

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Vegetable Oils

The use of vegetable oils, such as palm, soybean, sunflower, peanut and olive oils as alternative fuels for diesel engines dated back almost a century ago. Due to a rapid decline in crude oil reserves, the use of vegetable oils as diesel fuels is promoted in many countries. Depending upon climate and soil conditions, different nations are looking into different vegetable oils for diesel fuels. For example, soybean 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 are being considered as substitutes for diesel fuels (Srivastava and Prasad, 2000).

Vegetable oils are triglycerides, which are esters of one glycerol with three long-chain acids (which can be different types), commonly called fatty acids. The major component of vegetable oils is triglycerides. Vegetable oils comprise 90 to 98% triglycerides and small amounts of mono- and diglycerides. They contain free fatty acids (generally 1 to 5%) and traces of water (Srivastava and Prasad, 2000). The general formation of triglyceride is shown in Figure 2.1.

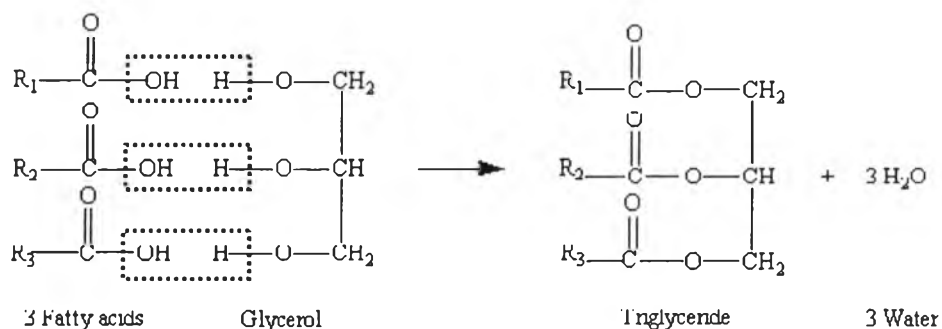


Figure 2.1 General formation of triglyceride (Swern, 1979).

As shown in 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. Different fatty acids have

different carbon chain length and number of double bonds. This reason leads to the different characteristics of vegetable oil. The common fatty acids found in vegetable oils are, palmitic, stearic, oleic, linoleic and linolenic. The name and chemical structure of common fatty acids are shown in Table 2.1. Fatty acid compositions in different types of vegetable oils are summarized in Table 2.2 and some properties of the vegetable oils are shown in Table 2.3.

Table 2.1 Chemical structure of common fatty acids (Srivastava and Prasad, 2000)

Fatty acid	Systematic name	Structure ^(a)	Formula
Lauric	Dodecanoic	12:0	C ₁₂ H ₂₄ O ₂
Myristic	Tetradecanoic	14:0	C ₁₄ H ₂₈ O ₂
Palmitic	Hexadecanoic	16:0	C ₁₆ H ₃₂ O ₂
Stearic	Octadecanoic	18:0	C ₁₈ H ₃₆ O ₂
Arachidic	Eicosanoic	20:0	C ₂₀ H ₄₀ O ₂
Behenic	Docosanoic	22:0	C ₂₂ H ₄₄ O ₂
Lignoceric	Tetracosanoic	24:0	C ₂₄ H ₄₈ O ₂
Oleic	cis-9-Octadecenoic	18:1	C ₁₈ H ₃₄ O ₂
Linoleic	cis-9,cis-12-Octadecadienoic	18:2	C ₁₈ H ₃₂ O ₂
Linolenic	cis-9,cis-12,cis-15-Octadecatrienoic	18:3	C ₁₈ H ₃₀ O ₂
Erucic	cis-13-Docosenoic	22:1	C ₂₂ H ₄₂ O ₂

^(a)xx:y indicates x carbons with y double bonds in fatty acid chain

Table 2.2 Fatty acid composition in different types of vegetable oils (Srivastava and Prasad, 2000, and Ramos *et al.*, 2009)

Vegetable oil	Fatty acid composition, wt.%									
	14:0	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Palm	1	37	7	tr ^(a)	0	tr ^(a)	46	0	9	tr ^(a)
Corn	0	7	2	tr ^(a)	0	0	66	0	25	tr
Cottonseed	0	28	1	0	0	0	13	0	58	0
Crambe	0	2	1	2	1	1	19	59	9	7
Linseed	0	5	2	0	0	0	20	0	18	55
Peanut	0	11	2	1	2	1	48	0	32	1
Rapeseed	0	3	1	0	0	0	64	0	22	8
Safflower	0	9	2	0	0	0	12	0	78	0
H.O. Safflower	tr	5	2	tr	0	0	79	0	13	0
Sesame	0	13	4	0	0	0	53	0	30	0
Soya bean	0	12	3	0	0	0	23	0	55	6
Sunflower	0	6	3	0	0	0	17	0	74	0

^(a)tr = traces

As shown in Table 2.3, 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 petroleum-based diesel fuels. Due to the high viscosity of vegetable oils, the injection process is interfered and led to poor fuel atomization. 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. In the long-term operation, vegetable oils normally develop gumming, injector coking and ring sticking (Srivastava and Prasad, 2000). Therefore, considerable efforts must be made to develop vegetable oil derivatives that close to the properties and performance of the petroleum-based diesel fuels.

Table 2.3 Properties of the vegetable oils (Marchetti *et al.*, 2007)

Vegetable oil	Kinematic 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	N/D ^(a)	176	0.883	33.6
Soybean	4.5	45	1	-7	178	0.885	33.5
Babassu	3.6	63	4	N/D ^(a)	127	0.875	31.8
Palm	5.7	62	13	N/D ^(a)	164	0.880	33.5
Sunflower	4.6	49	1	N/D ^(a)	183	0.860	33.5
Tallow	N/D ^(a)	N/D ^(a)	12	9	96	N/D ^(a)	N/D ^(a)
Diesel	3.06	50	N/D ^(a)	-16	76	0.855	43.8
20% biodiesel blend	3.2	51	N/D ^(a)	-16	128	0.859	43.2

^(a)Not determined

2.2 Derivatives of Triglycerides as Biodiesel

As previously described, there are many problems associated with the use of vegetable oils directly as fuels for diesel engine since they have high viscosity, low volatility and some polyunsaturated fatty acids. To overcome these problems, the oil requires slight chemical modifications, which mainly are pyrolysis, dilution, microemulsification, and transesterification. Among these processes, transesterification is the most commonly used method to produce the cleaner and environmentally safer biodiesel from vegetable oils.

Transesterification or alcoholysis is the reaction of fat or oil with an alcohol to form esters and glycerol. A catalyst (a strong acid or base) is usually used to improve the reaction rate and yield. This process has been widely used to reduce the high viscosity of triglycerides (Meher *et al.*, 2006). The transesterification reaction is represented by a general equation, as shown in Figure 2.2.

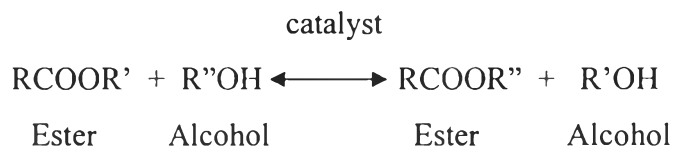


Figure 2.2 General equation of transesterification reaction (Srivastava and Prasad, 2000).

Generally, the alcohols used in the transesterification process are methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are the most frequently used, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides, and NaOH catalyst is easily to dissolve in it (Fangrui and Hanna, 1999). If methanol is used in this process, it is called methanolysis, as presented in Figure 2.3.

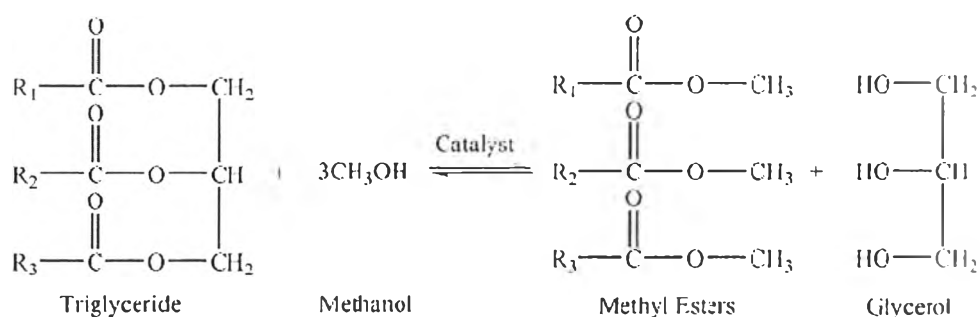


Figure 2.3 Methanolysis of triglyceride (Srivastava and Prasad, 2000).

Due to the fact that the transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants, the excess methanol is required to shift the equilibrium to the products side. To complete a transesterification stoichiometrically, a 3:1 molar ratio of methanol to triglycerides is needed. In practice, the ratio needs to be higher to drive the equilibrium to a maximum methyl ester yield. The methyl ester products (known as biodiesel) are attractive as alternative diesel fuels. The details on biodiesel are given below.

2.3 Biodiesel

Biodiesel is monoalkyl esters of long chain fatty acids derived from renewable feedstock, such as vegetable oils or animal fats, for using as alternative fuel in diesel engine. Biodiesel is usually prepared by the transesterification reaction of triglyceride, which is the main component in vegetable oils with methanol, and called fatty acid methyl ester (FAME). The resulting biodiesel is quite similar to conventional diesel fuel, especially its main characteristics; therefore, it is considered as a possible substitute to conventional diesel fuel.

The properties of biodiesel and petroleum-based diesel fuels are compared and shown in Table 2.4. From this table, it shows that several kinds of biodiesel produced from various vegetable oils have a viscosity close to that of petroleum-based diesel fuels. Their heating values are a little lower, but they have high cetane numbers and flash points. Since the characteristics of biodiesel are generally similar to those of petroleum-based diesel fuels; thus, biodiesel is a strong candidate to replace the petroleum-based diesel fuels.

Table 2.4 Comparison between properties of biodiesel and petroleum-based diesel fuels (Fukuda *et al.*, 2001)

Vegetable oil methyl ester	Kinematic viscosity (mm ² /s)	Cetane number	Lower heating value (MJ/kg)	Cloud point (°C)	Flash point (°C)	Density (g/l)	Sulfur (wt.%)
Peanut	4.9 (37.8°C)	54	33.6	5	176	0.883	N/D ^(a)
Soybean	4.5 (37.8°C)	45	33.5	1	178	0.885	N/D ^(a)
Babassu	3.6 (37.8°C)	63	31.8	4	127	0.879	N/D ^(a)
Palm	5.7 (37.8°C)	62	33.5	13	164	0.880	N/D ^(a)
Sunflower	4.6 (37.8°C)	49	33.5	1	183	0.860	N/D ^(a)
Rapeseed	4.2 (40.0°C)	51–59.7	32.8	N/D ^(a)	N/D ^(a)	0.882	N/D ^(a)
Used rapeseed	9.48 (30.0°C)	53	36.7	N/D ^(a)	192	0.895	0.002
Used corn oil	6.23 (37.0°C)	63.9	42.3	N/D ^(a)	166	0.884	0.0013
Diesel fuel	1.2–3.5 (40.0°C)	51	43.8	N/D ^(a)	N/D ^(a)	0.830– 0.840	N/D ^(a)
JIS-2D (gas oil)	2.8 (30.0°C)	58	42.7	N/D ^(a)	59	0.833	0.05

^(a)Not determined

There are many advantages for using biodiesel. For example, it is renewable resource, biodegradable, nontoxic and essentially contains very low content of sulfur and aromatics, resulting lower emissions of SO_x, CO, un-burnt hydrocarbon and particulate matter as compared to conventional diesel fuel (Karmee *et al.*, 2005).

However, biodiesel properties depend on natural characteristic of starting vegetable oil. Chemical structures that affect the fuel properties of biodiesel are chain length, branching of the chain, degree of saturation, and geometric configuration (*cis* or *trans*) of double bond (Benjumea *et al.*, 2011). Degree of saturation of fatty acid has strong effects on the quality of biodiesel especially oxidative stability and cold flow properties. Biodiesel produced from vegetable oil, which contains high amount of saturated fatty acid has better oxidative stability. However, the higher amount of saturated fatty acid gives worse cold flow property (Sonthisawate *et al.*, 2008). The amount of unsaturation in fatty acid can be determined by iodine value, which is the mass of iodine in grams being consumed by 100 grams of a chemical substance (Ramos *et al.*, 2009). The comparison of typical fatty acid methyl ester (FAME) compositions, iodine value (IV), cloud point (CP), as well as pour point (PP) of the corresponding biodiesel obtained from different types of vegetable oil are shown in Table 2.5

Table 2.5 Comparison of typical fatty acid methyl ester (FAME) compositions, iodine value (IV), cloud point (CP), as well as pour point (PP) of the corresponding biodiesel obtained from different types of vegetable oil (Moser *et al.*, 2007)

Oil:	Rapeseed	Sunflower	Palm	Soybean	Beef tallow	Grease
Region:	Europe	Europe	Tropical	USA	USA	USA
14:0	tr ^(a)	tr	tr	tr	3	1
16:0	4	4	44	11	27	17
18:0	2	5	4	4	7	11
16:1	tr	tr	tr	tr	11	2
18:1	56	81	40	22	48	56
18:2	26	8	10	53	2	10
18:3	10	tr	tr	8	tr	2
Other	2	2	2	2	2	1
IV	94–120	78–90	50–55	120–143	35–48	N/A ^(b)
CP	-3	0	16	0	17	8
PP	-9	-3	13	-2	15	6

^(a)tr = trace

^(b)N/A = not available

2.4 Oxidative Stability of Biodiesel

The oxidative stability of biodiesel has been found to be concerned when the biodiesel is stored over an extended period of time due to the presence of significant amount of unsaturated FAMES. Typically, oxidative stability of biodiesel, determined by induction period with Rancimat test, is an indicator for the stability of biodiesel during its storage. An oxidative stability of minimum 6 hours at 110°C is required according to EN14112 standard. The storage problems can be caused by storage conditions like exposure to air, light, as well as temperature. Oxidation of biodiesel is due to the unsaturation in FAME molecule, which offers high level of

reactivity with oxygen; especially, when it is placed in contact with air or water. The primary oxidation products of double bonds are allylic hydroperoxides, which are unstable and easily to form a variety of secondary oxidation products. This includes the rearrangement of product of similar molecular weights to give short chain aldehydes, acids, and high molecular weight materials (Jain *et al.*, 2010). This fuel instability leads to the sediment and gum formation and fuel darkening. Moreover, hydroperoxides, aldehydes, ketones, and acids, which are produced during the oxidation process, also cause operational problems like fuel filter plugging, injector fouling, and deposit formation in engine combustion chamber (Yamane *et al.*, 2007). Hence, the method to increase biodiesel stability is important.

It is generally known that biodiesel is more active to oxidation than petroleum-based diesel (Yoshimura, 2008). The number of unsaturated bonds in FAME molecules dramatically influences the oxidative and thermal stability of biodiesel. It has been reported that relative oxidation rates of C18:3, C18:2, and C18:1 FAMES are 98, 41, and 1, respectively (Frankel, 1998). This means C18:3 can be oxidized about two times more easily than C18:2 and almost hundred times than C18:1. Figure 2.4 shows the oxidative stability of model compounds (Aldrich reagent, >99% purity) of methyl stearate (C18:0), methyl oleate (C18:1), methyl linoleate (C18:2), and methyl linolenate (C18:3). It apparently shows that as the number of double bonds increases, the oxidative stability decreases dramatically. Therefore, saturation of unsaturated FAMES by hydrogenation is a promising way to improve biodiesel stability without the addition of any antioxidant.

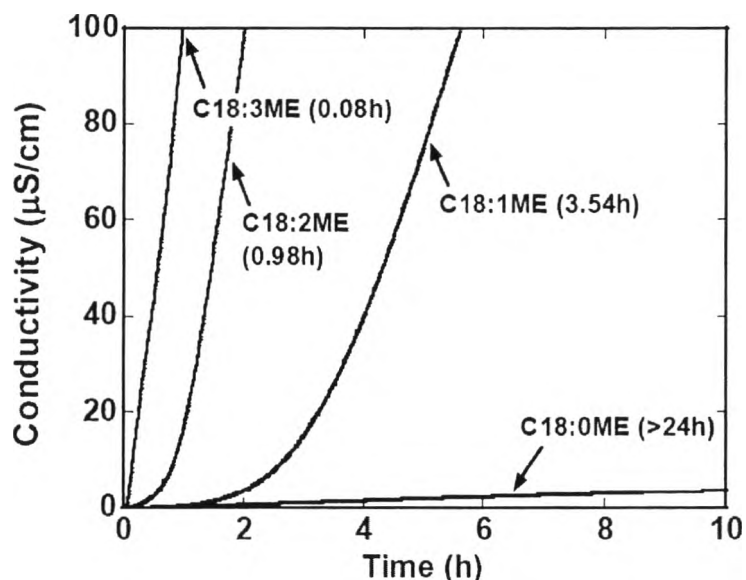


Figure 2.4 Oxidative stability of model compounds of FAMES obtained from Rancimat test (Yoshimura, 2008)

2.5 Improvement of Biodiesel Oxidative Stability by Partial Hydrogenation

Partial hydrogenation is a process that hydrogen atoms are added to partially saturate double bond in the FAME structure. This process requires low pressure and low temperature at about 0.1–0.5 MPa and 80–120°C, respectively. (Yoshimura, 2009). As the number of double bonds contained in the fatty acid part of FAME molecules decreases, the oxidative stability improves. However, the higher amount of single bonds in FAME molecules, the worse cold flow properties become (Yoshimura, 2008). A tradeoff relationship between oxidation stability and cold flow properties is presented in Figure 2.5. Therefore, the main objective of partial hydrogenation is to saturate the polyunsaturated FAMES (C18:3 and C18:2) to the monounsaturated one (C18:1), in order to obtain biodiesel product with relatively high oxidative stability and good cold flow properties (Yoshimura, 2009). The schematic of partial hydrogenation of polyunsaturated FAME is shown in Figure 2.6.

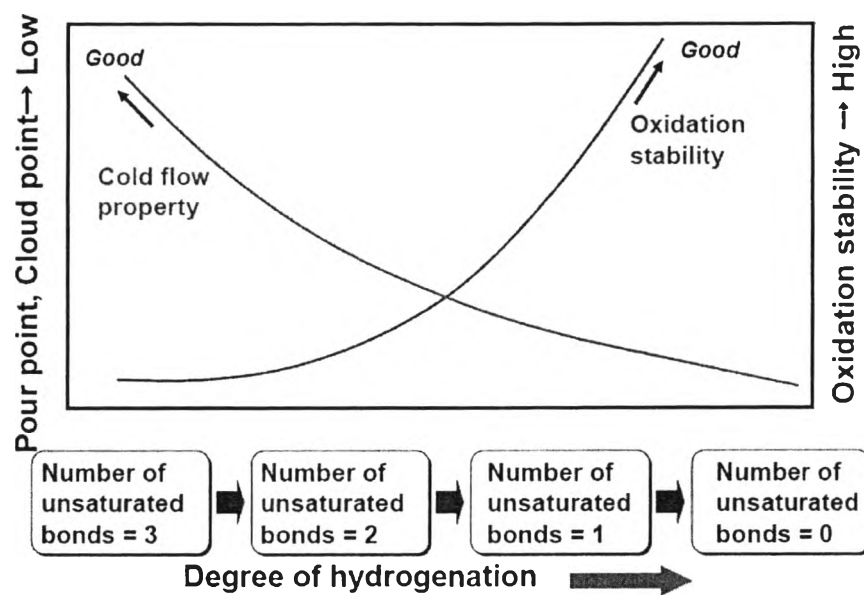


Figure 2.5 Concept of partial hydrogenation of polyunsaturated FAMES (Yoshimura, 2008)

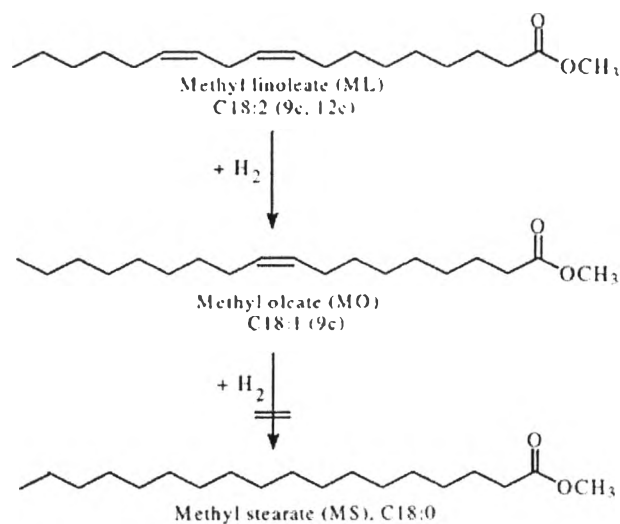


Figure 2.6 Partial hydrogenation of polyunsaturated FAMES (Nicolau *et al.*, 2009)

As previously described, the catalytic partial hydrogenation of polyunsaturated FAMES is possible under the reaction conditions of 80–120°C and 0.1–0.5 MPa hydrogen partial pressure. This low-pressure requirement provides an advantage in the possibility of using supplementary equipment along with the conventional biodiesel production process as shown in Figure 2.7. In this process, a batch type or continuous type reaction methods are possible, while slurry bed or fixed bed reactors can be used (Yoshimura, 2008).

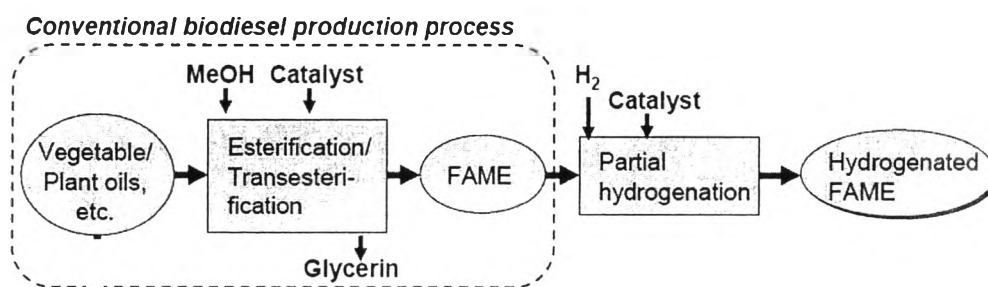


Figure 2.7 Schematic partial hydrogenation of polyunsaturated FAMES for upgrading conventional biodiesel (Yoshimura, 2008)

In 2009, Nikolaou and co-workers studied the partial hydrogenation of polyunsaturated methyl esters of sunflower oil to monounsaturated methyl esters by using highly active rhodium sulfonated phosphite (Rh/STPP) complexes as a catalyst at 90°C, 5 MPa, and 1,600 rpm stirring rate. They found that partial hydrogenation of polyunsaturated FAMES selectively to monounsaturated FAMES substantially increased the oxidative stability and greatly improved the storage properties. However, the catalyst used in their study is homogeneous catalyst, which leads to the difficulty of catalyst separation. Despite this, the major disadvantage is the fact that homogeneous catalyst cannot be reused. Thus, the homogeneous catalysts are expected to be replaced by the heterogeneous catalysts.

Heterogeneous catalyst especially supported metal (Ni, Mo, Pd, Rh, Pt, and etc.) is commercially attractive for liquid phase catalytic hydrogenation. The major advantages of supported metal catalysts are their relatively high activity, mild process conditions, easy separation, and better handling properties (Panpranot *et al.*,

2005). The high activity of heterogeneous catalyst in partial hydrogenation of polyunsaturated FAMES can be found in the work done by Sonthisawate and co-workers in 2009. They studied the upgrading of biodiesel obtained from various feedstocks such as palm oil, refined palm oil, rapeseed oil, and jatropha oil, by partial hydrogenation process under the atmospheric pressure using Pd-Pt supported on Yb-modified USY zeolite. They found that after 1 h of partial hydrogenation at 100°C, the oxidative stability of all biodiesels improved to over 24 h.

2.6 Heterogeneous Catalyst for Partial Hydrogenation of Polyunsaturated FAMES

Generally, the catalyst employed in the partial hydrogenation of polyunsaturated FAMES is the catalyst for hydrogenation of fats and oils such as Ni, Cu, and noble metals. The catalyst used in commercial hydrogenation of fats and oils is usually Ni catalyst supported on silica or alumina, and mostly used in the slurry phase. These Ni catalysts are cheaper than the noble metal catalysts but more severe hydrogenation pressure is required for the former compared with the latter ones (Allen *et al.*, 1982). On the other hand, noble metal catalysts like Pd and Pt are disadvantageous in terms of their cost. However, they require lower reaction pressure, which is low enough that the hydrogenation reaction is possible under atmospheric pressure (Yoshimura, 2008).

Several studies have been done on the hydrogenation of vegetable oil to increase its shelf life by improving its oxidative and thermal stability. The different metals exhibit different catalytic activity as well as *cis-trans* isomerization selectivity (Schmidt 2000 and Patterson 2011).

In 2011, McArdle and co-workers studied the selective hydrogenation of sunflower oil using Pd and Pt supported on Al₂O₃, ZrO₂, and TiO₂ catalysts and compared their catalytic activity with a conventional Ni catalyst. They found that Pd catalysts were much more active than the Ni catalyst while the Pt catalysts were not much active as Pd but produced lower *trans*-fatty acid during hydrogenation. The *trans*-fatty acid usually occurs from the isomerization of naturally *cis*-isomers during the hydrogenation reaction (Allen *et al.*, 1982; Schmidt, 2000; and Patterson, 2011).

Similarly, the isomerization of original *cis*-monounsaturated FAMES to *trans*-monounsaturated FAMES also commonly takes place during hydrogenation of FAMES. In biodiesel utilization point of view, the *cis*-monounsaturated FAME is preferable in terms of cold flow properties since its melting point is lower than that of *trans*-isomers, for example; -20.2°C for *cis*-C18:1 FAME, but 9.9°C for *trans*-C18:1 FAME (Knothe *et al.*, 2009).

Moreover, the trend of activity, selectivity, and *cis-trans* isomerization of metal catalysts in hydrogenation of fats and oils has been reported by many researchers (Rylander, 1970; Jang *et al.*, 2005; Dijkstra, 2006; Beers, 2007; and Cheng *et al.*, 2012). They found that the Pd catalyst is the most active metal and also causes the most *cis-trans* isomerization and migration of double bonds; whereas, Pt has lower hydrogenation activity than Pd, but exhibits higher selectivity towards *cis*-isomers. On the other hand, Ni shows the lowest hydrogenation activity.

In addition, several recent publications have addressed various solid supports used for the liquid phase hydrogenation such as carbon (Harada *et al.*, 2007; Tamai *et al.*, 2009; Wadumesthrige *et al.*, 2009; Simakova *et al.*, 2008; Bueres *et al.*, 2008; Zhu *et al.*, 2009; Ge *et al.*, 2010), silica (Rodríguez *et al.*, 1997; Ahn *et al.*, 2009), alumina (Jackson *et al.*, 2007; Pattamakomsan *et al.*, 2011), and zeolite (Schmitz *et al.*, 1996; Huang *et al.*, 2007). They found that Pd supported on these supports were effective for the hydrogenation of many reactants. Due to the difference in nature and structure of each support, the type of support is believed to affect catalytic activity and selectivity of the catalyst. Moreover, the same support with different pore size also affects the rate and selectivity of the reaction (Allen *et al.*, 1982).