CHAPTER II

LITERATURE REVIEW

2.1 Polybenzoxazine

Phenolic resins have been well known as addition-cure thermosetting polymers widely used in various applications due to their several desirable properties such as good mechanical strength, electrical insulation, and dimensional stability, resistance against many types of solvents, flame retardation, and low smoke emission from burning. However, many shortcomings of these materials are from their brittleness, short shelf life, requirement of acid or base catalyst for the resin preparation, which potentially causes corrosion in the processing equipments. Furthermore, the by-products when curing of the resins are such as ammonium compounds, water, and so forth. These generated volatiles could have an effect on the properties of cured resins because of void formation in the final products. In order to overcome these problems, a novel class of high performance thermosetting phenolic resin, namely polybenzoxazine (PBZ), has been developed. The polybenzoxazines have been attracted great attention as versatile materials for structural and engineering applications because they possess good flame retardance, and thermal properties of phenolic resins including their high mechanical properties, with good sound and noise absorbance (Endo *et al.*, 2009)

Typically, benzoxazine resins are synthesized from phenol (or substituted phenols), aldehyde (such as formaldehyde, acid aldehyde, or pyromucic aldehyde), and amine groups. Even though these resins were firstly produced by Holly and Cope (Holly *et al.*, 1944), the capability of polybenzoxazine has become well known recently (Liu *et al.*, 1996). This novel kind of polymers can be synthesis via either solvent or solventless technology. In addition, the curing of the resins involves ring-opening polymerization with no need of any catalyst or curing agent and there is no by-product during curing, which leads to no void in the products. Interestingly, benzoxazine resins are also able to undergo hybrid network formation with various other resins or polymers, therefore rendering a novel class of resin systems with intriguing properties (Kimura *et al.*, 2001). Additionally, polybenzoxazines have many reported

outstanding characteristics such as high glass transition temperature (Tg), high thermal stability, fast mechanical property development, near-zero volumetric shrinkage or expansion upon cure, high processability due to low melt viscosity before polymerization, low water uptake, high char yield, and low coefficient of thermal expansion (CTE). Moreover, the polymers render low dielectric constant and dissipation loss, high mechanical performance and great molecular design flexibility.

Polybenzoxazines are a novel class of phenolic resins and they can be used as excellent matrix for high-performance composites. The thermal stability of polybenzoxazines in different atmospheric environments attracts the interest of many researchers, and much effort has been devoted to investigating the thermal and thermooxidative degradation behavior of various polybenzoxazines and their blends. Most studies monitored the weight changes of various polybenzoxazines with temperature rising by thermogravimetry (TG) and identified the evolved gases by coupling of TG to an on-line analytical technology, such as Fourier transform infrared (FTIR) spectroscopy as well as gas chromatography with mass spectrometry (MS). These researches show that the variation in the thermal stability of various polybenzoxazines is due to the difference in their molecular structures, namely, the thermal stability of polybenzoxazines is affected by the molecular structures of the starting phenols and amines with which the corresponding benzoxazines are synthesized. In addition, the char yield in nitrogen at 800 °C varies with the structure changes of phenols and amines, and it is in the range of about 28–81% for various polybenzoxazines (Liu *et al.*, 2011).

2.2 Porous Carbon

Porous materials, especially porous carbon, have been extensively studied over the past decade and have been used in various applications, such as water purification, gas separation, catalyst supports, electrode material for energy storage devices, adsorbents, molecular sieves, thermal insulation, etc. Porous materials can be classified into three categories based on their pore sizes: microporous (pore size <2 nm), mesoporous (2-50 nm), and macroporous (>50 nm).

The demand for porous carbon materials is because of not only their excellent physical and chemical properties, such as thermal conductivity, electrical conductivity, low density, and chemical stability, but also their wide availability.

Porous carbon materials have been conventionally prepared by pyrolysis and physical or chemical activation of organic precursors, such as coals, woods, polymers, etc. at elevated temperatures in inert atmospheres. These porous carbon materials, such as activated carbon and molecular sieving carbons (MSCs), generally have broad pore size distributions in both micro- and mesopore ranges. Unlike other inorganic molecular sieves, such as zeolites, MSCs are hydrophobic and have great corrosion resistance. However, microporous carbons have some limitations including collapse of pore structures during high-temperature treatments and limited mass transport due to pore size restriction.

To produce well-defined micro- and mesoporous carbon materials, the template synthesis method has been investigated. The conventional template synthesis consists of the following steps:

(1) preparation of the carbon precursor and inorganic template composite

(2) carbonization, and

(3) removal of the inorganic templates.

Various inorganic materials such as zeolites, silica nanoparticles, and mesoporous silica compounds have been used as templates. This template synthesis approachis appropriate for certainapplications in which uniform pore sizes are required. For applications in which uniform pore sizes are not required, the carbonization of organic aerogels, cryogels, and xerogels is an attractive approach because of the simplicity of synthesis and, in the case of xerogels, the possibility of large-scale production.

Phenolic resins have been extensively used as organic precursors of carbon aerogel as they are easily available. In addition, their properties and cost are quite reasonable. In the 1990s, Pekala et al. developed resorcinol-formaldehyde (RF) aerogel through a sol-gel polycondensation of resorcinol and formaldehyde by using base (Na_2CO_3) as catalyst. To preserve the gel skeleton and prevent shrinkage during drying, the solvent was removed under CO_2 supercritical conditions. Carbon aerogel was then obtained by pyrolysis of RF aerogel at high temperature in an inert atmosphere.

Tao et al. recently reported a method to develop highly mesoporous carbon aerogels (HMCAs) with hydrophilicity controlled pore walls. CO_2 supercritical drying was used to form interconnected micropores and small mesopores, at the same time using colloidal silica nanocasting to form larger mesopores and increase pore volume. Controlled partial silica removal resulted in a silica-modified carbon aerogel (SMCA). If silica was controllably moved from carbon aerogel using aqueous HF solution, the product was called HMCA. The removal of silica also modified the hydrophilicity of the pore walls. The pore characteristics of HMCA and SMCA compared with a carbon aerogel without silica template (CA) and silica-templated mesoporous carbon (TMC) without CO_2 supercritical drying.

As mentioned earlier, organic gels are usually dried by supercritical drying after solvent exchange in order to eliminate the surface tension which can cause shrinkage. Another approach is to use freeze-drying by freezing organic gels before solvent removal using sublimation under low pressure, yielding a "cryogel". However, both supercritical drying and freeze-drying are quite expensive and impractical for the industrial level. highly porous carbon materials called "carbon xerogels" could be produced by direct evaporative drying and pyrolysis of aqueous RF gels if the operating parameters were correctly evaluated. When pH was lower than 5.5, the obtained sample was micro and macroporous with poor mechanical strength. However, when pH was in the range of 5.5-6.25, micro- and mesoporous carbon material was obtained. On the other hand, the material was nonporous when pH exceeded 6.25. Hence, the pore texture of carbon material obtained after drying and pyrolysis was controllable by the pH of the solution.

Carbon aerogel is a 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 they obtained organic aerogel is transformed into carbon aer-

ogel via pyrolysis (Pekala *et* al., 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 supercritical drying. The experimental results indicated that it was easy to avoid the accumulation of polymerization heat during gelation, and easy to take out the products from the reaction container. (Liu *et al.*, 2006)

Carbon aerogels are obtained by pyrolysis of organic aerogels, which are mostly produced by the polycondensation reaction of resorcinol and formaldehyde in different solvents and using different catalysts (Figure 2.1). They are generally supercritical dried prior to pyrolysis of the organic aerogels to preserve their pore texture (Fairén-Jiménez *et al.*, 2006).
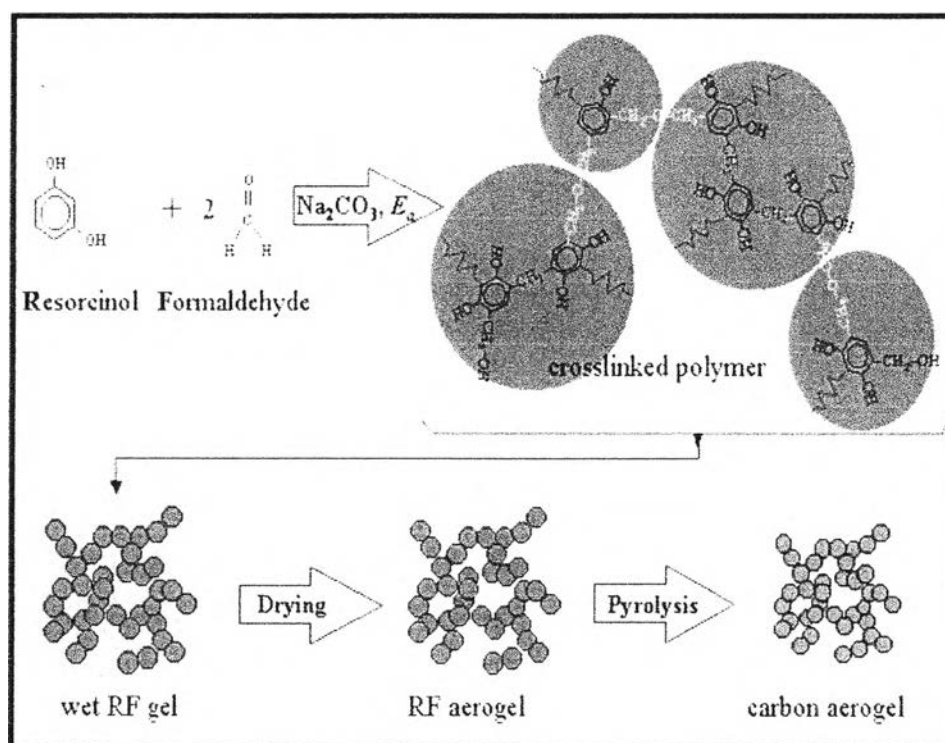

Figure 2.1 Schematic diagram of the reaction of resorcinol with formaldehyde (Berthon-Fabry and Achard, 2003).

The organic and carbon aeorgel processing normally uses resorcinol (R) and formaldehyde (F) as the precursor. 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. Lorjai et al.(2009) prepared carbon aerogel from bisphenal-A and aniline base polybenzoxazine (Figure 2.2). They found that pore structure of carbon aerogel can be tailored by varying monomer concentration.
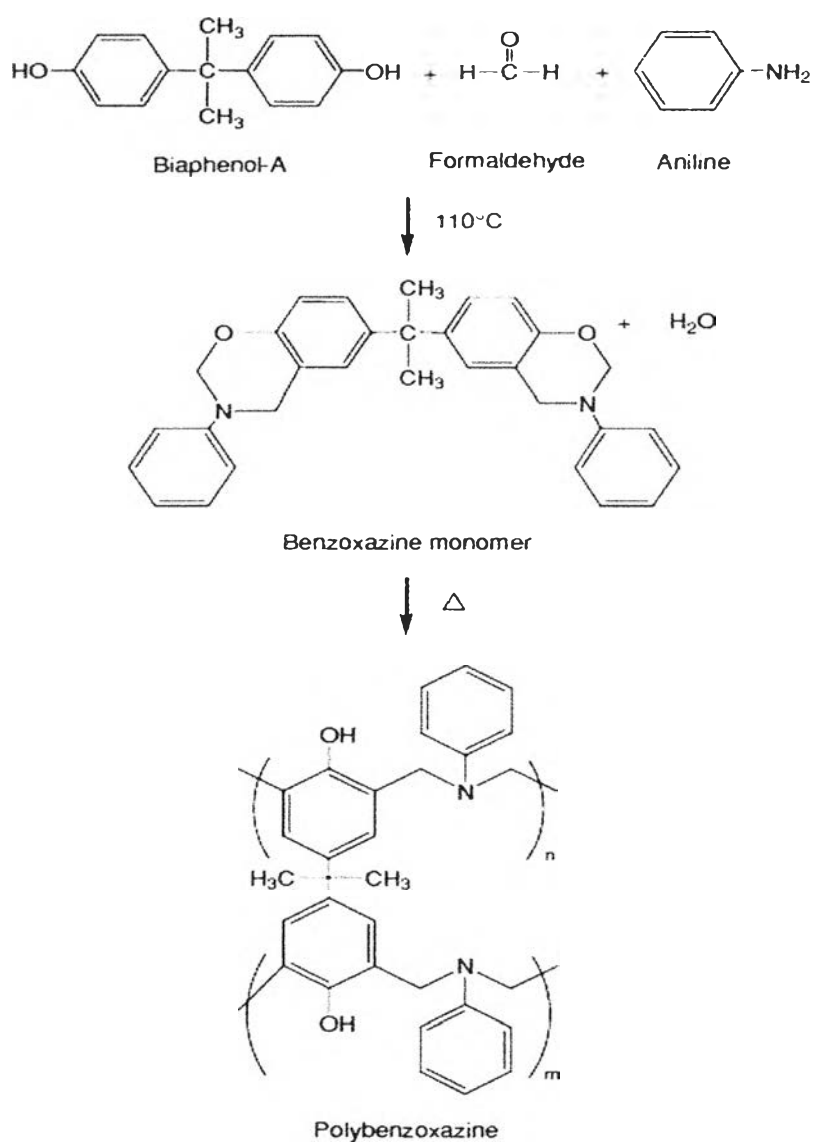
Figure 2.2 Schematic Precursors and the polybenzoxazine synthetic reaction.

The work done by Horikawa and co-workers in year 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 high temperature nitrogen under a 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, RF aerogel particles with a truly spherical shape and controlled particle size were prepared. The spherical RF carbon aerogel particles had an average diameter of 20 μm, a BET surface area of about $800m^2/g$ and a uniform mesopores radius of 1.78 nm.

Tamon H. and co-workers (1998) studied the mesoporous structure of organic and carbon aerogels by taking into account the synthesis conditions of the RF aquagels. They concluded that the mesoporous radius of the RF aerogel could be controlled in the range of 2.5-9.2 nm by changing the mole ratio of resorcinol to sodium carbonate used as a catalyst and the ratio of resorcinol to distilled water used as a diluent. Shrinkage also played a role in control of the mesopore redius. As the pyrolysis temperature increased, the mesopore volume became small but the peak radius of pore distribution was maintained. It was also noticed that with an increase in the pyrolysis temperature, ethane adsorption became larger than ethylene adsorption on the aerogels. The carbon aerogels prepared by pyrolysis at 1000°C had the same ethane and ethylene adsorption characteristics as activated carbons did.

Mahingsupan N.(2010) studied effect of activation process on the pore structure of polybenzoxazine-derived carbon aerogel. By activating carbon aerogel at 900°C in CO_2 it was found that the activated carbon aerogel had a high surface area with large amount of micropores whereas the non-activated sample had lower surface area, but larger pore size are summarized in Table 2.1.

Table 2.1 Surface areas, pore volume and pore diameter of carbon aerogels prepared from benzoxazine precursor.

Parameter	CA	Heat-treated CA	Activated CA
BET surface area (m^2/g)	360	372	910
Total pore volume (cm^3/g)	0.24	0.25	0.54
Average pore size (nm)	2.69	2.65	2.40
Micropore volume (cm^3/g)	0.14	0.16	0.40
Mesopore volume (cm^3/g)	0.13	0.11	0.17
*Mesoporosity (%)	54.2	44.0	31.5
*Microporosity (%)	58.3	64.0	74.1

*Mesoporosity = (mesopore volume/total pore volume) · 100

*Microporosity = (micropore volume/total pore volume) · 100

2.3 Activated carbon

Activated carbon is a carbonaceous material with a highly developed internal surface area and with a strong adsorptive capacity. Activated carbon has an abundant pore structure. Pyrolytic char can be converted into activated carbon by an appropriate physical activation process. Activated carbons produced from tire chars possess surface areas comparable with those of commercially available activated carbons. A pore system is developed using oxidizing agents such as carbon dioxide, air or steam, heated to 700–1000°C, creating new porous surfaces and with oxygenated functional groups (Helleur *et al.*, 2001). Activated is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions.

Porous carbon materials are characterized by their highly developed internal surface area and porosity. The development of micro- and mesopores is of especially great importance because it allows the carbons to absorb large amount and various types of chemicals from gases or liquids. (Cai *et al.*, 2004)

There are many raw materials available for preparing activated carbons, which can be divided into two completely different kinds. One includes grade low

coal (such as peat and lignite), waste pulp solution, waste plastics and various agricultural byproducts. The other includes synthetic resins and fibers. In the former, although raw materials of producing activated carbon are cheap, the applications of activated carbon obtained from these raw materials are limited because of its low surface area and not inefficient adsorption capacity (Yang *et al.*, 2004). With increasing aggravation of energy problem, it has become using synthetic resins and fibers to prepare high grade activated carbon (Ozaki *et al.*, 1997).
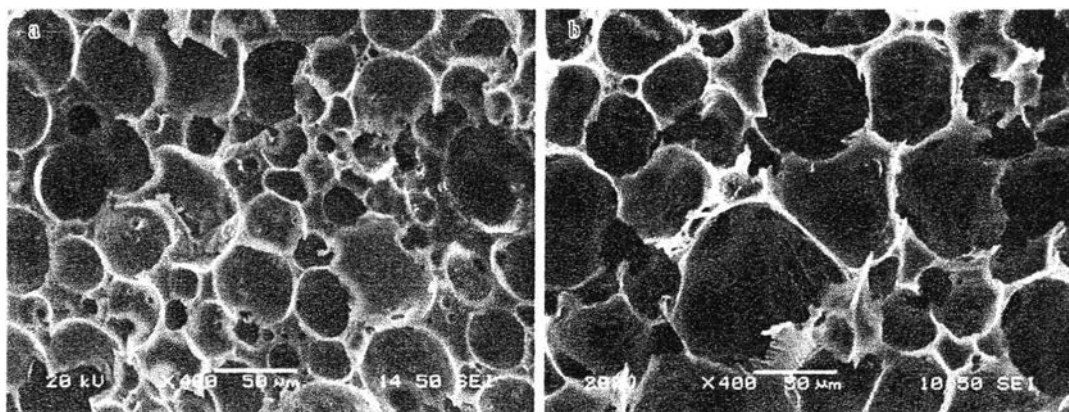

Figure 2.3 SEM image of phenolic resin carbon foam before (a) and after (b) activation (Xuefei *et al.*, 2009).

The SEM image shows that the pore structure of the activated carbon foam became honeycomb, and had thinner and smoother pore wall (Figure 2.3)

2.4 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 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% tri-glycerides and small amounts of monogylcerides 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 below.
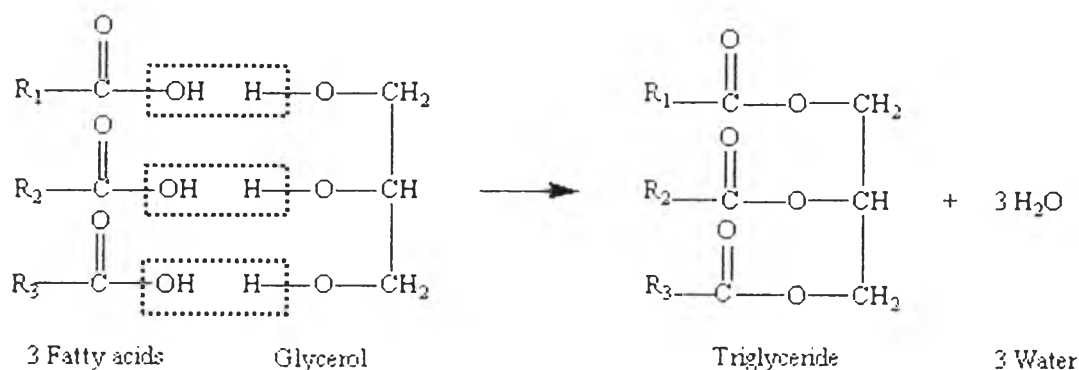

Figure 2.4 General formation of triglyceride (Swern, 1979).

From Figure 2.4, 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 2.2. 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 2.4.

Table 2.2 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	$C_{20}H_{40}O_2$

Fatty acid	Systematic name	Structure[a]	Formula
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 2.3 Fatty acid composition in different types of vegetable oils (Marchetti *et al.*, 2007).

Fatty acid	Soybean	Cottonseed	Palm	Lard	Tallow	Coconut
Lauric	0.1	0.1	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1.0	1.4	2.8	19.2
Palmitic	10.2	20.1	42.8	23.6	23.3	9.8
Stearic	3.7	2.6	4.5	14.2	19.4	3.0
Oleic	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic	53.7	55.2	10.1	10.7	2.9	2.2
Linolenic	8.6	0.6	0.2	0.4	0.9	0.0

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

| VegeTable oil	Kinematics viscosity (mm^2/s)	Cetane number	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)	Lower heating value (MJ/kg)
Peanut	4.9	54	5	-	176	0.883	33.6
Soya bean	4.5	45	1	-7	178	0.885	33.5
Babassu	3.6	63	4	-	127	0.875	31.8
Palm	5.7	62	13	-	164	0.880	33.5
Sunflower	4.6	49	1	-	183	0.860	33.5

VegeTa-ble oil	Kinematics viscosity (mm^2/s)	Cetane number	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)	Lower heating value (MJ/kg)
Tallow	-	-	12	9	96	-	-
Diesel	3.06	50	-	-16	76	0.855	43.8
20% bio-diesel blend	3.2	51	-	-16	128	0.859	43.2

As shown in Table 2.4, the use of vegetable oils directly as diesel fuels leads to a number of problems. The injection, atomization and combustion characteristics of vegetable oils in diesel engines are significantly different from those of 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.

2.5 Transesterificattion

The transesterification reaction proceeds with catalyst or without any catalyst by using primary or secondary monohydric aliphatic alcohols (Demirbas 2005).

Triglycerides + Monohydric alcohol $\rightleftharpoons$ Glycerin + Mono-alkyl esters
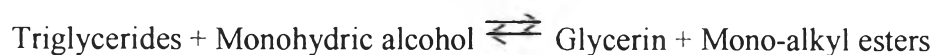
2.5.1 Acid-catalyzed Processes

The transesterification process is catalyzed by acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow. The alcohol/vegetable oil molar ratio is one of the main factors that influence the transesterification. An excess of alcohol favors the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically.

2.5.2 Alkali-catalyzed Processes

The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps. The alkali-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction.

2.5.3 Enzyme-catalyzed Processes

Although the enzyme-catalyzed transesterification processes are not yet commercially developed, new results have been reported in a recent article. The common aspects of these studies consist in optimizing the reaction conditions (solvent, temperature, pH, type of microorganism which generates the enzyme, etc) in order to establish suitable characteristics for an industrial application.

2.5.4 Non-catalytic Supercritical Alcohol

A non-catalytic biodiesel production route with supercritical methanol has been developed that allows a simple process and high yield because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids.

2.5.5 Transesterification by Microwave Flow System

The production of methyl esters from soybean transesterification by the use of a microwave flow system has been investigated. A household microwave was modified as a biodiesel reactor for continuous transesterification. This system consists of a polytetrafluoroethylene (Teflon) tubing reactor of 28 mm ID and 150 mL of total volume. The transesterification reaction under microwave radiation yielded similar results but with very fast heating rates (Encinar *et al.*, 2012).

2.6 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, which can be used in unmodified diesel-engine vehicles. Biodiesel is distinguished from the straight vegetable oil (SVO) (sometimes referred to as "waste vegetable oil", "WVO", "used vegetable oil", "UVO", "pure plant oil", "PPO") used as fuels in some converted diesel vehicles. "Bio diesel" is standardized as mono-alkyl ester and other kinds of diesel-grade fuels of biological origin are not included.

Biodiesel, (Ramos *et al.*, 2009) is produced through a reaction known as transesterification. In a transesterification or alcoholysis reaction, one mole of triglyceride reacts with three moles of alcohol (molar ratio of methanol to vegetable oil of 3:1) to form one mole of glycerol and three moles of the respective fatty acid alkyl esters. The process is a sequence of three reversible reactions, in which the triglyceride molecule is converted step by step into diglyceride, monoglyceride and glycerol.

Biodiesel is a biodegradable and non-toxic alternative fuel produced from animal fats or used vegetable oil that is produced from renewable resources (Meher *et al.*, 2009). It can be used in any Diesel engine without modification. Pure biodiesel has the highest BTU 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 and not from 40,000,000 year old organic matter, it is renewable. Moreover, the carbon dioxide taken up by plants during photosynthesis helps to mitigate the carbon dioxide emitted from using biodiesel so there is no net carbon introduced to the atmosphere. Compared to diesel fuel, 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, carbon monoxide and total unburned hydrocarbons from biodiesel are each much less than those from petroleum diesel.

There are many advantages for using biodiesel. For example, it is renewable resource, biodegradable, higher flash point, inherent lubricity, reduction of most reg-

ulated exhaust emissions (Knothe 2008), nontoxic and essentially free of sculpture and aromatics, makes it has low emissions of SO_x, CO, NO_x, unburn hydrocarbon and particulate matter as compared to conventional diesel fuel (Karmee *et al.*, 2005). It can be used without engine modification, generates good engine performance and improves combustion because of its oxygen content. Furthermore, it offers good lubrication properties and ability to be blended in any proportion with regular petroleum-based diesel fuel.

2.7 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. So, catalysts are required to reduce the operating temperature and pressure for this reaction to be useable.

Partial hydrogenation is a process that hydrogen atoms are added to partially saturate double bond in the fatty acid methyl esters (FAMEs) structure. This process requires low pressure and temperature at about 1–5 bar and 80–120°C. 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 2.5
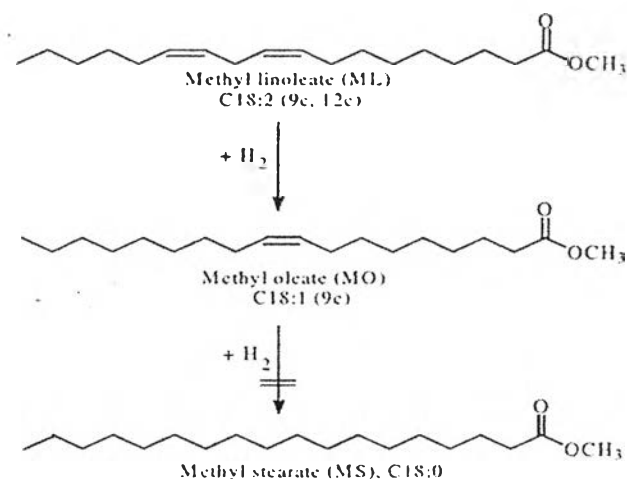
Methyl linoleate (ML)
C18:2 (9c, 12c)

+ H₂

Methyl oleate (MO)
C18:1 (9c)

+ H₂

Methyl stearate (MS), C18:0

Figure 2.5 Partial hydrogenation of polyunsaturated FAME(Papadopoulos *et al.*, 2010).

From previous work of Kapilla and co-workers showed 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. So, they can conclude that hydrogenation is a good method to increase oxidative stability as well as higher cetane number, which are two key parameter for biodiesel. However, the poorer cold flow properties of hydrogenated FAME make it unsuitable for cold weather condition.

In addition, Nicolous and co-workers studies the partial hydrogenations of polyunsaturated FAMEs selectively to monounsaturated compounds using active rhodium sulfonated phosphate (Rh/STPP) complexes. They found that partial hydrogenation substantially increase the oxidative stabilities and greatly improve the ageing/storage properties of biodiesel product and is not influence to cold flow property.

In 2006 Snare and co-worker studied and the result showed that Pd supported on carbon is the best partial hydrogenation catalyst in term of high activity and high selectivity compare to other metal catalyst on different supports.

Furthermore, the previous work done by Tamai et al. in year 2009 showed that Pd particles supported mesoporous activated carbons were prepared by immersing mesoporous activated carbons in a dispersion of Pd particles and their catalytic activities for the hydrogenation of methyl linoleate were investigated. As a result,

they found that Pd particles were mainly supported on mesopores. Pd supported mesoporous activated carbons exhibited high catalytic activities, compared with Pd supported microporous activated carbon. It is indicated that Pd particles supported on mesopores play an important role in the catalytic activity.

2.8 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. To distinguish these types, petroleum-derived diesel is increasingly called petrodiesel Ultra-low sulfur diesel (ULSD) is a term used to describe a standard for defining diesel fuel with substantially lowered sulfur contents.

Because of diesel engine have a difference size, so diesel fuel must have suitable properties for each diesel engine

2.8.1 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 the cetane number. The higher cetane number, the better the ignition quality. Higher cetane number shortens the ignition delay period, which translates to smoother combustion and thereby optimising the power generated. Cetane number also influences cold start performance, white smoke, engine noise, and emission.

2.8.2 Sulphur Content

Sulphur content of On-Road Diesel Fuel cannot exceed 22 mg/kg after September 1, 2006 and 15 mg/kg after October 15, 2006. These ultra-low sulphur

levels are mandated by Federal legislation and required for all 2007 model year vehicles that will be equipped with advanced emission control systems utilizing diesel particulate filters (DPFs) in exhaust systems. High sulphur fuel will be potentially harmful because it will result in premature filter plugging with sulphates.

2.8.3 Lubricity

Lubricity is the ability to reduce friction between two surfaces in relative motion. It is a measure of fuel's effectiveness as a lubricant. Diesel fuel also functions as lubricant in fuel injection equipment such as rotary or distributor- type injection pumps, and injectors. The severe hydro treatment 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 hydro treated 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.

2.8.4 Cloud Point

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

2.8.5 Flash Point

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

2.8.6 Viscosity

Viscosity is a measure of a liquid's resistance to flow under pressure and is dependent upon temperature. At higher temperature, the viscosity of the fuel decreases and at lower temperature its viscosity increases. Viscosity of diesel fuel influences engine performance in two ways: injection pump and injector performance, and injected fuel spray pattern and atomization. A very low viscosity fuel can cause internal leakages in the injection pump causing low pressure build up resulting to fuel starvation in the combustion chamber of the engine. This could also lead to undesirable spray pattern that promotes incomplete combustion. Fuel starvation and incomplete combustion will both contribute to reduced power and excessive emission. A very low viscosity fuel also causes excessive wear in the injection system and poor hot re-start.

On the other hand, a very high viscosity fuel will cause poor atomization during injection. As a result, the fuel is not evenly distributed in the combustion chamber to mix well with the air - a requisite for good combustion.

2.8.7 Volatility (Distillation)

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

2.8.8 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. Interestingly, it has been reported that the oxidative stability problem is more pronounced in 20% blended biodiesel (B-20) than in neat soy-based biodiesel (B-100), presumably due to the fact that ultra-low sulfur diesel (ULSD) is a much poorer solvent as compared to B-100. Another factor which may contribute to the

oxidative instability is the presence of metal ions and additives in ULSD. This paper will examine three fundamental aspects: 1. The oxidative stability of individual fatty acid esters and soy-based biodiesel when blended with ULSD; 2. The effectiveness of synthetic and natural antioxidants as a function of concentration, storage time and conditions, in B-20; and 3. the catalytic effects of transition metal ions on the oxidative degradation of biodiesel and biodiesel blends. The oxidative stability will be evaluated by measuring the acid number, peroxide value, kinematic viscosity and Rancimat induction period. Based on the findings, the possible mechanisms leading to the oxidative degradation in B-20 will be discussed. Various approaches to minimize oxidative stability problems in B-20 will be examined.