

CHAPTER II



Background and Literature Review

2.1 Bio-oil and biodiesel

Bio-oils and biodiesel refer to triglycerides based fuels produced from vegetable oils or animal fats to substitute the use of petroleum diesel. Here bio-oil is defined as triglycerides either used directly or modified to achieve the properties required as engine fuels. Biodiesel is also a bio-oil but it specifically refers to fatty acid alkyl esters produced from triglycerides. The background and literature reviews on the development of the bio-oil and bio-diesel are summarized in this chapter.

2.1.1 Bio-oil

2.1.1.1 Direct use and blending

Beginning in 1980, there was considerable discussion regarding use of vegetable oil as fuel (Bartholomew, 1981) with most advanced work at that period was with sunflower oil which took place in South Africa. Caterpillar Brazil in 1980 used pre-combustion chamber engines with a mixture of 10% vegetable oil to maintain total power without any alteration or adjustments to the engines. At that point, it was not practical to substitute 100 % vegetable oil for diesel fuel. But a blend of 20 % vegetable oil and 80 % diesel fuel was successful. Some short-term experiments were successfully carried out using up to 50/50 ratio. Nevertheless, the problem appeared after the engine has been operating on vegetable oil for longer period of time. Schlick et al. (1988) evaluated the performance of a direct injection 2.59 L, 3-cylinder 2600 series ford diesel engine operating on mechanically expelled- unrefined soybean oil and sunflower oil blended with number 2 diesel fuels on 25.75 v/v basis. The power remained constant throughout 200 h of operation. Excessive carbon deposition on all combustion chamber part precludes the use of these fuel blends, at least in this engine and under the specified Engine Manufacturers' Association operating conditions.

In conclusion of these experiments, direct use of vegetable oil and/ or the use of blends of the oils has generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines, the high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and composition, carbon deposits and lubricating oil thickening.

2.1.1.2 Microemulsions

To solve the problem of the high viscosity of vegetable oils, microemulsions with solvents such as methanol, ethanol, and 1-butanol have been studied. A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimension generally in the 1-150 nm range, formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles (Schwab et al., 1987). It was found that microemulsions can improve spray characteristic by explosive vaporization of the low boiling constituent in the micelles (Pryde, 1984). In short term performances, ionic and non-ionic microemulsions of aqueous ethanol in soybean oil were nearly as good as that of No. 2 diesel, in spite of the lower cetane number and energy content (Goering et al., 1982). However, fuels formulated as microemulsions have low cetane numbers and low heating values as compared with No. 2 diesel fuel (Bagby, 1987).

2.1.1.3 Thermal cracking (pyrolysis)

Pyrolysis is strictly defined as the conversion of one substance into another by means of heat or by heat with the aid of a catalyst. It involves heating in the absence of air or oxygen and cleavage of chemical bond to yield small molecules (Weisz et al., 1979). Pyrolytic chemistry is difficult to characterize because of the variety of the reaction paths and the variety of reaction products that may be obtained from the reaction that occur. The pyrolyzed materials can be vegetable oils, animal fats, natural fatty acids and methyl ester of fatty acids. The pyrolysis of fats has been investigated for more than 100 years especially in those areas of the world that lack deposits of petroleum (Sonntag, 1979).

Since World War I, many investigators have studied the pyrolysis of vegetable oil to obtain products suitable for fuel. In 1947, a large scale of thermal cracking of

tung oil calcium soaps was reported (Chang and Wan., 1947). Tung oil was first saponified with lime and then thermally cracked to yield a crude oil, which was refined to produce diesel fuel and small amounts of gasoline and kerosene. It was found that 68 kgs of the soap from the saponification of tung oil produced 50 L of crude oil. Grossley et al., (1962) studied the temperature effect on the type of products obtained from heated glycerides. For pyrolysis, various catalysts, largely metallic salts, have been studied and used in many investigations, to obtain paraffin and olefins similar to those present in petroleum sources.

The equipment for thermal cracking and pyrolysis is expensive for modest throughput. In addition, while the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. Furthermore, it produced some low value materials and, sometimes produces more gasoline than diesel fuel.

2.1.2 Biodiesel

Biodiesel is defined as fatty acid methyl or ethyl esters produced by transesterification of vegetable oils or animal fats when they are used as fuel in diesel engine and heating system. In this context, Biodiesel shows the following general advantages (Vicente et al., 2003)

1. It is biodegradable and non- toxic, assuring safe handling and transport.
2. It does not contain sulfur or aromatic compounds and thus it contributes to the reductions of the diesel engine exhaust emission level.
3. It comes from renewable source such as vegetable oil.
4. It can be produced domestically, reducing a country's dependency on foreign fuel.

2.2 Transesterification (Alcoholysis)

Transesterification (also called Alcoholysis) means taking a triglyceride molecule or a complex fatty acid, neutralizing the free fatty acid, and removing the glycerin and creating an alcohol ester. The general equation of this reaction is shown in Figure 2.1. R_1 , R_2 , and R_3 of the oil molecules are long chain hydrocarbon

constituting fatty acids which may be the same or different. A catalyst is usually used to improve the reaction rate and yield. Theoretically, the transesterification reaction is an equilibrium reaction. In this reaction, a larger amount of alcohol is generally used to shift the reaction equilibrium to the right side and produce more methyl ester products.

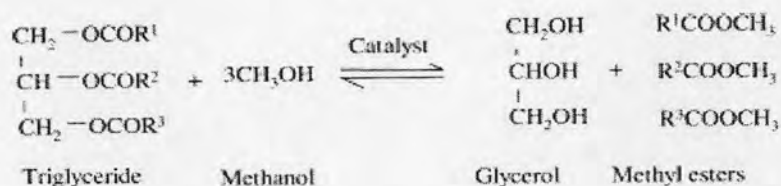


Figure 2.1 Transesterification of triglycerides (Mether et al., 2004)

Alcohols used in the transesterification can be primary or secondary monohydric aliphatic alcohol having 1- 8 carbon atoms. Among these alcohols, methanol and ethanol are used most frequently. Ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the reaction in the environment. However, methanol is used in practice because of its physical and chemical advantages of having shortest chain, making it easy to react. In general, transesterification reaction can be carried out with a catalyst using alkalis, acids, or enzymes. Noncatalytic transesterification in supercritical alcohols is also carried out.

2.2.1 Catalytic transesterification method

Acid – catalyzed Processes

The transesterification process can be catalyzed by acids such as sulfuric or hydrochloric acids (Freedman et al., 1986). These catalysts give very high yield in alkyl esters, but the acid catalyzed reactions are generally slow, and typically require, temperatures above 100 °C and more than several hours to complete. Methanolysis of soybean oil in the presence of 1 mol % of H₂SO₄ with an alcohol/oil molar ratio of 30:1 at 65 °C takes 50 h to reach complete conversion of the vegetable oil (>99 %)

while the butanolysis (at 117°C) and ethanolysis (at 78°C) using the same quantities of catalyst and alcohol, take 3 and 18 h, respectively (Freedman et al., 1986).

The alcohol/vegetable oil molar ratio is one of the main factors that influences transesterification. An excessive amount of alcohol favors the formation of the products. On the other hand, it makes the recovery of the glycerol difficult, so that ideal alcohol/oil ratio has to be established empirically, considering each individual process.

The mechanism of the acid catalyzed transesterification of vegetable oils is shown in figure 2.2 for a monoglyceride. However, it can be extended to diglyceride and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation I which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III. Elimination of glycerol forms the new ester IV, and regenerates the catalyst H^+ .

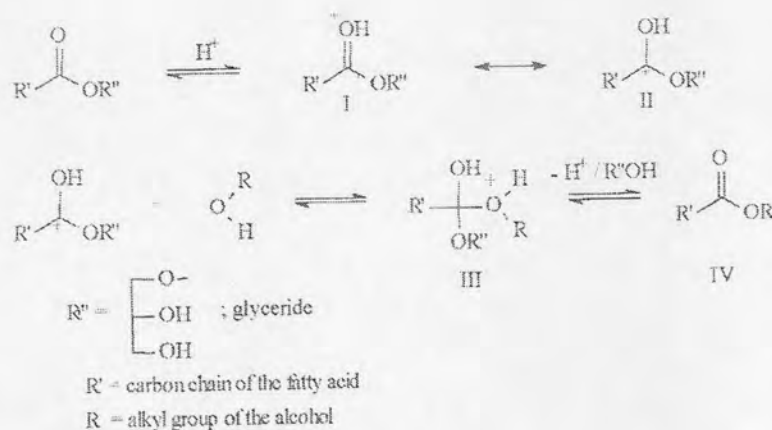


Figure 2.2 Mechanism of the acid catalyzed transesterification of vegetable oil (Schuchardt et al., 1997)

According to this mechanism, carboxylic acids can be formed by the reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid catalyzed transesterification should be carried out in the absence of water in order to avoid the competitive formation of carboxylic acid which reduces the yield of alkyl esters.

Base – Catalyzed Processes

Base catalyzed transesterification of vegetable oils is known to proceed faster than the acid catalyzed reaction. Due to this reason, together with the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favor base catalyst such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates. The mechanism of the base catalyzed transesterification of vegetable oils is shown in Figure 2.3.

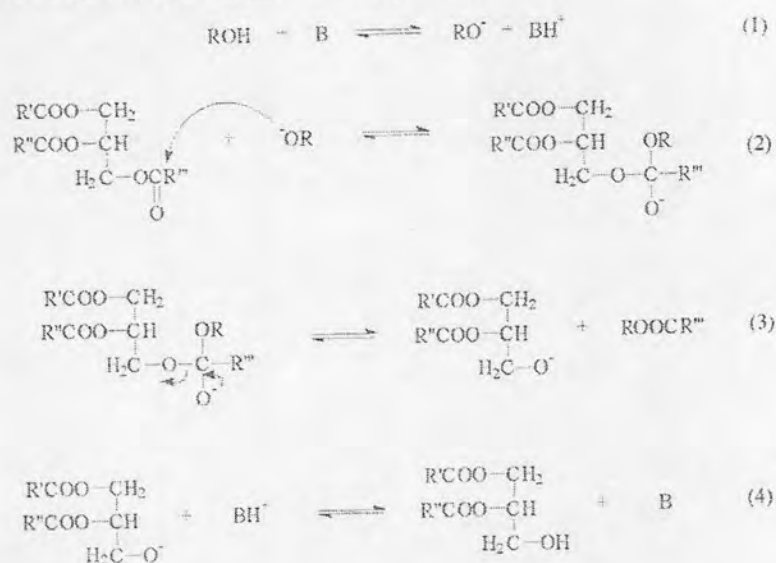


Figure 2.3 Mechanism of the base-catalyzed transesterification of vegetable oils
(Schuchardt et al., 1997)

The first step (equation 1) is the reaction between the base and alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate in equation 2 from which the alkyl ester and the corresponding anion of the diglyceride are formed in equation 3. The latter deprotonates the catalyst, thus regenerating the active species which is now able to react with a second molecule of the alcohol, starting another catalytic cycle (equation 4). Diglycerides and monoglycerides are converted by the same mechanism to form a mixture of alkyl esters and glycerol.

Alkaline metal alkoxides (denoted as CH_3ONa for the methanolysis) are the most active catalyst, since they give very high yields (> 98 %) in short reaction time of about 30 minutes, even when they are applied at low molar concentrations (0.5 mol

%). However, they require the absence of water which makes them inappropriate for typical industrial processes. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxide, but less active. Nevertheless, they are a good alternative since they can give the same high conversions just by increasing the catalyst concentration to 1 or 2 mol %. However, even if water free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester with consequent soap formation as shown by the reaction in figure 2.4. This undesirable saponification reaction reduces the ester yields and thus makes it considerably difficult for the recovery of the glycerol due to the formation of emulsions.

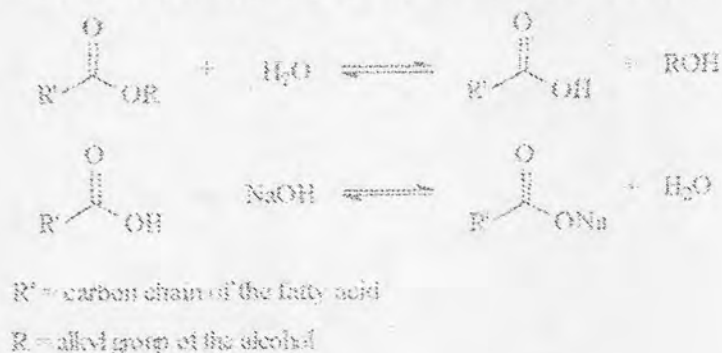


Figure 2.4 Saponification of the produced fatty acid alkyl esters
(Schuchardt et al., 1997)

Lipase catalyzed Processes

Due to their ready availability and the ease of handling, hydrolytic enzymes have been widely applied in organic synthesis. They do not require any coenzymes, are reasonably stable, and often tolerate organic solvents. Their potential for regioselective and especially for enantioselective synthesis makes them valuable tools

Although the enzyme catalyzed transesterification processes are not yet commercially developed, new results have been reported in recent articles and patent (Posorske, 1984). The common aspects of these studies consists of optimizing the reaction conditions (solvent, temperature, pH, type of microorganism which generate the enzyme, etc.) in order to establish the suitable characteristics for industrial application. However, the reaction yields as well as the reaction times are still unfavorable compared to the base catalyzed reaction system.

2.2.2 Non-Catalytic transesterification method (Supercritical Methanol)

With the aim of developing a novel methanolysis process for oil without using any catalyst, Saka and Kusdiana (2001a) conducted a fundamental study of biodiesel production in supercritical methanol. They demonstrated that rapeseed oil could be converted to methyl ester in 240s by supercritical methyl transesterification at 350 ° C. While the quality of methyl ester produced were basically the same as those obtained in the conventional method with alkali catalyst, the methyl ester yield of the supercritical methanol method was higher due to the smaller number of steps were required for product separation and purification. A reaction temperature of 350 ° C and a molar ratio of methanol to rapeseed oil of 42 to 1 were considered to be the most appropriate condition (Saka and Kusdiana, 2001 b). Since supercritical methanol has a hydrophobic nature with a lower dielectric constant, non polar triglycerides can be well solvated with supercritical methanol to form a single phase oil/methanol mixture. The oil to methyl ester conversion rate was found to increase dramatically in the supercritical state.

Free fatty acid contained in crude oils and fats could also be converted efficiently to methyl ester in supercritical methanol, leading to increase of the total yield of methyl ester from use oils (Saka and Kusdiana. 2001 c). In addition, because the process is non-catalytic, the purification of product after the transesterification reaction is much simpler and the process is more environmentally friendly compared with the alkali-catalyzed method in which all the catalyst and saponified products have to be removed to obtain biodiesel fuel.

2.3 Production of biodiesel from fatty acids

2.3.1 Fatty acids

Fatty acids are merely carboxylic acids with long hydrocarbon chains. The hydrocarbon chain length may vary from 10-30 carbons (most usual is 12-18). The non-polar hydrocarbon alkane chain is an important counter balance to the polar acid functional group. In acids with only a few carbons, the acid functional group dominates and gives the whole molecule a polar character. However, in fatty acids, the non-polar hydrocarbon chain gives the molecule a non polar character. The most

common fatty acids are listed in Table 2.1. There are two groups of fatty acids: saturated and unsaturated fatty acids. Unsaturated fatty acid refers to the presence of one or more double bonds between carbon atoms as in alkenes, whereas saturated fatty acids have all bonding positions between carbons occupied by hydrogen. Generally, the melting points for the saturated fatty acids follow the boiling point principle, that is, as the molecular weight increases, the melting point increases. For fatty acids with the same number of carbon atoms, the unsaturated fatty acids have lower melting points than the saturated fatty acids. The reason for this phenomenon can be found by a careful consideration of molecular geometries. This molecular structure allows many fatty acid molecules to be rather closely "stacked" together. As a result, close intermolecular interactions result in relatively high melting points. On the other hand, the introduction of one or more double bonds in the hydrocarbon chain in unsaturated fatty acids results in one or more "bends" in the molecule. The geometry of the double bond is almost always a cis configuration in natural fatty acids. These molecules do not "stack" very well. The intermolecular interactions are much weaker than saturated molecules. As a result, the melting points are much lower for unsaturated fatty acids.

Table 2.1 Common saturated and unsaturated fatty acid

Saturate	Unsaturated
Capric acid	Oleic acid
Lauric acid	Linoleic acid
Myristic acid	Linolenic acid
Palmitic acid	
Stearic acid	

Table 2.2 Composition of palm fatty acid (Fangrui Ma, Milford A. Hanna, 1999)

Fatty Acid	Composition
Palmitic Acid	42.80%
Stearic Acid	4.50%
Oleic Acid	40.50%
linoleic Acid	10.10%
linolenic Acid	0.20%

Palm fatty acids

The majority of fatty acids constituting palm oil are shown in Table 2.2. The general characteristics of each of the fatty acids are described below and summarized in Table 2.3.

Palmitic acid

The scientific name of palmitic acid is “hexadecanoic acid”. It has a molecular formulae of $C_{16}H_{32}O_2$ (see Figure 2.5). Other Names include 1-Pentadecanecarboxylic acid; n-hexadecanoic acid; n-hexadecoic acid, cetylic acid. Palmitic acid is a saturated acid, since there are no double bonds between neighboring carbon atoms. The palmitic acid has a molecular weight of 256.5, melting point of palmitic acids is between 61 - 64 °C, the boiling point is at 352 °C, and the density is approximately 0.84 g cm⁻³ at room temperature.

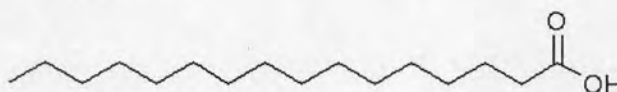


Figure 2.5 Structure of palmitic acid (Richardson J.F., 1983)

Stearic Acid

The scientific name of stearic acid is “octadecanoic acid”, having a molecular formulae of $C_{18}H_{36}O_2$ (see Figure 2.6). Other name is 1-heptadeca necarboxylic acid. Stearic acid has a molecular weight of 284.5, melting point of 67-69 °C, boiling point of 355.2 °C, and density of 0.8390 g cm⁻³.

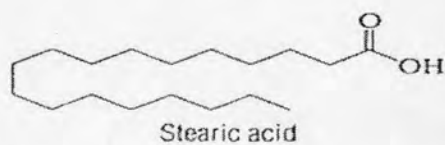


Figure 2.6 Structure of Stearic acid (Richardson J.F., 1983)

Oleic Acid

The scientific name of otearic acid is “9-Octadecenoic acid” Oleic acid is a fatty acid found in animal and vegetable oils having a molecular formulae of $C_{18}H_{34}O_2$ (see Figure 2.7), molecular weight of 282.47, and melting point of $13\text{ }^{\circ}\text{C}$, and boiling point of $360\text{ }^{\circ}\text{C}$ and density of 0.8935 g cm^{-3} . It is called a mono-unsaturated fatty acid because of the single double bond between the carbons.

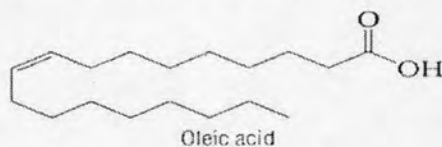


Figure 2.7 Structure of Oleic acid (Richardson J.F., 1983)

Linolenic acid

The scientific name of linolenic acid “9,12,15-Octadecatrienoic acid”. Linolenic acid having a molecular formulae of $C_{18}H_{30}O_2$, molecular weight of 278.435, boiling point $230\text{ }^{\circ}\text{C}$, melting point $-11\text{ }^{\circ}\text{C}$ and density of 0.92 g cm^{-3} . Other Names include (Z,Z,Z)-9,12,15-Octadecatrienoic acid cis,cis,cis-9,12,15-Octadecatrienoic acid.

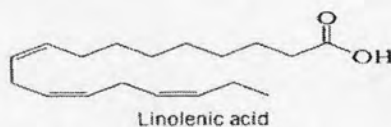


Figure 2.8 Structure of linolenic acid (Richardson J.F., 1983)

Linoleic Acid

The scientific name of linoleic acid “9, 12-Octadecadienoic acid”. Linoleic acid having a molecular formulae of $C_{17}H_{32}O_2$, molecular weight of 280.46, boiling

point 230 °C, melting point -5°C, and density of 0.9025 g cm⁻³ at room temperature. Other Names include 9-cis, 12-cis-linoleic acid; 9Z, 12Z-linoleic acid.

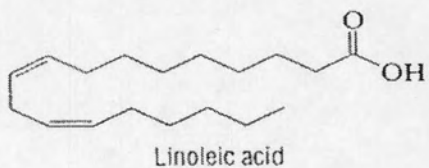


Figure 2.9 Structure of linoleic acid(Richardson J.F.,1983)

Table 2.3 Properties of palm fatty acid

Fatty Acid	Palmitic Acid	Stearic Acid	Oleic Acid	linoleic Acid	linolenic Acid
Scientific name	Hexadecanoic	Octadecanoic	9-Octadecenoic	9,12,15Octadecatrienoic	9,12Octadecadienoic
Molecular formulae	$C_{16}H_{32}O_2$	$C_{18}H_{36}O_2$	$C_{18}H_{34}O_2$	$C_{18}H_{30}O_2$	$C_{17}H_{32}O_2$
Molecular weight	256.5	284.5	282.47	278.44	280.46
Melting point (°C)	61 - 64	67-69	13	-11	-5
Boiling point(°C)	352	355.2	360	230.0	230
Density (g cm-3)	0.84	0.84	0.89	0.92	0.9

2.3.2 Esterification of fatty acids

Fatty acids can be used as raw materials to produce biodiesel by alkyl esterification. This occurs when fatty acids react with alcohol in the presence of a catalytic amount of mineral acid (Figure 2.10).

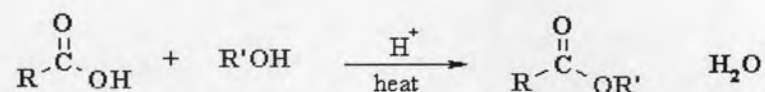


Figure 2.10 General equation for esterification

Fatty acids esterification with alcohol can not be catalyzed by alkali due to the competing saponification reaction which would produce soap rather than the desired alkyl esters. Therefore, acids catalyst must be used for this reaction. Under supercritical conditions however, fatty acids can readily be esterified with alcohol to form alkyl esters or biodiesel. Under such condition, care should be taken as water by product could react with the ester and hydrolyze the esters back into fatty acids.

2.4 Factors affecting biodiesel production

The processes of transesterification and esterification are affected by various factors, depending upon the reaction conditions used. The effects of these factors are described below.

2.4.1 Ratio of alcohol to oil or fatty acids

For transesterification, it is generally known that one of the most important variables affecting the yield of ester is molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole 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 in which a large excess of alcohol is required to drive the reaction to the right. For maximum conversion to the, a molar

ratio of 6:1 should be used. However, the high molar ratio of alcohol to vegetable oil interferes with separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it drives the equilibrium to back to the left, lowering the yield of esters.

For esterification, the molar ratio of alcohol to fatty acids is also of importance. In this case however, the stoichiometric ratio requires 1 to 1 mole ratio of the two reactants. Furthermore, no glycerol is produced. As a result, it is expected lower alcohol to fatty acids molar ratio would be needed compared with triglyceride transesterification.

2.4.2 Reaction temperature

The rate of reaction is strongly influenced by the reaction temperature. However, given enough time, the reaction will proceed to near completion even at room temperature. Generally, the catalytic reactions are conducted close to the boiling point of alcohol (60 to 70°C), under atmospheric pressure. For supercritical conditions, the reaction is carried out under high pressure (9000 kPa) and high temperature (above 240°C).

2.4.3 Reaction time

The conversion increases with reaction time. For example, Freedman et al. (1984) studied the transesterification of peanut, cotton-seed, sunflower and soybean oil under the condition of methanol to oil molar ratio of 6:1, 0.5 % sodium methoxide catalyst, and at 60°C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversion was almost the same (93-98%) for all four oils.

2.4.4 Use of organic co-solvent

An improved process was investigated by Krisnangkura and Simamaharnnop (1992) for methanolysis and ethanolysis of fatty acid glycerides such as those found in naturally occurring fats and oils derived from plant and animals. The processes comprise solubilizing oil or fat in methanol or ethanol by addition of toluene as co-

solvent in order to form a one phase reaction mixture in presence of an acid catalyst. The processes were found to proceed quickly, usually in less than 20 min, at ambient temperature, atmospheric pressure, and without agitation. The co-solvent increased the rate of reaction by making the oil soluble in methanol, thus increasing contact of the reactant. The lower alkyl fatty acid monoesters produced by the process can be used as biofuels and are suitable as diesel replacement or additives.

2.4.5 Purity of reactant

Impurities present in the oil also affect conversion levels. Under the same condition, 67 to 84 % conversion into ester using crude vegetable oils can be obtained, compared with 94 to 97 % when using refined oils. The free fatty acids in the original oils interfere with catalyst, however, under conditions of high temperature and pressure this problem can be overcome (Freedman et al., 1984).

2.4.6 Catalyst type and concentration

Catalysts used for transesterification of triglyceride are classified as alkaline, acid, among which alkaline are the most effective transesterification catalyst compared to acid catalyst. Sodium alkoxides are among the most efficient catalyst used, although KOH and NaOH can also be used. The alkaline catalyst concentration in range of 0.5 to 1 % by weight yields 94 to 99%. The acid could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Acid catalyst transesterification was studied with waste vegetable oil. The reaction was conducted at four different catalyst concentration, 0.5, 1.0, 1.5, and 2.25M HCl in presence of 100 % excess alcohol and result was compared with 2.25 M H₂SO₄. H₂SO₄ was found to have superior catalyst activity in the range of 1.5-2.25 M concentration (Mohamad, 2002).

2.4.7 Presence of water

In biodiesel production, it is well known that the vegetable oils used as a raw material for the transesterification should be water free since water has a negative effect on the reaction. As it consumes the catalyst and reduces catalyst efficiency. It

is generally recommended that for typical transesterification of vegetable oil, the water content should be kept below 0.06 % (Ma et al., 1998).

2.5 Fuel properties of vegetable biodiesel

2.5.1 Kinematic Viscosity

The standard procedure for measuring kinematic viscosity in diesel or biodiesel fuels is ASTM D 445. The summary of the test method as presented in the standard is “The time is measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature.” The repeatability of the test is within 0.5-1.0%, while the reproducibility is 1-2%. The test is usually conducted by measuring the time required for a volume of liquid to flow under gravity through a calibrated glass capillary tube. The kinematic viscosity is then equal to the product of this time and a calibration constant for the tube. Figure 2.11 shows a Cannon-Fenske style glass capillary tube that is commonly used for ASTM D 445. Biodiesel is more viscous than No. 2 diesel fuel, but only by a small amount. Depending on feedstock and the amount of oxidation, biodiesel’s viscosity will vary between 4.0 and 6.2, while No. 2 diesel fuels tend to fall in the a narrower range of 2.4 to 2.6.

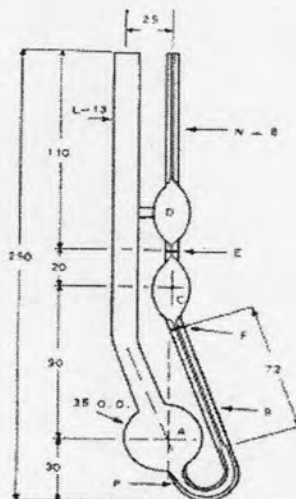


Figure 2.11 Cannon-Fenske Capillary Viscometer Tube

2.5.2 Density

Density is another important property of biodiesel. It is the weight of a unit volume of fluid. Specific gravity is the ratio of the density of a liquid to the density of water. The specific gravity of biodiesel ranges between 0.87 and 0.89g/ml. Since fuel injection equipment operates on a volume metering system, hence a higher density for biodiesel results in the delivery of a slightly greater mass of fuel.

2.5.3 Cetane number

The cetane is one of the prime indicators of the quality of diesel fuel. It relates to the ignition delay time of a fuel upon injection into the combustion chamber, and high CN implies short ignition delay. It is based on two compounds, namely hexadecane with a cetane number of 100 and heptamethylnonane with a cetane number of 15. The CN scale also shows that straight chain, saturated hydrocarbons have higher CN compared to branched chain or aromatic compounds of similar molecular weight and number of carbon atoms. The CN of biodiesel is generally higher than that of conventional diesel. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the CN will be. The CN of biodiesel from animal fats is higher than those from vegetable oils.

2.5.4 Cloud point and pour point

Two important parameters for low temperature applications of a fuel are cloud point (CP) and pour point (PP). The CP is the temperature at which wax first becomes visible when the fuel is cooled. The PP is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow. Biodiesel usually has higher CP and PP compared to conventional Diesel.

2.5.5 Flash point

The standard procedure for measuring the flash point for diesel and biodiesel fuels are ASTM D 93. Flash point is the lowest temperature of a liquid at which it gives off sufficient vapor to form an ignitable mixture with the air near the surface of the liquid or within the vessel used. The flash point can be determined by the open cup or the closed cup method.

2.6 Literature reviews

A number of studies on preparation of biodiesel from vegetable oils have been reported using a variety of oils, alcohols, different catalysts, and reaction conditions. For alkali catalyzed process, Aracil et al. (2004) used different basic catalysts (sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide) for transesterification of sunflower oil. The biodiesel purity near 100 wt.% was obtained for all catalysts. However, biodiesel yields near 100 wt.% were only obtained with the methoxide catalysts. Although all the transesterification reactions were quite rapid and the product achieved nearly 100% methyl ester concentrations, the reactions using sodium hydroxide turned out the fastest. Another example on alkali process is that of Meher et al., (2006), in which the transesterification of karanja oil with methanol was carried out using alkaline catalyst in a batch type reactor. At 65 °C, with a molar ratio of 1:6 of the karanja oil to methanol, using KOH as catalyst, the 97% conversion to methyl ester was obtained after 3 hrs. Although high purity and yield of biodiesel can be achieved in a short time with the alkali process. However, it is very sensitive to the purity of reactants. For example, the starting material (oil or fat) must be dried (moisture level <0.06%) and free of free fatty acid (FFA) (<0.5%). The presence of minor amount of FFA and moisture in the reaction mixture produces soap, which lower the yield of ester and renders the separation of ester and glycerol by water washing difficult. FFA also consumed the catalyst and reduced catalyst efficiency (Zullaikah et al., 2005).

An alternative to the alkali process is the acid catalyzed process. Mohamad et al., (2003) studied transesterification of waste palm oil using acid catalyst was under various conditions such as different H₂SO₄ and HCl concentrations. In this study,

ethanol at different excess levels was also used. They found that higher catalyst concentrations produced biodiesel with lower specific gravity, in much shorter reaction time than lower concentrations. The H_2SO_4 performed better than HCl, as it results in diesel with lower specific gravity in about 3 hrs. Moreover, a 100 % excess alcohol resulted in significant reductions in reaction time and lower specific gravity. Zheng et al., (2006) studied the reaction kinetic of acid catalyzed (H_2SO_4) transesterification of waste frying oil in excess methanol to form fatty acid methyl ester for possible use as biodiesel. The oil:methanol:acid molar ratios and temperature were the most significant factors affecting the yield of fatty acid methyl ester at 70 °C with oil:methanol:acid molar ratios of 1:245:3.8 and at 80 °C with oil:methanol:acid molar ratios in range 1:74:1.9-1:245:3.8. As a result of the large excess of methanol, the reaction completed ($99 \pm 1\%$ conversion) in 4hrs. Although acid catalyzed process does have advantages such as reduced purification costs, the reaction is much slower. Ramadhas et al., (2005) proposed a two-step transesterification process developed to convert the high free fatty acid (FFA) oil to its mono-ester in the first step via acid catalyzed esterification to reduce FFA content of the oil to less than 2%. Then, in the second step, alkaline catalyzed transesterification process converts the product of the first step to its mono-esters and glycerol. The major factors affecting the conversion efficiency of the process are such as oil to methanol molar ratio, the amount of catalyst, reaction temperature, and reaction duration. However, for this two-step process, long reaction time, no recovery of catalyst, and high cost of reaction equipment were still the major disadvantages (Wang et al., 2006).

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Acid and base catalyzed process may also be carried out heterogeneously using solid catalysts. These processes reduce the problems with of product separation in the homogeneous processes. Gorzawski et al. (1999), suggested that the production of alkyl ester will be simplified when heterogeneous catalysts are utilized. Furuta et al. (2004) studied transesterification of soybean oil and the esterification of n-octanoic acid with solid superacid catalysis such as sulfated tin and zirconium oxides and tungstated zirconia in a fixed bed reactor. They found that three types of solid superacid catalysts, tungstated zirconia-alumina is a promising catalyst for the production of biodiesel fuels from soybean oil because of its high performance in the conversions over 90% for the transesterifications as well as the esterification. Baba et al., (2005) studied transesterification of triolein with methanol and glycerolysis of triolein with glycerol are performed using this alkali metal salt-loaded alumina catalyst. A K_2CO_3 -loaded alumina catalyst prepared by evacuation at 823 K gives methyl oleate and glycerol in the highest yields of 94 and 89%, respectively, at 333 K in 1 h. This catalyst also effectively catalyzes the glycerolysis of triolein with glycerol to give dioleoyl glycerol at 71% yield at 453 K in 5 h. Despite these positive examples, there still appear to be some problems with this technique such as incomplete reaction and finding a suitable catalyst that is active, selective, and stable under the process conditions is the major challenge (Kiss et al., 2006).

Besides alkali and acid catalyzed process, enzyme catalyzed process are considered for the production of biodiesel. Liu et al., (2006) studied Lipase-catalyzed

alcoholysis of soybean oil deodorizer distillate (SODD) for biodiesel production. *Tert*-Butanol has been adopted as the reaction medium, in which both the negative effects caused by excessive methanol and by-product glycerol could be eliminated completely. There was no obvious loss in lipase activity even after being repeatedly used for 120 cycles. The highest biodiesel yield of 97% could be achieved with 3 Å molecular sieve as the adsorbent for water adsorption. The production of biodiesel fuel by enzymatic method has not been adopted industrially however, because of the high cost of enzyme catalyst. The process of enzyme immobilization was therefore developed in order to be able to use the enzyme catalyst repeatedly. Iso et al., (2001) studied the production of biodiesel fuel from triglycerides and alcohol using immobilized *Pseudomonas* lipase and found that the activity of immobilized lipase was highly increased in comparison with free lipase because its active sites became more effective. Immobilized enzyme could be repeatedly used without troublesome method of separation and the decrease in its activity was not largely observed.

Alternative to the catalytic process of biodiesel production as mentioned above, non-catalytic transesterification was investigated. Kudiana and Saka (2001) studied transesterification reaction of rapeseed oil in supercritical methanol. The experiment was carried out in the batch-type reaction vessel preheated at 350 and 400°C and at a pressure of 45- 65 MPa, and with a molar ratio of 1:42 of the rapeseed oil to methanol. It was consequently demonstrated that, at the temperature of 350°C, supercritical treatment of oil and methanol for 240 s was sufficient to convert the rapeseed oil to methyl ester and that, although the prepared methyl ester were basically the same as those of the common method with a basic catalyst, the yield of methyl ester by the former was found to be higher than that by the latter. In addition, it was found that the supercritical methanol process requires the shorter reaction time and simpler purification procedure. Nevertheless supercritical reaction requires high temperature and high pressure, thus resulting in high cost of product. In order to overcome these problems, Cao et al., (2005) studied the effect of co-solvents on transesterification of soybean oil in supercritical methanol. They found that, with propane as co-solvent in the reaction system, there was a significant decrease in the severity of the conditions required for supercritical reaction, which makes the production of biodiesel using supercritical methanol viable as an industrial process.

Other than the use of cosolvent, making appropriate choice of raw materials used for the production of biodiesel can also decrease the production cost. Fatty acids are by products of vegetable oil refinery and are produced at high purity, and therefore are considered an interesting inexpensive raw material for the production of biodiesel. Kusdiana and Saka (2003b) evaluated non-catalytic supercritical esterification of different fatty acids and found that, after 240 s, complete conversion of saturated fatty acids to methyl ester could be achieved at the temperatures above 400 °C, whereas the lower temperature of 350 °C was more appropriate for unsaturated fatty acids.

Table 2.4 Studies in production of biodiesel by alkali or acid catalyzed process.

Reference	Material	Method	Temp. (°C)	Pressure	Condition Molar ratio (MeOH:Oil)	Time	Volume reactor (ml)	Analysis	Objective
Freedman B. et al. (1984)	Refined vegetable oil (edible grade) and crude oils, NaOH, H ₂ SO ₄ , MeOH, EtOH, BuOH	Conventional (base and acid catalyst)	60-63	-	3:1 and 6:1	0.1 to 4 hr	100	TLC	1. To develop basic information for the transesterification reaction of crude and refined oils. 2. To delineate optimum reaction conditions for maximum conversion to fatty ester with alkali and acid catalyst.
S.Zheng et al.,(2006)	waste frying oil MeOH	acid catalyzed (H ₂ SO ₄)	70	-	1:6-1:24	1-3hrs	-	HPLC, HNMR	To investigate the rection variables affecting the transesterification such as concentration of catalyst, oil/alcohol ratio, temperature

Reference	Material	Method	Temp. (°C)	Pressure	Condition Molar ratio (MeOH:Oil)	Time	Volume reactor (ml)	Analysis	Objective
Mohamad et al., (2003)	waste palm oil Ethanol	Conventional (acid catalyst) H ₂ SO ₄ , HCl	90 to 110	-	6:1			GC	To investigated the reaction variables affecting the transesterification such as concentration of catalyst, temperature and compare concentration of acid catalyst
L.C. Mether et al.,(2006)	vegetable oil	Base catalyst	70	-	1:6-1:24	1-3hrs	-	HPLC, HNMR	To investigate the rection variables affecting the transesterification such as concentration of catalyst, oil/alcohol ratio, temperature

Table 2.5 Studies in production of biodiesel in supercritical alcohol process.

Reference	Material	Method	Temp. (°C)	Pressure	Condition Molar ratio (MeOH:Oil)	Time	Volume reactor (ml)	Analysis	Objective
S. Saka and D. Kusdiana (2001)	rapeseed oil MeOH	SC-MeOH	400	-	42:1	4-45 min	5	HPLC	To study the reactivity of transesterification of triglycerides and alkyl esterification of fatty acids in the supercritical alcohol process.
Saka et al. (2003 a)	rapeseed oil MeOH	SC-MeOH	300-450	-	42:1	10-240 s	5	HPLC	To study effect of free fatty acids and water in triglycerids on biodiesel fuel production.
Saka et al. (2003 b)	rapeseed oil MeOH	SC-MeOH	300-450	-			5	HPLC	To evaluate esterification reaction of free fatty acids.

Reference	Material	Method	Condition					Analysis	Objective
			Temp. (°C)	Pressure	Molar ratio (MeOH:Oil)	Time	Volume reactor (ml)		
Cao et al. (2005)	soybean oil, Methanol	SC-MeOH	200-310	-	-	13-15 min	-		To study the transesterification of soybean oil in methanol under supercritical conditions in the presence of propane as co-solvent.