

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Feedstocks for Biodiesel Production

Biodiesel is a fuel produced from vegetable oils, animal fats or waste vegetable oils, and has been widely studied. These categories of feedstocks have already been employed for the production of biodiesel. As earlier stated application of these feedstocks in biodiesel production could lower the cost of final biodiesel product (Atadashi *et al.*, 2012). Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdom that are made up of one mole of glycerol and 3 moles of fatty acids and are commonly known as triglycerides (Ramos *et al.*, 2009). Biodiesel contain fatty acids with different levels of unsaturation. The fuel properties of biodiesel are dependent on the amount of each fatty acid present in the feed stock. Important physical and chemical characteristics that influence the biodiesel production and its quality. Choosing the oils or fats for biodiesel production depends on both the process chemistry and economy of the process and most importantly the oil content of the feedstock. The oil content is of fundamental significance and in the future, is likely to become the competitive factor on international markets. Physical and chemical characteristics of virgin or used oils that affect the potential biodiesel production are free fatty acid (FFA) content, moisture content and other impurities, and calorific content. Different vegetable oils with various compositions of fatty acids can be used for biodiesel production. Recently, many studies are being carried out for biodiesel production from less common or unconventional oilseeds like tobacco, pongamia, jatropha, rubber seeds, etc. Though animal fats having chemical structures similar to vegetable oils with the difference only in the distribution of fatty acids are the excellent sources of biodiesel (Karmakar *et al.*, 2010). In general, biodiesel feedstocks can be divided into four main categories are edible vegetable oil, non-edible vegetable oil, waste or recycled oil, and animal fats.

2.2 Properties of Biodiesel Feedstocks

2.2.1 Free Fatty Acid Content

Free fatty acid (FFA) content is the amount of fatty acid (%wt) in oil which is not connected to triglyceride molecule. Heating of oil can cause breakage of long carbon chain and formation of FFAs. During transesterification process, free fatty acids react with alkali, and form soaps and water, both of which must be removed during ester purification process. Moreover, FFA attracts water because of their hygroscopic nature. Fatty acid profiles of different feedstocks are presented in Table 2.1.

2.2.2 Heat Content

The calorific content is the energy content of the oil. The energy content of the biodiesel depends on the energy content of the feedstock oil. Fuels with more unsaturation generally have lower energy (on a weight basis) while fuels with greater saturation have higher energy content. Denser fuels provide greater energy per gallon and since fuel is sold volumetrically, the higher the density, greater the potential energy.

2.2.3 Moisture, Impurities and Unsaponifiables (MIU)

Moisture, impurities and unsaponifiables (MIU) are the amount of water, filterable solids (such as bone fragments, food particles or other solids), and other non-triglycerides in an oil which cannot be converted to mono alkyl fatty esters by esterification or transesterification. Hence, MIUs must be removed before biodiesel production or during ester purification. Average amounts of MIU present in different feedstocks are presented in Table 2.2. The removal methods of MIU are discussed below.

2.2.3.1 *Removal of Water*

Water should be removed from transesterification reaction because at high temperature, water can hydrolyze the triglycerides to diglycerides and form a FFA. This FFA reacts with the alkali catalyst and forms soaps. Even the presence of very little amount (1%) of water will increase soap production and

considerably affect transesterification reaction. Heating breaks any emulsions between the water and oil; and then settled water at the bottom can be removed. Centrifuges can also be used to separate water and oil. Heating the oil under pressure and then spraying into a vacuum chamber can bring the water content to a very low level.

2.2.3.2 *Removal of Insoluble Impurities*

The insoluble impurities may consist of sand, dirt, and seed fragments in case of vegetable oil, and small particles of bones and gums in case of animal fats or used cooking oil. Feedstocks should always be filtered prior to entering the processing system. A 100 μm filter will suffice to remove particles from most feedstocks although all fuel leaving the plant should be filtered to 5 μm .

2.2.3.3 *Removal of Unsaponifiables*

Unsaponifiable matter consists of organics which do not react with base to form soaps. These include sterols, higher molecular weight alcohols, pigments, waxes, and hydrocarbons. These may be removed during crude oil refining. When biodiesel is produced directly from crude oil, these materials are mostly removed by water washing. Unsaponifiables can also be separated in the glycerol phase.

2.2.4 Titre

Temperature at which oil changes from solid to liquid is called titre. Titre is important since the transesterification process is basically a liquid process, and oils with high titre may require heating, which increase the energy requirements and production costs for a biodiesel plant. Acceptable titre values of different feedstocks are provided in Table 2.2 along with other physio-chemical properties of the feedstocks. Feedstocks like palm, neem, cotton seed, and yellow grease having high titres in the range of 30-45 $^{\circ}\text{C}$ have been used for biodiesel production (Karmakar *et al.*, 2010). As shown in Table 2.2, 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 diesel. 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 polymerization of vegetable oils causes 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 diesel.

Table 2.1 Fatty acid composition of some vegetable oils (%) (Balat *et al.*, 2008)

Vegetable oil	Fatty acid composition, wt.%					
	Palmitic 16:0	Stearic 18:0	Palmitoleic 16:1	Oleic 18:1	Linoleic 18:2	Others
Coconut oil	5.0	3.0	-	6.0	-	65.0
Olive oil	14.6	-	-	75.4	10.0	-
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
Rapeseed	3.5	0.9	0.1	54.1	22.3	9.1
Sunflower seed	6.4	2.9	0.1	17.7	72.8	0.1

Table 2.2 Physico-chemical properties of commonly used biodiesel feedstocks
(Barnwal *et al.*, 2005)

Vegetable Oil	Kinematic Viscosity at 38°C (mm ² /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
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
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
Diesel	3.06	50	43.8	-	-16.0	76	0.855

^a Cetane number (CN) is a measure of ignition quality of diesel fuel

2.3 Vegetable Oil

The use of vegetable oils as alternative fuels has been around for 100 years when the inventor of the diesel engine Rudolph Diesel first tested peanut oil, in his compression ignition engine (Shay, 1993). However, due to cheap petroleum products, such non-conventional fuels never took off. Vegetable oils occupy a prominent position in the development of alternative fuels although, there have been many problems associated with using it directly in diesel engine (especially in direct injection engine). These include;

1. Coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or even prevented as a result of plugged orifices,
2. Carbon deposits,
3. Oil ring sticking,
4. Thickening or gelling of the lubricating oil and

5. Lubricating problems.

Other disadvantages to the use of vegetable oils and especially animal fats are the high viscosity (about 11–17 times higher than diesel fuel), lower volatilities that causes the formation of deposits in engines due to incomplete combustion and incorrect vaporization characteristics. These problems are associated with large triglyceride molecule and its higher molecular mass and avoided by modifying the engine less or more according to the-conditions of use and the oil involved (Meher *et al.*, 2006).

The major components of vegetable oils are triglycerides (Gerpen *et al.*, 2004). Which are esters of one glycerol with three long-chain fatty acid. 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 2.1.

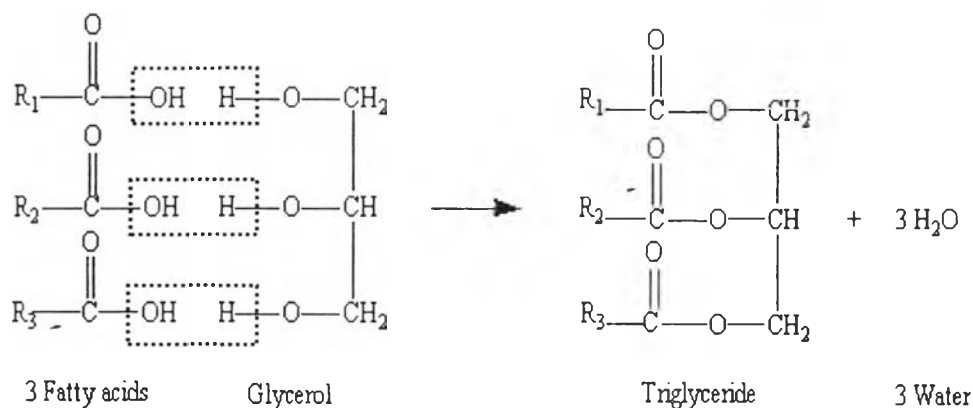


Figure 2.1 General formation of triglyceride (Swern, 1955).

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 properties of the triglyceride and the biodiesel fuel are determined by amounts of each fatty acid that shown 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).

2.4 Transesterification of Vegetable Oil

One popular process for producing biodiesel from the fats/oils is transesterification of triglyceride by methanol (methanolysis) to make methyl esters of the straight chain fatty acid. The purpose of the transesterification process is to lower the viscosity of the oil (Demirbas, 2008).

2.4.1 Transesterification Kinetics and Mechanism

The transesterification reaction is represented by the general equation, as shown in Figure 2.2.

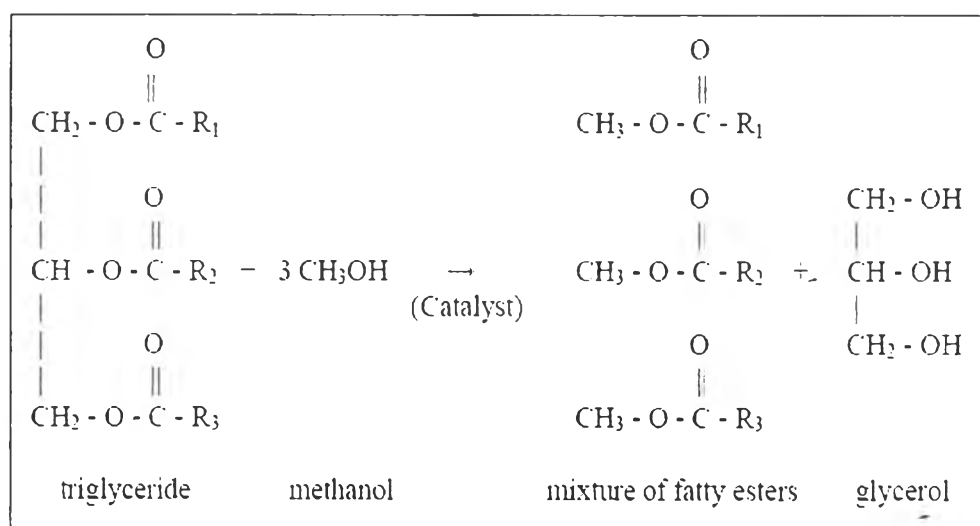


Figure 2.2 Transesterification reaction (Gerpen *et al.*, 2004)

Where R_1 , R_2 , and R_3 are long chains of carbons and hydrogen atoms, sometimes called fatty acid chains. There are five types of chains that are common in soybean oil and animal fats (others are present in small amounts):

Palmitic: $R = -(\text{CH}_2)_{14}-\text{CH}_3$ 16 carbons (16:0)

Stearic: $R = -(\text{CH}_2)_{16}-\text{CH}_3$ 18 carbons, 0 double bonds (18:0)

Oleic: $R = -(\text{CH}_2)_7 \text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3$ 18 carbons, 1 double bond (18:1)

Linoleic: $R = -(\text{CH}_2)_7 \text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}(\text{CH}_2)_4\text{CH}_3$ 18 carbons, 2 double bonds (18:2)

Linolenic: $R = -(CH_2)_7CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH_3$ 18 carbons, 3 double bonds (18:3).

These chains are designated by two numbers separated by a colon. The first number designates the number of carbon atoms in the chain and the second number designates the number of double bonds. Note that the number of carbon atoms includes the carbon that is double bonded to the oxygen atom at one end of the fatty acid (called the carboxylic carbon). This is the end that the methanol attaches to when methyl esters are produced (Gerpen *et al.*, 2004).

When the transesterification reaction with alcohol proceeds, the first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and of monoglycerides to glycerol, yielding one methyl ester molecule per mole of glyceride at each step (Freedman *et al.*, 1986). These conversion steps are presented in Figure 2.3.

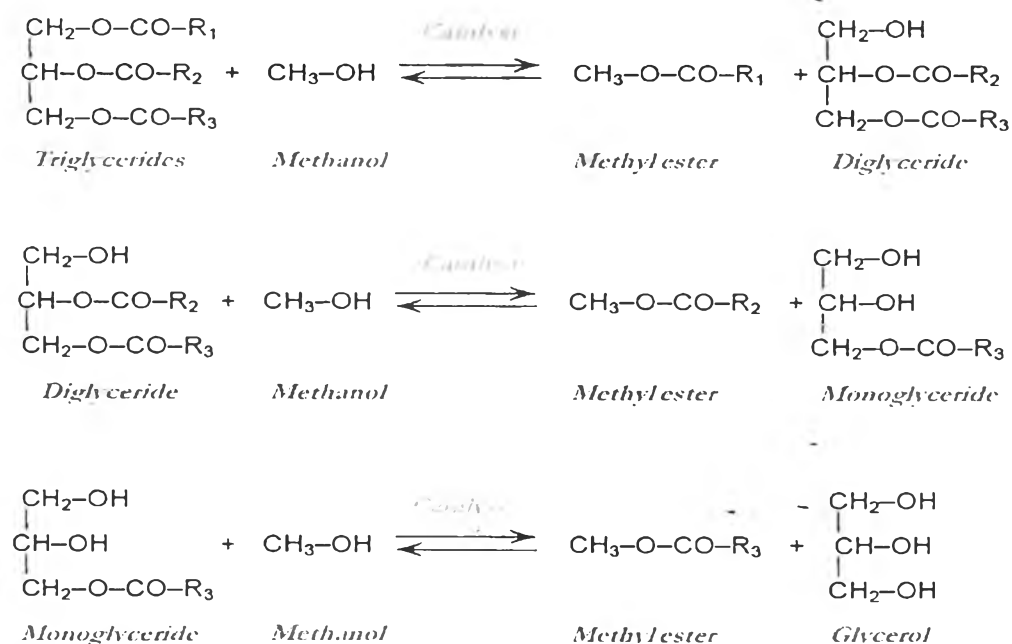


Figure 2.3 Transesterification reaction steps (Borges and Díaz, 2012)

The stepwise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the forward reaction is pseudo-first order and the reverse reaction is found

to be second order. It was also observed that transesterification is faster when catalyzed by alkali (Freedman *et al.*, 1986). The mechanism of alkali-catalyzed transesterification is described in Figure 2.4. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule which results in the formation of a tetrahedral intermediate. The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step. In the last step the rearrangement of the tetrahedral intermediate gives rise to an ester and a diglyceride (Ma, 1999).

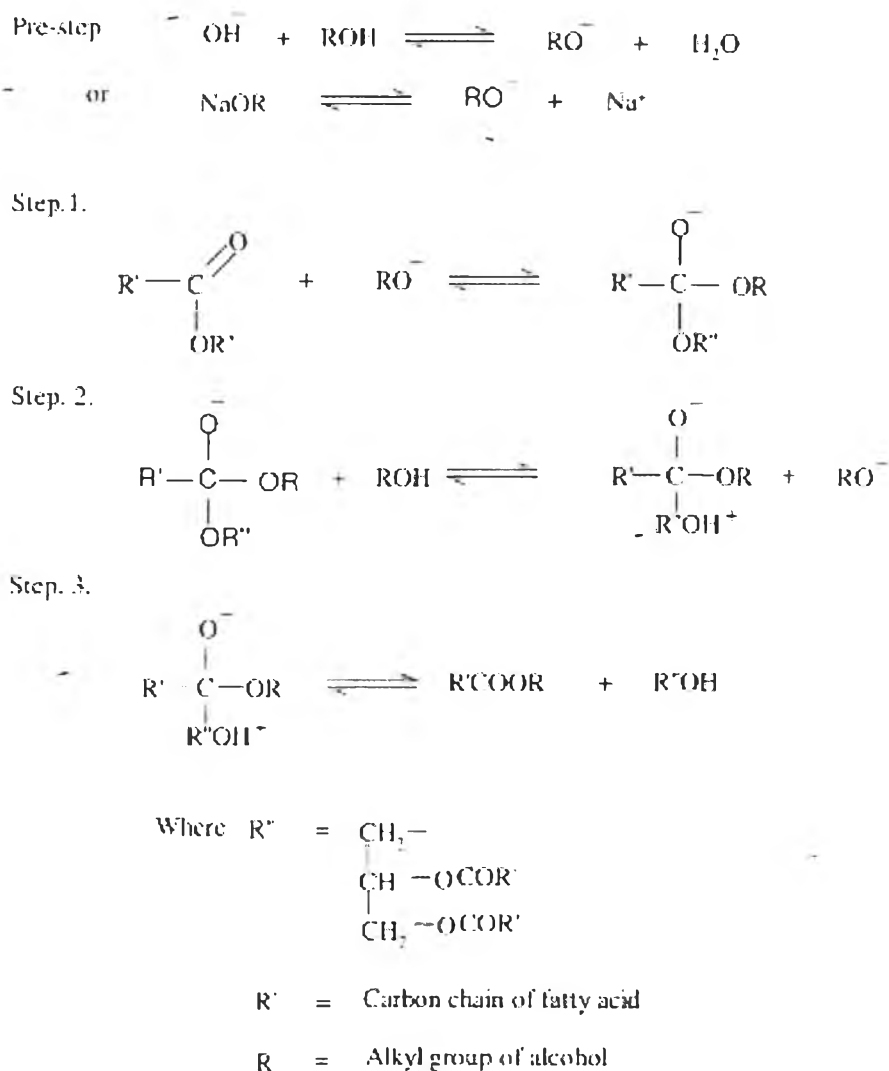


Figure 2.4 Mechanism of base catalyzed transesterification (Meher *et al.*, 2006).

Transesterification can be catalyzed by Bronsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters but these reactions are slow, requiring typically temperature above 100 °C and more than 3 h to complete the conversion (Schuchard *et al.*, 1998). The mechanism of acid catalyzed transesterification of vegetable oil (for a monoglyceride) is shown in Figure 2.5. However, it can be extended to di- and tri-glycerides. The protonation of carbonyl group of the ester leads to the carbocation which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst (Freedman *et al.*, 1986).

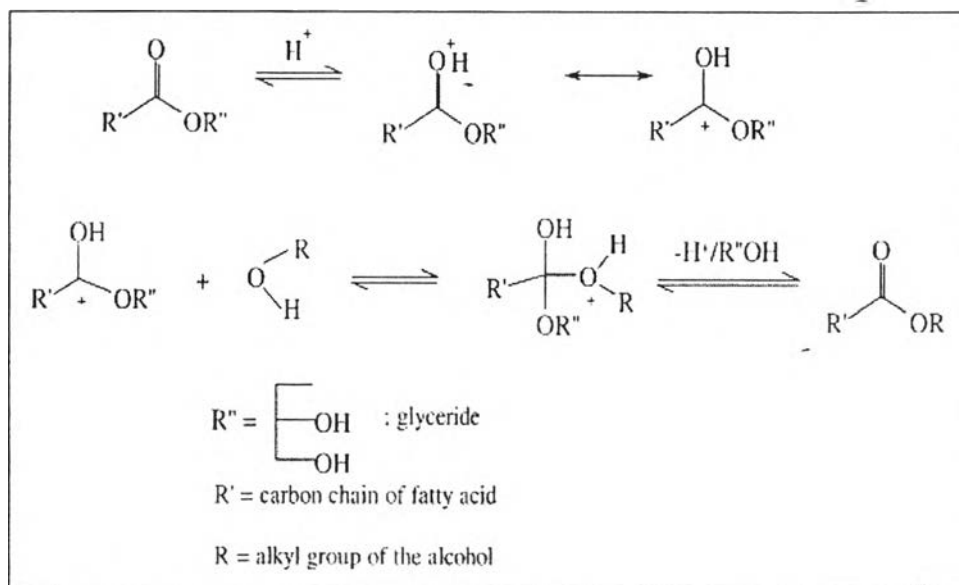


Figure 2.5 Mechanism of acid catalyzed transesterification (Meher *et al.*, 2006).

2.4.2 Variables Affecting Transesterification Reaction

The process of transesterification is affected by various factors depending upon the reaction condition used. The effects of these factors are described below.

2.4.2.1 Effect of Free Fatty Acid and Moisture

The free fatty acid and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. To carry the base catalyzed reaction to completion; free fatty acid (FFA) value lower than 3% is

needed. The higher the acidity of the oil, smaller is the conversion efficiency. Both excess as well as insufficient amount of catalyst may cause soap formation (Dorado *et al.*, 2002).

2.4.2.2 Catalyst Type and Concentration

Catalysts used for the transesterification of triglycerides are classified as alkali, acid, enzyme or heterogeneous catalysts, among which alkali catalysts like sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide are more effective (Ma, 1999). If the oil has high free fatty acid content and more water, acid catalyzed transesterification is suitable. The acids could be H_2SO_4 , H_3PO_4 , or $RS(O)_2-OH$. Methanolysis of beef tallow was studied with catalysts NaOH and NaOMe. Comparing the two catalysts, NaOH was significantly better than NaOMe (Ma *et al.*, 1998). The NaOH and NaOMe catalysts reached their maximum activity at 0.3 and 0.5% w/w of the beef tallow, respectively. CH_3ONa causes formation of several byproducts mainly sodium salts which are to be treated as waste. In addition, high quality oil is required with this catalyst (Ahn *et al.*, 1995).

2.4.2.3 Molar Ratio of Alcohol to Oil and Type of Alcohol

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. For maximum conversion to the ester, a molar ratio of 6:1 should be used. The molar ratio has no effect on acid, peroxide, saponification and iodine value of methyl esters (Tomasevic *et al.*, 2003). However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution it helps drive the equilibrium to back to the left, lowering the yield of esters. The transesterification of oil with ethanol was studied at molar ratios between 3:1 and 15:1. The ester yield increased as the molar ratio increased up to a value of 12:1. The best results were for molar ratios between 9:1 and 12:1. For molar ratios less than 6:1, the reaction was incomplete. For a molar ratio of 15:1 the separation of glycerin is difficult and the apparent yield of esters decreased because a part of the glycerol

remains in the biodiesel phase. Therefore, molar ratio 9:1 seems to be the most appropriate (Enciner *et al.*, 2002).

2.4.2.4 Effect of Reaction Time and Temperature

Transesterification can occur at different temperatures, depending on the oil used. The literature has revealed that the rate of reaction is strongly influenced by the reaction temperature. However, the reaction is conducted close to the boiling point of methanol (60-70 °C) at atmospheric pressure for a given time. Such mild reaction conditions require the removal of free fatty acids from the oil by refining or pre-esterification. Therefore, degummed and deacidified oil is used as feedstock (Freedman *et al.*, 1984).

2.4.2.5 Mixing Intensity

It has been observed that during the transesterification reaction the reactants initially form a two-phase liquid system. The mixing effect has been found to play a significant role in the slow rate of the reaction. As phase separation ceases, mixing becomes insignificant. The effect of mixing on the kinetics of the transesterification process forms the basis for process scale-up and design (Barnwal *et al.*, 2005).

2.5 Biodiesel

Biodiesel is defined by ASTM as a fuel comprised of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated B100 (Bart *et al.*, 2008). The vegetable and animal derived feedstocks used to produce biodiesel are known as triacylglycerides (TAGs), or more simply, triglycerides. Biodiesel is produced by a chemical process known as transesterification, by which the triglycerides are reacted with alcohols in the presence of a catalyst to produce fatty acid alkyl esters. A byproduct of transesterification is glycerine also known as glycerol. Since the most common alcohol used to produce biodiesel is methanol another name for biodiesel is fatty acid methyl esters (FAME). Unless otherwise indicated the term biodiesel refers to neat material i.e. 100% FAME often designated as B100. Lower concentrations such as B20, are properly referred to as biodiesel blends, not biodiesel itself. Renewable diesel fuel (also known as Green Diesel) is

produced by catalytic hydroprocessing of the same triglyceride feedstocks used to produce biodiesel (Kalnes *et al.*, 2007 and Mikkonen, 2008). In this process, an alcohol is not required the products are hydrocarbons rather than fatty acid alkyl esters and no glycerol byproduct is formed. The general term biodistillate is used to refer to both biodiesel and renewable diesel (Hoekman *et al.*, 2012).

The produced biodiesel such as, it is mainly consisting of fatty acid methyl esters (FAME) of vegetable oils and it is a renewable, biodegradable, safe (cause of its relatively high flash point), non-toxic, low in sulfur fuel. More importantly it has a negative CO₂ balance and a low emissions profile (emits less CO, hydrocarbons, particulates and smoke). In addition, it also presents better lubricity characteristics compared with petroleum diesel (Dermibas, 2005; Huber *et al.*, 2006; Knothe, 2005, 2006; Ma and Hanna, 1999).

In the transport sector, it can be used as blended with conventional diesel fuel or in pure methyl esters form. However, biodiesel is still faced with technical challenges, such as its oxidative stability, low temperature performance and nitrogen oxides (NO_x) emissions (Imahara *et al.*, 2006; Knothe, 2005, 2006; McCormick *et al.*, 2001).

It is evident that biodiesel final quality, meaning all its critical properties, initially depends on the fatty acid composition of its raw materials (vegetable oils, fats, etc.). However, the produced methyl esters qualitative and quantitative composition in biodiesel virtually defines its properties and its quality in the end. Subsequently, the properties of the various fatty acid methyl esters are determined by the structural features of the fatty acid and the alcohol moieties that comprise a fatty ester. Structural features that influence the physical and fuel properties of a fatty ester molecule are chain length, degree of unsaturation, and branching of the chain. Important fuel properties of biodiesel that are influenced by the fatty acid profile and, in turn by the structural features of the various fatty esters are cetane number and ultimately exhaust emissions, cold flow performance, oxidative stability, heat of combustion, viscosity, and lubricity (Knothe, 2005). The strong adverse effects of the degree of saturation of fatty acid methyl esters on a number of biodiesel quality properties and particularly those related with oxidative stability and cold flow

behavior has been extensively researched (Bouaid *et al.*, 2009; Falk and Meyer-Pittroff, 2004; Knothe, 2005; Ramos *et al.*, 2009).

As shown in Table 2.3, the properties of biodiesel and petroleum based diesel fuels are compared. This table shows that biodiesel produced from various vegetable oils gives 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 2.3 Comparison between properties of biodiesel and petroleum-based diesel fuels (Fukuda *et al.*, 2001)

Vegetable oil methyl ester	Kinetic viscosity (mm ² /s)	Cetane number	Lower heating value (MJ/l)	Cloud point (°C)	Flash point (°C)	Density (g/l)	Sulfur (wt.%)
Soybean	4.5 (37.8°C)	45	33.5	1	178	0.885	-
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
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

2.6 Production of Biodiesel

Different methods of producing biodiesel from various feedstocks have been developed. These methods are classified as follows: direct oil use/blends with diesel fuel, direct use and blending, pyrolysis, microemulsion, and transesterification. The most often used technique to produce biodiesel is the transesterification reaction of vegetable oils with short-chain alcohol, usually methanol (Abreu *et al.*, 2005).

Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side. Transesterification is the process used to make biodiesel fuel as it is defined in Europe and in the USA. It also is used to make methyl esters for detergents and cosmetics (Ma, 1999).

2.7 Biodiesel Properties

2.7.1 Iodine Value

The iodine value (IV) or iodine number is a stability index measuring levels of unsaturation in organic compounds such as FAME. The IV is defined as the mass of iodine (grams) that can be formally added to 100 g of the sample measured according to the standard test method EN 14111. It is an indicator of the number of double bonds presents in the sample; the higher the IV, the higher the number of double bonds. The IV of a particular triacylglycerides is almost identical to that of the corresponding methyl esters although IV decreases with higher alcohols used in transesterification (Knothe *et al.*, 2005). Iodine value is one of the oldest and most common methods for determining the level of unsaturation in a fatty oil or ester (Waynick, 2005). It can be seen that IV depends on the MW of the component unsaturated compounds. The idea behind the use of IV is that it would indicate the propensity of an oil or fat to oxidize and so may indicate the tendency of biodiesel to polymerize and form engine deposits. Hence an IV maximum-of 120 is specified by EN 14214.

However, IV does not depend on the exact nature of the double bonds in the structure; it establishes only the relative concentration of unsaturation within a sample. It provides no information on the distribution of double bonds in an ester chain molecule so that the number of allylic and bis-allylic sites remains unknown. Iodine value treats all double bonds as being equally reactive; therefore, it cannot be a predictor of oxidation stability (Knothe and Dunn, 2003). It has been shown that different fatty acid structures can give the same IV. Two samples with the same IV can therefore exhibit entirely different oxidization behavior (Pullen and Saeed, 2012).

2.7.2 Cetane Number

Cetane number (CN) is widely used as diesel fuel quality parameter related to the ignition delay time and combustion quality. Higher the cetane number is better it is in its ignition properties (Meher *et al.*, 2006). An adequate cetane number is required for good engine performance. High cetane numbers help ensure good cold start properties and minimize the formation of white smoke. Cetane number is measured by matching against the blends two reference fuels namely n-cetane and α -methyl-naphthalene. It is not always possible to carry out engine tests to determine cetane number because of the cost of the reference fuels and the more effort required. It is well known that biodiesel cetane number depends on the feedstock used for its production. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the cetane number (Bajpai and Tyagi, 2006; Dermibas, 2005; Knothe *et al.*, 1998). The cetane number for biodiesel should be a minimum of 51. Low cetane numbers have been associated with more highly unsaturated components such as the esters of linoleic (C18:2) and linolenic (C18:3) acids (Knothe *et al.*, 2003). High cetane numbers were observed for esters of saturated fatty acids such as palmitic (C16:0) and stearic (C18:0) acids (Ramos *et al.*, 2009).

2.7.3 Oxidation Stability

Oxidation and thermal instability can result in the degradation of biodiesel fuel properties and affect engine performance. Instability is fundamentally

a consequence of fatty acid chain unsaturation (carbon double bonds C=C). Both of these instability types are determined by the amount and configuration of fatty acid chain unsaturation (Waynick, 2005). Instability is greatly poor if two or more carbon double bonds are present in the fatty acid chain (Graboski *et al.*, 1998), so that more highly unsaturated fatty acid chains are relatively less stable. In the process of oxidative degradation, unsaturated sites of a fatty acid chain undergo free radical attack; where a hydrogen atom is abstracted from the fatty acid chain. Ambient oxygen then readily reacts at the site, subsequently forming hydroperoxide. This oxidation process is a self-sustaining chain reaction that proceeds slowly at first and then suddenly much more rapidly after an initial induction period has elapsed. Once formed hydroperoxides accumulate and then later decompose, inter-reacting to form numerous problematic secondary oxidation products including aldehydes, alcohols, short chain carboxylic acids, and higher molecular weight oligomers. Therefore, oxidation affects an increase of insoluble sediments, acidity, and viscosity (McCormick *et al.*, 2007).

Stability of fatty compounds is influenced by factors such as presence of air, heat, traces of metal, peroxides, light, or structural features of the compounds themselves, mainly the presence of double bonds (Bajpai and Tyagi, 2006). The oxidation stability decreased with the increase of the contents of polyunsaturated methyl esters (Ramos *et al.*, 2009).

2.7.4 Kinematic Viscosity

Viscosity is a measure of resistance to flow of a liquid due to internal friction of one part of a fluid moving over another. This is a critical property because it affects the behavior of fuel injection. In general, higher viscosity leads to poorer fuel atomization. High viscosity can cause larger droplet sizes, poorer vaporization, narrower injection spray angle, and greater in-cylinder penetration of the fuel spray. This can lead to overall poorer combustion, higher emissions, and increased oil dilution. The viscosity of biodiesel is typically higher than that of petroleum diesel (Hoekman *et al.*, 2012; Su *et al.*, 2011; Allen *et al.*, 1999; Ceriani *et al.*, 2007).

2.7.5 Flash Point

Flash point is inversely related to fuel volatility. The biofuel specifications for flash point are meant to guard against contamination by highly volatile impurities principally excess methanol remaining after product stripping processes (Hoekmana *et al.*, 2012). The flash point values of vegetable oil methyl esters are much lower than those of vegetable oils. An increase in density from 860 to 885 kg/m³ for vegetable oil methyl esters or biodiesels increases the viscosity from 3.59 to 4.63 mm²/s and the increases are highly regular. There is high regression between the density and viscosity values of vegetable oil methyl esters. The relationships between viscosity and flash point for vegetable oil methyl esters are irregular (Demirbas, 2009).

2.7.6 Density

The airfuel ratio and energy content within the combustion chamber are influenced by fuel density. In general, densities of biodiesel fuels are slightly higher than those of petroleum diesel and increasing the level of biodiesel blends increases the blend's density. FAME density is strongly affected by the degree of unsaturation with higher unsaturation leading to increased density. It has been reported that biodiesel density is also affected by chain length with higher chain length leading to lower fuel density (Hoekmana *et al.*, 2012; Ramirez-Verduzco *et al.*, 2012; Tesfa *et al.*, 2010; Gopinath *et al.*, 2009).

2.7.7 Cloud Point, Pour Point and Cloud Filter Plugging Point

Two important parameters for low temperature applications of a fuel are cloud point (CP) and pour point (PP). Cloud point is defined as the temperature below which wax in diesel or biowax in biodiesels form a cloudy appearance. The presence of solidified waxes thickens the oil and clogs fuel filters and injectors in engines. Pour point is the temperature at which the amount of wax out of solution is sufficient to gel the fuel. Biodiesel has a higher CP and PP compared to conventional diesel. Cold filter plugging point (CFPP) is the lowest temperature, expressed in 1 °C, at which a given volume of diesel type of fuel still passes through a standardized filtration device in a specified time when cooled under certain conditions. It is

important as in cold temperature countries, a high CFPP will clog up vehicle engines more easily (Demirbas *et al.*, 2009; Su *et al.*, 2011; Gopinath *et al.*, 2009).

2.8 Partial Hydrogenation

The partial hydrogenation of vegetable oils is of the special interest in the process of modification of edible fats and oils. The advantages of partial hydrogenation include that low pressure operation (0.1-0.5 MPa), low temperature operation, and improve oxidative stability, as shown in Figure 2.6 (Yoshimura, 2009).

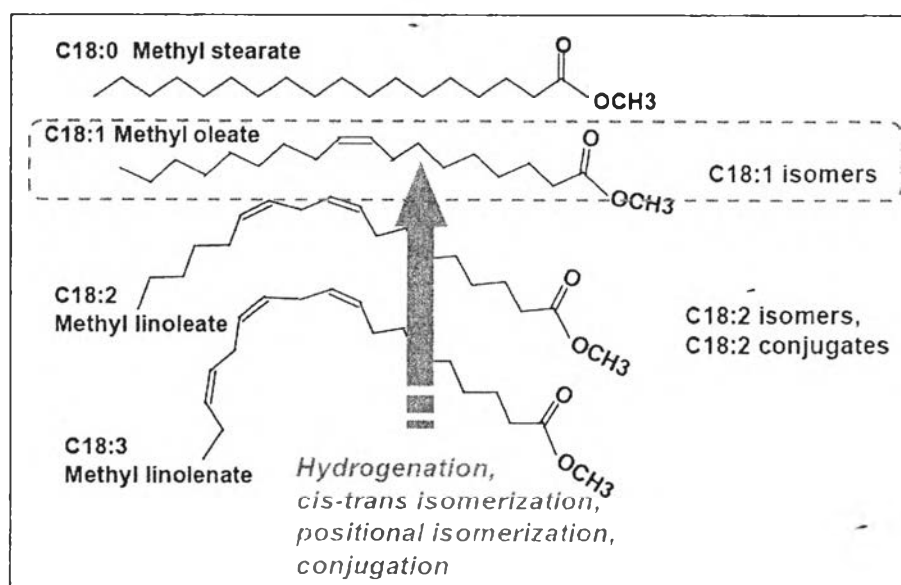
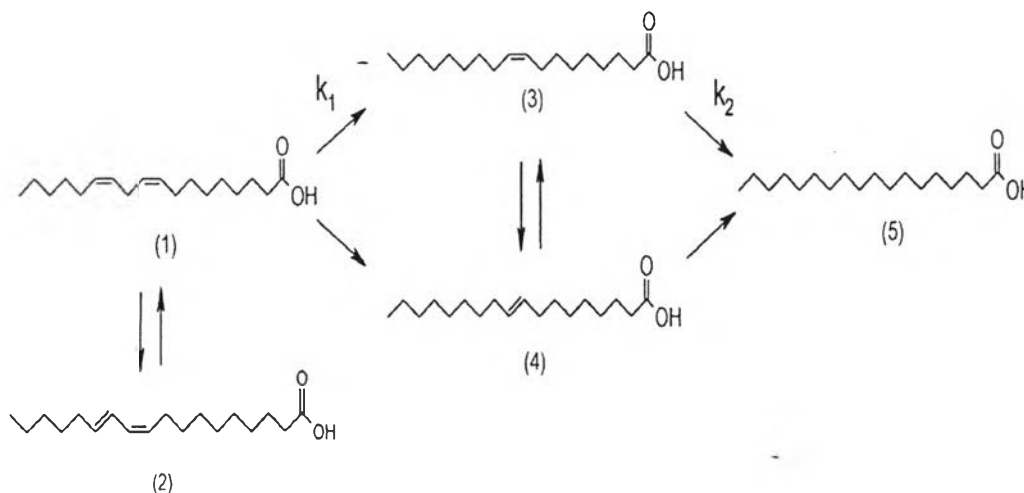


Figure 2.6 Partial hydrogenation of FAME for improving the oxidation stability (Yoshimura, 2009).

The reaction takes place in the presence of a catalyst usually 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. Consequently, the hydrogenation reaction involves consecutive saturation of C18:2 to *cis*-C18:1 and subsequent *cis*-C18:1 isomerizes to *trans*-C18:1 and C18:0,



respectively, as shown in Figure 2.7 (Schmidt and Schomacker, 2007).

Figure 2.7 Reaction mechanism for the hydrogenation of fatty acid; (1) linoleic acid, (2) *trans* linoleic acid (3) oleic acid, (4) elaidic acid, and (5) stearic acid (Schmidt and Schomacker, 2007).

Typically, common vegetable oils contain a low percentage of saturated fatty acids and a high percentage of monounsaturated and polyunsaturated fatty acids with the double bonds in *cis*-configuration (Schmidt and Schomacker, 2007). 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 isomerizes 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 as shown in Figure 2.8 (Mozaffarian *et al.*, 2006). Several public health organizations have consequently recommended that the intake of TFA be lowered as much as possible (Stender and Dyerberg, 2003). The *trans*-isomers lead to a much

higher melting point than those of the corresponding *cis*-isomers. The melting point of *trans*-C18:1 FAME is 9.9 °C, whereas it is only -20.2 °C for *cis*-C18:1 FAME. Therefore, *cis*-isomers are preferable in term of cold flow properties point of view (Numwong *et al.*, 2012). This causes the increased demand for reduction of *trans*-fatty acid formation during hydrogenation.

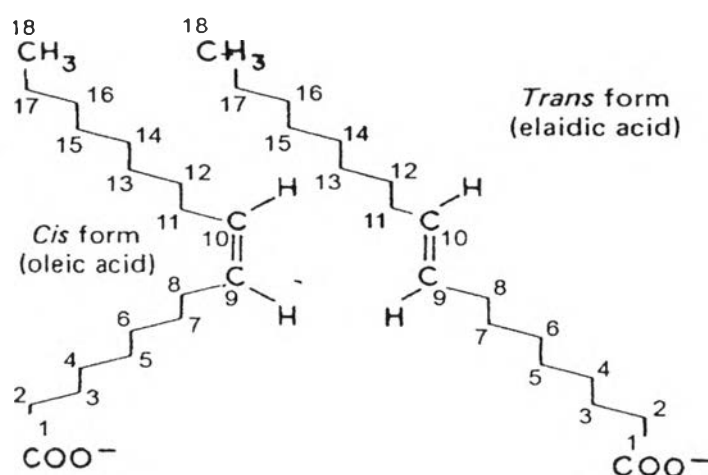


Figure 2.8 The geometric structure of oleic acid (*cis*-C18:1) and elaidic acid (*trans*-C18:1) (Kummerow, 2009).

From these considerations arises the need to search for alternatives that improve the catalytic process in order to reduce the *trans*-isomers content in hydrogenated edible oils. A field where much progress has been made is the design of new hydrogenation catalysts. Supports with specific properties and a sharply defined pore structure have been studied; several active metals have been used (Pt, Pd, Rh, In) obtaining differences in the *cis/trans* and saturate compounds selectivity. Active metals, i.e., Pd, Cu, Ru, Co, Pt, have been researched, especially for the purpose of reducing *trans*-fatty acids contents. The performance parameters, e.g., activity and selectivities, vary significantly with the catalyst types and reaction conditions (Simonetti *et al.*, 2013).

Nikolaou *et al.* (2009) studied the partial hydrogenation of renewable methyl esters of linseed and sunflower oils to high quality biodiesel catalyzed by water soluble rhodium trisulfonated triphenylphosphine (TPPTS) complexes in

aqueous/organic two phase systems. They reported the partial hydrogenation of polyunsaturated methyl esters of sunflower oil selectively to monounsaturated fatty esters catalyzed by rhodium sulfonated triphenylphosphite (STPP) complexes in conventional organic media in order to improve the quality of biodiesel in terms of increased oxidative stability, higher cetane numbers, and lower NO_x emissions.

Bouriazos *et al.* (2010) studied the selective hydrogenation of polyunsaturated methyl esters of vegetable oils for upgrading biodiesel. From these studies, they found that the partial hydrogenation gives high selectivities up to 79.8 mol% of C18:1 ester and also upgrades the biodiesel oxidative stability property.

Tonetto *et al.* (2009) studied the partial hydrogenation of sunflower oil with minimum *trans*-isomer formation was studied, using a Pd/ γ -alumina catalyst modified with promoters allowed for human diet: ethyl benzoate and magnesium glycinate. Regarding the *cis/trans*-selectivity, significant differences were found: ethyl benzoate increases the formation of *trans*-isomers, whereas magnesium glycinate decreases it. These results can be interpreted in terms of different effects: change in the electron density of Pd, which affects the relative adsorption strength of the reactant, intermediates and hydrogen; and a block of part of the surface, by the promoters.

From the previous background and literature review, the purposes of this work were to investigate the performance of Pd, Pt, and Ni supported on mesoporous SiO₂ in the partial hydrogenation of polyunsaturated FAMEs, and to study the effect of modifier of the Pd-Mg, Pt-Mg, and Ni-Mg supported on SiO₂. In addition, the reaction temperature was varied from 80 °C to 120 °C, to observe the *trans*-isomer formation during the partial hydrogenation of polyunsaturated FAMEs. Moreover, the important fuel properties were also investigated after partial hydrogenation reaction.