# CHEPTER II
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 ten decades ago. Due to the rapid decline in crude oil reserves, the use of vegetable oils as diesel fuels is again promoted in many countries. Depending upon climate and soil conditions, different nations are looking into different vegetable oils for diesel fuels. For example, soy bean oil in the United States, rapeseed and sunflower oils in Europe, palm oil in Southeast Asia (mainly Malaysia and Indonesia), and coconut oil in the Philippines are being considered as substitutes for diesel fuels (Srivastava et al, 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 di-glycerides. They contain free fatty acids (generally 1 to 5%) and traces of water (Srivastava et al, 2000). The general formation of triglyceride is shown in Figure 2.1.

| 3 Fatty acids | Glycerol | Triglyceride | 3 Water |
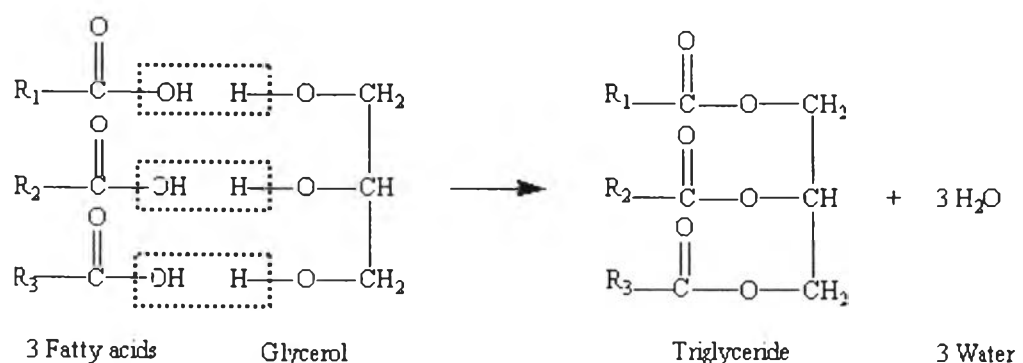
Figure 2.1 General formation of triglyceride (Swern et al, 1979).

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. Different fatty acids have different carbon chain length and number of double bonds. This reason leads to make different characteristics of vegetable oil. The common fatty acids found in vegetable oils are stearic, palmitic, oleic, linoleic, and linolenic. The name and chemical structure of common fatty acids are shown in Table 2.1. 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 *et al.*, 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)

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
Corn	0	12	2	Tr	0	0	25	0	6	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.

Table 2.3 Properties of the vegetable oils

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

As shown in Table 2.3, 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 leads 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.

2.2 Derivatives of Triglycerides as Diesel Fuels

As previously described, there are many problems associated with the use of vegetable oils (triglycerides) directly as fuels for diesel engine since they have high viscosity, low volatility, and polyunsaturated fatty acids. Therefore, the properties and performance of vegetable oils derivative must be improved in order to be able to use in diesel engine. These can be done by four major ways as follows.

2.2.1 Direct Use and Blending

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

2.2.2 Microemulsion

Microemulsion is a dispersion of fluid particle that suspended in another fluid. The objective of this method is to solve the high viscosity problem of vegetable oil and animal fats by use solvent such as methanol, ethanol, and 1-buthanol in microemulsion. This method can adjust injection to spray vegetable oil or animal fats from injector.

2.2.3 Thermal Cracking or Pyrolysis

Pyrolysis is a process of thermal cracking, also known as thermal decomposition. This process occurs when organic or carbonaceous material is heated to high temperatures in the absence of air or oxygen. Any volatile organic compounds are cracked and subsequently released (vaporized) from the solid state and a carbon char product remains.

2.2.4 Transesterification

Transesterification is a reaction of vegetable oils or animal fats with alcohol in the presence of a strong acid or base, producing a mixture of fatty acid alkyl esters and glycerol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed.

2.3 Biodiesel

Biodiesel refers to a non-petroleum-based diesel fuel consisting of short chain alkyl (methyl or ethyl) esters, made by transesterification of vegetable oil or animal fat (tallow), which can be used alone, or blended with conventional petro diesel in diesel-engine vehicles. Biodiesel is a biodegradable and non-toxic alternative fuel produced from new or used vegetable oil that is produced from renewable resources. Pure biodiesel has the highest heating content of any alternative fuel. It also has the highest energy balance of any fuel. For every unit of fossil energy needed to produce biodiesel, more than 3 units of energy are gained. As for gasoline and diesel, every one unit put in, yields only about one half units. Because biodiesel is made from plant oil or animal fat; therefore, it is renewable. Moreover, the carbon dioxide taken up by plants during photosynthesis helps to mitigate the CO_2 emitted from using biodiesel so there is no net carbon introduced to the atmosphere. Compared to diesel, biodiesel emissions are substantially better for the environment and, in turn, better for the health of the environment's inhabitants. Specifically, the emissions of particulate matter, CO, and total unburned hydrocarbons from biodiesel are each much less than those from petroleum diesel.

The properties of biodiesel and petroleum-based diesel fuels are compared and shown in Table 2.4. From this table, it shows that biodiesel produced from various vegetable oils have viscosities close to those of petroleum-based diesel fuels. Their heating values are a little lower, but they have higher cetane numbers and flash points. Since the characteristics of biodiesel are generally similar to those of petroleum-based diesel fuels; therefore, biodiesel is a strong candidate to replace 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 (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 (370°C)	63.9	42.3	-	166	0.884	0.0013
Diesel fuel	12-3.5 (40°C)	51	35.5	-	-	0.830	-
Gas-oil	2.8 (30°C)	58	42.7	-	59	0.833	0.05

There are many advantages for using biodiesel. For example, it is renewable resource, biodegradable, nontoxic, and essentially free of sculpture and aromatics, makes it has low emissions of SO_x, CO, NO_x, unburnt hydrocarbon and particulate matter as compared to conventional diesel (Karmee *and Chadha.*, 2005). However, the use of biodiesel is limited by some of its characteristics. Two of important properties which are suspected to be the limitations, are the oxidative stability and cold flow properties. The oxidative properties depend on the degree of unsaturation of the FAME chain (Kapila *et al.*, 2009). If the degree of unsaturation is higher, the oxidative stability of FAME will be lower. On the other hand, if the degree of saturation is too high, the cold flow properties will be bad.

2.4 Partial Hydrogenation

Hydrogenation is the chemical reaction that results from the addition of hydrogen (H_2). The process is usually employed to reduce or saturate organic compounds. This process typically constitutes the addition of pairs of hydrogen atoms to a molecule, since non-catalytic hydrogenation takes place only at very high temperature and pressure. Therefore, catalysts are required to reduce the operating temperature and pressure for this reaction to be useful.

Kapila and co-workers (2009) reported that the properties of hydrogenated FAME strongly depend on the hydrogenation time. The total percentage of saturated fatty acid (SFA) increased from 29.3% to 76.2% after 2 h of hydrogenation. It can be concluded that hydrogenation is a good method to increase oxidative stability as well as higher cetane number, which are the two important key parameters for biodiesel upgrading. However, the poorer cold flow properties of hydrogenated FAME make it unsuitable for cold weather condition.

In 2009, Nikolaou and co-workers studied the partial hydrogenation of polyunsaturated FAMEs selectively to monounsaturated compounds using active rhodium sulfonated phosphite (Rh/STPP) complexes. They found that partial hydrogenation substantially increase the oxidative stability and greatly improve the aging/storage properties of biodiesel product and is not influence to cold flow property.

In addition, Sonthisawate and co-worker (2009) studied the upgrading of biodiesel fuel quality by partial hydrogenation process. They found that the partial hydrogenation can improve the oxidation stability at the minimal cost of cold flow property and decrease the sludge formation after polymerization without adding the antioxidant.

In 2006, Snare and co-worker studied the deoxygenation of stearic acid to biodiesel and the result showed that Pd supported on carbon is the best partial hydrogenation catalyst in terms of high catalytic activity and high selectivity compared to other metal catalysts on different supports.

Tamai and co-worker (2009) prepared Pd supported on microporous and mesoporous activated carbons by immersing the activated carbons in a Pd solution. The catalytic activities of the prepared catalysts for the hydrogenation of methyl linoleate were investigated. As a result, they found that Pd particles were mainly supported on mesopores. Moreover, the Pd supported mesoporous activated carbons exhibited higher catalytic activities when compared with Pd supported on microporous activated carbons. It indicated that Pd particles supported on mesopores play an important role in the catalytic activity.

2.5 Polybenzoxazine (Carbon Aerogel)

Carbon aerogel are highly solid porous material, which extremely low densities, large open pore, and high specific surface areas; moreover, its pore size can be controlled by changing starting material. The morphology of aerogel can be modified by using different synthesis parameters. This characteristic makes the aerogel particularly well adapted for various applications such as fuel cells, host material of catalysts, thermal insulators, and molecular sieves. The traditional process for organic aerogel preparation is typical via the sol-gel polymerization of an organic solution followed by supercritical drying of the obtained hydrogel to extract the solvent in the gel structure; and then the obtained organic aerogel is transformed into carbon aerogel via pyrolysis (Pekala, R.W.,1989). The total process of carbon aerogel preparation requires approximately 2 weeks. Recently, many attempts have been made to shorten the process, such as using alcohol-sol–gel polymerization

and drying with supercritical acetone to avoid the solvent exchanging period (Qin, G and Guo, S., 2001). The organic and carbon aeorgel processing normally uses resorcinol (R) and formaldehyde (F) as the precursors. The RF aerogels consist of a highly crosslinked aromatic polymer. In order to obtain carbon aerogel, the RF gel is carbonized in an inert atmosphere. Basically, the crosslink density of organic gel is a key parameter that needs to be considered for aerogel applications. Highly crosslinked organic gel not only provides high structural stability in order to preserve its structure after solvent removal, but also introduces high char yield after pyrolysis to construct the carbon aerogel. In order to find a reactant to synthesize the organic aerogel and transform it to carbon aerogel, these two characteristics of the synthesized gel need to be considered (Lorjai *et al.*, 2009).

Furthermore, the work done by Horikawa *et al.* in 2003 showed that spherical resorcinol-formaldehyde (RF) aerogel particles were synthesized by emulsion polymerization of resorcinol with formaldehyde in a slightly basic aqueous solution, followed by supercritical drying with carbon dioxide. RF carbon aerogel particles were prepared by carbonizing of the RF aerogel at a high temperature under nitrogen atmosphere. By changing the viscosity of the RF sol added to the cyclohexane containing a surface-active agent for preparation of the spherical RF hydrogels, they investigated the influence of the apparent viscosity of the RF sol on the size of the generated RF carbon aerogel particles. They could successfully prepare the RF carbon aerogel particles with a truly spherical shape and control their size in the range from about 10 to 500 μm by changing the apparent viscosity of the RF sol. The spherical RF carbon aerogel particles with an average diameter of 20 μm have a BET surface area of about 800 m^2/g and a uniform mesopores radius of 1.78 nm.

2.6 Diesel Fuel

Diesel or Diesel fuel in general is any fuel used in diesel engines. The most common is a specific fractional distillate of petroleum fuel oil, but alternatives that are not derived from petroleum, such as biodiesel, biomass to liquid (BTL) or gas to liquid (GTL) diesel, are increasingly being developed and adopted. Because

many types of diesel engine, diesel fuel must have suitable properties for each diesel engine. The properties of diesel fuel as follows:

2.6.1 Ignition Quality (Cetane Number)

The performance of diesel engines is critically dependent upon the ignition quality of the fuel. The diesel engine relies on the high pressures and temperatures generated during the compression stroke to bring about auto-ignition of the air-fuel mixture. Auto-ignition is defined as the condition when the air-fuel mixture spontaneously ignites without an external source of ignition, such as flame or spark. The tendency of the diesel fuel to ignite under these conditions is known as its ignition quality, which is conveniently expressed in terms of cetane number. The higher the cetane number, the better the ignition quality. Higher cetane number shortens the ignition delay period, which translates to smoother combustion and thereby optimizing the power generated. Cetane number also influences cold start performance, white smoke, engine noise, and emission in premature filter plugging with sulphates.

2.6.2 Lubricity

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

2.6.3 Cloud Point

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

2.6.4 Flash Point

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

2.6.5 Viscosity

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

2.6.6 Volatility (Distillation)

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

2.6.7 Oxidation Stability

One important problem associated with renewable fuel derived from vegetable oil and animal fats (i.e., biodiesel) is poor oxidative stability. This is especially true for soy-based biodiesel which has significantly higher levels of polyunsaturation. The oxidative stability will be evaluated by measuring the acid number, peroxide value, kinematic viscosity, and Rancimat induction period.