which is much lower as compared to diesel fuels.

Although the low sulfur content in biodiesel is not harmful to human, one of the major problems associated with the use of platinum and palladium in hydrogenation reaction is their high sensitivity to sulfur compounds that are usually present in feedstocks (Barbier *et al.*, 1990). The sulfur poisoning of noble metals has been shown to occur via two routes, (i) a direct poisoning of the metal surface and (ii) a sintering and a growth of metal particles due to a decrease of metal–support interactions (Simon *et al.*, 2003). Numwong *et al.* (2012) studied the effect of support acidic properties on sulfur tolerance of Pd catalysts for partial hydrogenation reaction using rapeseed oil as biodiesel feedstock. They proposed that after adding additional sulfur, the activity decreased by about 30–50 % of the original activity. In the same year, Yu *et al.* also suggested that weak adsorption of tetralin on metal site causes the *trans*-decalin isomer to be preferred. In addition, with a higher sulfur content in rapeseed BDF, a lower composition of *trans*-isomers was obtained. This was attributed to a decrease in metal sites, with the hindrance effect, after adding more sulfur, resulting in a greater difficulty in the rotation of the partial hydrogenated intermediate to generate the *trans*-form.

2.4.2 Iodine Value (IV)

The iodine value is also known as iodine adsorption value, iodine number, or iodine index. This value is the mass of iodine in grams that is consumed by 100 grams of a chemical substance. Iodine value is often used to measure the amount of unsaturated fatty acids which are in the form of double bonds. The higher the iodine value, the more C=C bonds are present in the fat.

ASTM D6751 does not include a specification for IV, while EN 14214 has a maximum IV specification of 120 mg of I_2/100 g FAME. Rapeseed biodiesel is just below this value of 120, whereas soybean and sunflower biodiesel are just over the limit. Biodiesel from camellia and safflower have even higher IV levels, and would clearly be "off-spec" with respect to EN 14214, while all other biodiesel types investigated here are well below the 120 IV level. Coconut-derived

biodiesel is highly saturated, and has an exceptionally low IV of about 19 (Hoekman *et al.*, 2012).

2.4.3 Cold Flow Properties

Cold flow properties of a fuel defined its behavior in a given climate conditions. Partial solidification is the reaction that a fuel may have in cold weather and can cause clogged fuel supply lines and filters, which creates problems for engine ignition (Mittelbach and Remschmidt, 2006). The most regularly used parameters to determine the cold flow properties of diesel are cloud point (CP) at which crystallization begins, cold-filter plugging point (CFPP) at which fuel starts to plug a fuel filter, and pour point (PP) at which fuel no longer pours (Tang, 2008). Generally, these parameters measure the temperature at which the fuel begins to have changes in its liquid phase and it gets crystallized, producing changes in its fluidity and leading to performance problems (Zuleta *et al.*, 2012). Cold flow properties of biodiesel also depend on the structure of alkyl esters. The melting point increases with chain length and decreases with the increase of double bonds. At room temperature, saturated fatty acids with 10 or more carbons are solid, while unsaturated fatty acids are liquid. Among the saturated fatty acids, even-chain fatty acids have higher melting points than odd-chain fatty acids. In addition, the *cis* configurations and/or the presence of –OH groups in the chain significantly reduce the melting point (Asadauskas and Erhan, 1999).

The African oil palm (*Elais guinehensis*) is the oilseed species with the highest oil production per hectare (4 ton/half year) (Rival, 2007). It is the main source of biodiesel production in tropical countries. In addition, this biodiesel provides good oxidative stability because of the high content of saturated fatty acids and natural antioxidants. Unfortunately, this high content of saturated fatty acids causes poor cold flow properties.

2.4.4 Oxidative Stability

The oxidative stability of biodiesel is another extremely important property, particularly in places with warm climate, as this property provides an estimate of the storage time of biodiesel in normal conditions. It is thus a parameter that describes the degradation tendency of biodiesel and is of great importance in the

context of possible problems with engine parts. Oxidation of biodiesel is due to several factors, among which, the most important, are: the number of double bonds and the existence of allylic and bis-allylic hydrogens (Karavalakis *et al.*, 2010). Esters with large amounts of unsaturated fatty acids are much more susceptible to oxidation than those that are rich in saturated fatty acids (Freire *et al.*, 2012). Oxidation is a very complex process which involves with several stages including initiation, propagation, and termination, as represented in Figure 2.4.

Initiation	$RH \rightarrow R^{\bullet}$
Propagation	$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$
	$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$
Termination	$R^{\bullet}, ROO^{\bullet} \rightarrow$ Stable products
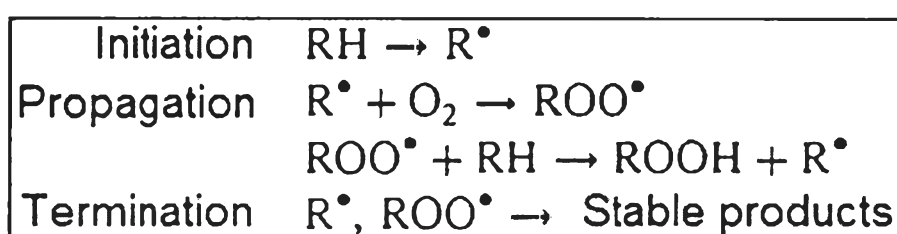
Figure 2.4 Stages involved in oxidation of lipids (Zuleta *et al.*, 2012).

After the oxidation reaction proceeds, the main oxidation products are peroxides and hydroperoxides. During further degradation, these products form shorter-chain compounds such as low molecular weight acids, aldehydes, ketones, and alcohol (Tang *et al.*, 2008). The appearance of alcohols decreases the flash point, whereas the appearance of acids increases the total acidity and the risk of corrosion. Further reactions with the unstable hydroperoxide species with another fatty acid chain may form high molecular weight materials such as dimer or trimer acids which may lead to filter blocking, injector failures and deposit formation (Karavalakis *et al.*, 2010). Zuleta *et al.* (2012) studied about oxidative stability and cold-filter plugging points (CFPP) of blends of biodiesel from palm, sacha-inchi, jatropha, and castor oils. They found that a higher content of polyunsaturated methyl esters decreases the oxidative stability and a higher content of saturated methyl esters increases the CFPP. For their experiment, oxidation stability varies in the sequence of castor>palm>jatropha>sacha-inchi. As for the cold flow properties, the CFPP varies in the order sacha-inchi>castor>jatropha>palm. Castor oil biodiesel has a CFPP (-7 °C) slightly lower than the melting point of methyl ricinoleate (-5.85 °C) which is explained because this biodiesel is mostly made of this methyl ester

(89.4 %). Therefore, the presence of small amounts (8.6 %) of unsaturated methyl esters (oleate, linoleate, and linolenate) contributes to the lowering of CFPP.

Since these fuel instabilities can increase the formation of unwanted substances in biodiesel and its blend, when such fuel is used, for example, it diminishes the engine performance due to fuel filter plugging, injector fouling, and deposit formation in engine combustion chamber. Therefore, the method to increase biodiesel stability is important. Amongst various types of method, partial hydrogenation is widely used in order to improve the oil properties and stability.

2.5 Partial Hydrogenation

The partial hydrogenation of vegetable oils is of the special interest in the process of modification of edible fats and oils. The first purpose of this process is to change the normal liquid oil into a semisolid product with a desired consistency in a certain temperature range. The second one is to reduce the diene and triene contents of the product to a minimum, thus contributing to the stability of the product against oxidative rancidity (Gabrovska *et al.*, 2006).

This is a chemical process by which hydrogen is added to a carbon–carbon double bond in the glycerides of an oil molecule (M *et al.*, 2011). The reaction takes place in the presence of a catalyst, usually Raney nickel or Ni supported on silica or alumina. However, Ni is known to have toxicity if not completely removed especially using in conventional industrial processes. In addition, the *trans*-fatty acid content from industrial processes using Ni is relatively high. The use of catalyst can be divided into 2 types: homogeneous catalysts and heterogeneous catalysts. Heterogeneous catalysts have several advantages over homogeneous ones, including separation, recovery, ease of handling and recycling, and stability (Hindle *et al.*, 2006 and Qiu *et al.*, 2011). Therefore, they are widely used.

As shown in Figure 2.5, the partial hydrogenation of polyunsaturated methyl esters of linseed (MELO), sunflower (MESO), and soybean oils (MESBO) to their monounsaturated (C18:1) counterparts catalyzed by Rh/TPPTS complexes in aqueous/organic two-phase systems. The term "regiomers" refers to all regio-isomers obtained from hydrogenation and/or positional isomerization (along the carbon

chain) reactions and all other geometric isomers formed via *cis/trans* isomerization reactions. The results showed that the partial hydrogenation gives high selectivities up to 79.8 mol% of C18:1 esters which is upgraded as the 1st generation biodiesel fuel of improved oxidative stability (Bouriazos *et al.*, 2010).
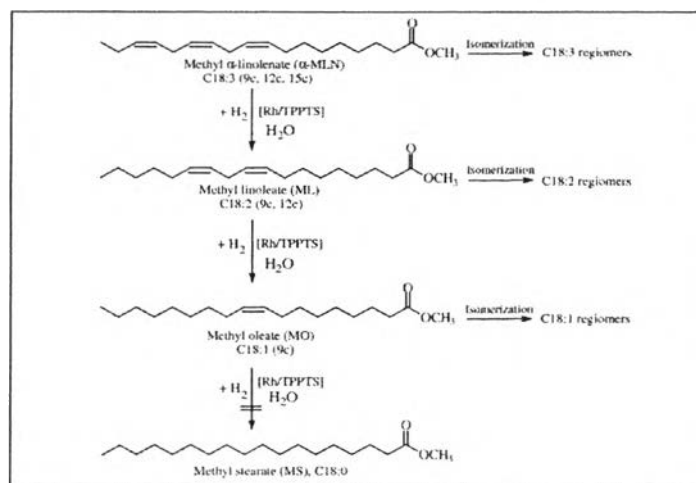

Figure 2.5 Selective hydrogenation of polyunsaturated methyl esters of linseed (MELO), sunflower (MESO) and soybean oils (MESBO) (Bouriazos *et al.*, 2010).

The quality and physical properties of the hydrogenated oil are not only greatly influenced by the number of double bonds present but also by the *cis-trans*-isomers of fatty acids. During the hydrogenation, the monounsaturated fatty acids originally present or formed as products may isomerize to form the *trans*-fatty acids, which are nutritionally inferior to the naturally occurring *cis*-isomers. The *trans*-fatty acids (TFA) have been reported to be unfavorable to human diet due to undesirable health effects. It is associated with increased risk of coronary heart disease (CHD). Studies on dietary fat intake suggest a four- to five-fold higher risk of CHD per gram of TFA than per gram of saturated fat (Mozaffarian *et al.*, 2006). Several public health organizations have consequently recommended that the intake of TFA should be lowered as much as possible (Stender and Dyerberg, 2003). This causes the increased demand for reduction of *trans*-fatty acid formation during hydrogenation.

To replace the supported Ni catalysts, supported noble metals catalysts have been tried as substitutes. The use of noble metals provide more active and/or more

selective as compared to Ni. The other advantages of supported noble metal catalysts are mild process conditions, easy separation, and better handling properties. The most commonly reported as active catalysts are platinum (Pt) and palladium (Pd). The established order for increasing *trans* formation amongst all reported oil hydrogenation catalysts is: Pt<Rh<Ir<Ni<Pd<Cu (Veldsink *et al.*, 1997).

In 2004, Nohair and co-workers studied the selective hydrogenation of ethyl esters of traditional sunflower oil (SOEE) in the presence of monometallic catalysts containing noble metals (Pd, Pt, Ru) supported over silica. They reported that the activity decreases in the order Pd>Pt>Ru at 40 °C under 10 bar of hydrogen. However, the three noble metals are not selective in *cis* oleic isomer since *trans* oleic and stearic derivatives were produced in large amounts.

McArdel *et al.* (2011) studied the selective hydrogenation of sunflower oil using a variety of heterogeneous catalysts. The reaction was carried out in a batch reaction at 170 °C under 3 bar. Palladium and Platinum supported on Al_2O_3, ZrO_2, and TiO_2 were screened. From the experiment, they found that Pd based catalysts are more active than the conventional Ni catalyst and Pt based catalysts for the hydrogenation of vegetable oil. However, the Pt-based catalysts in general produced less *trans*-fatty acids during hydrogenation. The level of *trans* could be further reduced by increasing the operating pressure to 10 bar and reducing the reaction temperature to 100 °C. The reduction in *trans* formation was most significant for the Pt based catalyst.

There are many researches which studied about the effect of support on activity and selectivity of metal supported catalysts, for example, Fernández and co-workers (2009) reported that Pd catalysts showed a higher activity, similar *trans*-isomer formation, and were more selective towards monounsaturated fatty acid formation than Ni catalysts. On the other hand, under the studied operating conditions (100 °C and 4.135 bar for 1 h, using 250 cm^3 of commercial refined sunflower oil), the different supports did not improve significantly the selectivity or the activity of the reaction. In addition, they found that most Pd particles (2–4.5 nm) were not located in the micropores of the samples, suggesting that the microporosity did not affect the activity of the catalysts. This study supported the work done by

Nohair *et al.* (2005). They studied the selective hydrogenation of ethyl esters of sunflower oil (SOEE) in the presence of supported Pd catalysts at low temperature (40 °C) in ethanol as solvent. They found that the use of various oxide supports (α-Al_2O_3, γ-Al_2O_3, TiO_2, MgO, ZnO, CeO_2, $CeZrO_2$) to deposit palladium did not improve the selectivity of the reaction toward the *cis* C18:1 compared to Pd/SiO_2 catalysts.

Although the types of support do not significantly influence the activity and selectivity of the hydrogenation reaction, the pore size and shape of support have an effect on it. Jonker *et al.* (1998) reported that the transport limitations on the hydrogenation and the oil have a strong influence on both the selectivity and the activity. Therefore, an adequately porous support is required to facilitate the transfer of bulky triglyceride molecules and hydrogen to active sites on the catalyst (McArdle *et al.*, 2010).

The use of suitable porous support is supported by several researches. For example, Mäki-Arvela et al. (2008) studied about the catalytic hydrogenation using different Pd- and Ru-supported catalysts. The result showed that supported Ru was more prone to deactivation by coking than Pd. In addition, they reported that the use of mesoporous structure of the catalyst was preferable to achieve fast hydrogenation of the intermediate products, thus promoting the formation of stearic acid.

Furthermore, Tamai and co-workers (2009) prepared the Pd supported on microporous and mesoporous activated carbons in order to investigate their catalytic activities for the hydrogenation of methyl linoleate. They found that the mesopore surface area volume decreased with supporting Pd particles. The amounts of Pd particles supported on mesoporous supports are higher than those on microporous one. From this point, Pd supported mesoporous exhibited the higher catalytic activities than microporous support catalyst.

The mesoporous material has a elaborate framework which came from the co-operative assembly of an inorganic precursor, for example, a silica source with an organic structure directing template. By using surfactant as a templating agent gives the advantage of capability to adjust the surface properties directly through the addition of organic modifiers. Because of the advantage of tailored structural

properties, the use of these mesoporous materials, particularly silica, as catalysts in the oils and fats industry is growing (Mbaraka and Shanks, 2006). In addition, there are many authors that are using solid mesoporous silica support in their works such as Plourde *et al*. (2004), Cepeda and Calvo (2008), and Belkacemi *et al*. (2006).

The most popular family of mesoporous molecular sieves is named MCM-41. These supports have already been used for the transition metals, such as Ni, Pt, Pd, and Cu, and the obtained materials have been applied in several processes for example, desulfurization, deodorization, and selective oxidation (Wojcieszak *et al*., 2004). MCM-41 material exhibits extremely interesting textural properties (high specific surface area in the 600–1000 m^2/g) and possesses a hexagonal arrangement of uniformly sized unidimensional mesopores (homogeneous pore diameter from 1.5 to 10 nm), which are required when bulkier molecules need to be processed (Wojcieszak *et al*., 2004 and Nava *et al*., 2009). However, mesoporous MCM-41-type silica, with a uniform pore diameter of 3.5 nm, is almost inactive, because the small number of acid sites strong enough to catalyze the hydrogenolysis/ring-opening reactions. Therefore, the introduction of heteroatoms (such as Al, Ti, or Zr) into the siliceous framework is applied to increase the acidity of mesoporous solids (Albertazzi *et al*., 2004). In 2003, Albertazzi and co-workers investigated the behavior of single noble-metal ions inserted in a mesoporous MCM-41 aluminosilicate framework for hydrogenation of naphthalene. In their work, the acidity and dimensions of the uniform system of channels was tailored by selecting the Si:Al ratio and the dimension of the template, respectively. Furthermore, MCM-41 also has another important advantage over zeolitic materials, that is a   lower strength of acidic OH groups than those in zeolites. Therefore, it leads to lower coke formation when using MCM-41 as supports.

Apart from MCM-41, mesoporous silicon dioxide (SiO_2) is also broadly used because it is not expensive as well as there is an easy and cheap way for its preparation. In addition, it is highly robust and has higher long term stability compared with the zeolitic materials. Besides, the work done by Hoelderich and co-workers demonstrated that the cheap silica support performs similar properties and yields as the very expensive MCM-41 based catalysts. Moreover, the use of SiO_2 support was sustained by Yingxin *et al*., 2007's work. They studied the effects of

various supports (SiO$_2$, TiO$_2$, γ-Al$_2$O$_3$, MgO, and diatomite carriers) on the activity of supported nickel catalysts for hydrogenation of *m*-dinitrobenzene to *m*-phenylenediamine. The results showed that, among the catalysts tested, SiO$_2$ supported Ni catalyst exhibited highest activity and selectivity towards *m*-phenylenediamine. Higher activity could be attributed to the weaker metal-support interaction due to Ni species present as crystallized Ni metal particles.