

CHAPTER II

BACKGROUND & LITERATURE REVIEWS

2.1 Biodiesel as engine fuel

Biodiesel is referred to as the monoalkyl ester of long chain fatty acids derived from vegetable oil and animal fats, for use in diesel engine and heating system. Biodiesel as a possible replace of petroleum diesel and is consisted of fatty acid alkyl ester, obtained from triglycerides in vegetable oils by transesterification with alcohol. Biodiesel is a clear amber-yellow liquid with a viscosity similar to petroleum diesel. In the environmental aspect, biodiesel has better properties than petroleum diesel such as renewable, biodegradable, non-toxic, and no sulfur or aromatic compounds.

2.2 The production of biodiesel

2.2.1 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 appeared in South Africa. Caterpillar Brazil, a company in Brazil, in 1980 used pre-combustion chamber engines with a mixture of vegetable oil and diesel fuel at 10 % v/v and found that the total power could be maintained 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. However, the advantages of vegetable oils as diesel fuel are (1) liquid nature-portability, (2) heat content (80% of diesel fuel), (3) ready availability and (4) renewability. The disadvantages are (1) higher viscosity, (2) lower volatility and (3) the reactivity of unsaturated hydrocarbon chains (Pryde, 1983). Nevertheless, the problem appeared after the engine has been operating on vegetable oil for longer period of time, especially with direct-injection engines. The problems include (1) coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of

plugged orifices, (2) carbon deposits, (3) oil ring sticking and (4) thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils (Ma et al., 1999). Schlick et al. (1988) evaluate 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, FFA content, as well as gum formation due to oxidation and polymerization during storage and composition, carbon deposits and lubricating oil thickening. The probable reasons for the problems and the potential solutions are shown in Table 2.1.

Table 2.1 Problems and potential solutions for using vegetable oils as engine fuels (Harwood, 1984; Ma et al., 1999)

Problem	Probable cause	Potential solution
<i>Short-term</i>		
1. Cold weather starting	High viscosity, low cetane, and low flash point of vegetable oils	Preheat fuel prior to injection. Chemically alter fuel to an ester
2. Plugging and gumming of filters, lines and injectors	Natural gums (phosphatides) in vegetable oil. Ash.	Partially refine the oil to remove gums. Filter to 4 microns
3. Engine knocking	Very low cetane of some oils. Improper injection timing.	Adjust injection timing. Preheat fuel prior to injection. Chemically alter fuel to an ester
<i>Long-term</i>		
4. Coking of injectors and carbon deposits on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load.	Heat fuel prior to injection. Switch engine to diesel when operating at part load. Chemically alter the vegetable oil to an ester.
5. Excessive engine wear	High viscosity, incomplete combustion of fuel. Poor combustion at part load. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil.	Heat fuel prior to injection. Switch engine to diesel when operating at part load. Chemically alter the vegetable oil to an ester. Increase lubricating oil changes. Lubricating oil additives to inhibit oxidation.
6. Failure of engine lubricating oil due to polymerization	Collection of poly-unsaturated vegetable oil blow-by in crank-case to the point where polymerization occurs	Same as in 5.

2.2.2 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). Ziejewski et al. (1984) prepared an emulsion of 53 % (vol) alkali-refined and winterized sunflower oil, 13.3 % (vol) 190-proof ethanol and 33.4 % (vol) 1-butanol. This nonionic emulsion had a viscosity of 6.31 cSt at 40 °C, a cetane number of 25 and an ash content of less than 0.01 %. Lower viscosities and better spray patterns (more even) were observed with an increase of 1-butanol. However, fuels formulated as microemulsions have low cetane numbers and low heating values as compared with No. 2 diesel fuel (Bagby, 1987).

2.2.3 Pyrolysis

Pyrolysis (or thermal cracking) 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 oils 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 mechanism of pyrolysis of triglycerides for the formation of alkanes, alkenes, alkadienes, aromatics and carboxylic acids is shown in Figure 2.1. Generally, thermal decomposition of these structures proceeds through either a free-radical or carbonium ion mechanism. The formation of homologous series of alkanes and alkenes is described as the generation of the RCOO radical from triglyceride cleavage and subsequent loss of carbon dioxide. The formation of aromatics is supported by the Diels-Alder reaction which is an organic chemical reaction (specifically, is cycloaddition) between a conjugate diene and substituted alkene, commonly termed the dienophile to form a substituted cyclohexane system. Soybean oil could be thermally decomposed and distilled in air and nitrogen sparged with a standard ASTM distillation apparatus (Niehaus et al., 1986; Schwab et al., 1988).

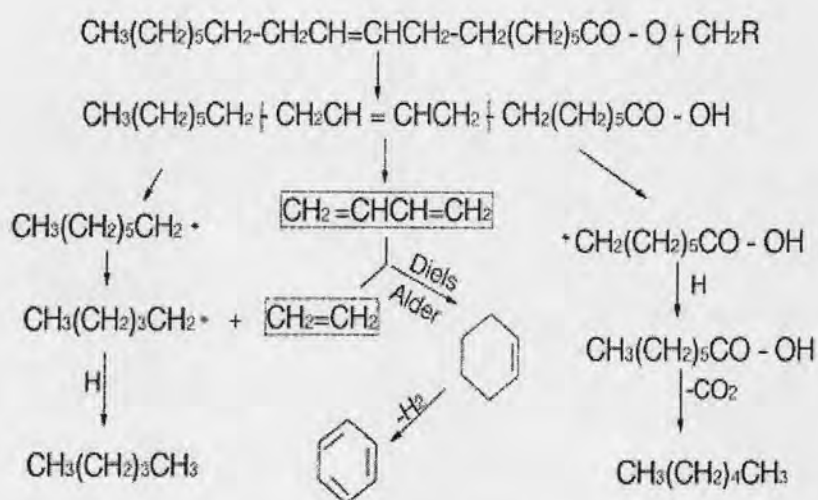


Figure 2.1 The mechanism of pyrolysis of triglycerides (Schwab et al., 1988)

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.

2.2.4 Transesterification (Alcoholysis)

Transesterification (also called Alcoholysis) means taking a triglyceride molecule or a complex fatty acid, neutralizing the FFA, and removing the glycerin and creating an alcohol ester. The general equation of this reaction is shown in Figure 2.2. 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.

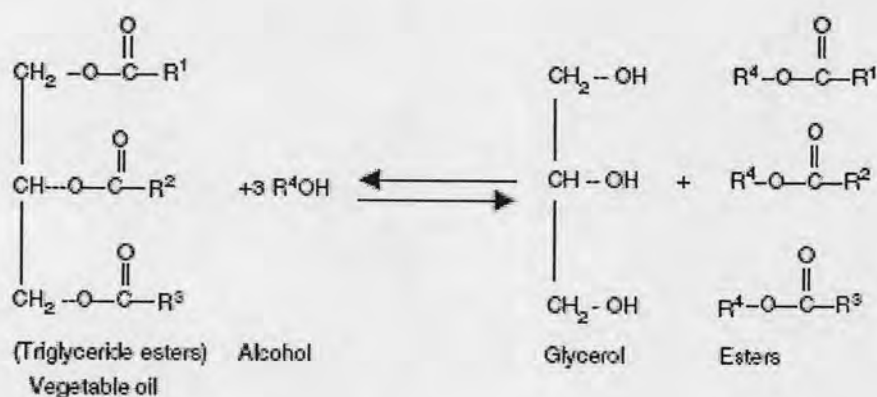


Figure 2.2 Chemical reaction of transesterification

The stoichiometry requires three moles of alcohol and one mole of triglyceride to produce three moles of fatty esters and one mol of glycerol. However, this reaction is reversible, and therefore excess alcohol is used in reaction to shift the equilibrium to the right side (products). Typically, the variables affecting reaction rate and yield include: type and amount of catalyst, type of alcohol, reaction temperature, reaction time, molar ratio of vegetable oil and alcohol, glycerol separation and quality of vegetable oil such as fatty acid composition.

The transesterification reaction shown in Figure 2.2 is indeed the overall reaction for three stepwise reactions with intermediate formation of diglyceride and monoglyceride (Figure 2.3). In the first reaction, triglyceride (TG) react with alcohol

to produce diglyceride (DG), then in the second reaction, diglyceride (MG) react with alcohol to form monoglyceride (MG). Finally, in the third reaction, monoglyceride (MG) react with alcohol to give glycerol.

Stepwise Reaction:

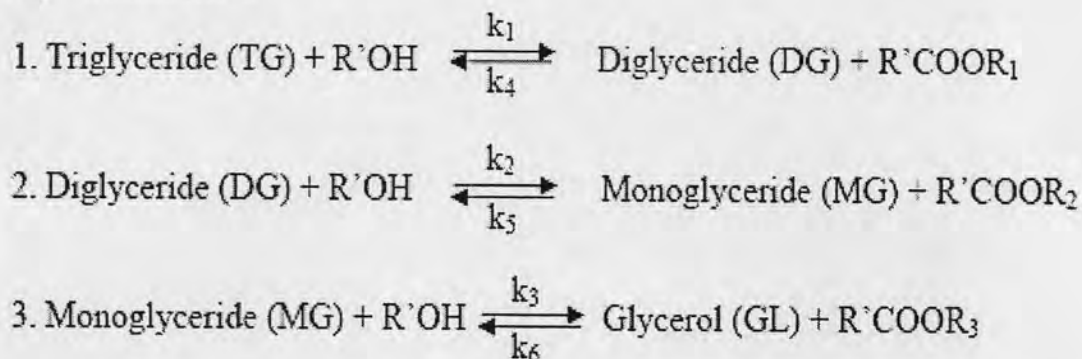


Figure 2.3 The transesterification reactions of vegetable oil with alcohol to esters and glycerol (Freedman et al., 1986)

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. Non-catalytic transesterification in supercritical alcohols is also carried out.

2.2.4.1 Catalytic transesterification method

Alkali-catalyzed process

All commercial biodiesel production today employs an alkali-catalyzed transesterification process. Alkali-catalyzed transesterification of vegetable oils is known to proceed faster than the acid catalyzed reaction. It is reported that the rate could be as high as 4000 times, compared to that using an acid catalyst (Fukuda et al., 2001). This process is accomplished by mixing methanol (alcohol) with sodium

hydroxide or potassium hydroxide to make sodium methoxide. Then the sodium methoxide is added to vegetable oil in a reactor at molar ratio of oil and alcohol 6:1. The mixture was stirred and heat at 60-63 °C. After complete reaction mixture is allowed to cool to room temperature, and the ester and glycerol in were separated. Glycerol is left on the bottom and methyl esters, or biodiesel, is left on top. The ratio of 6:1 was found to be the best condition because methanol/oil molar ratio less than 6:1 the reaction resulted in incomplete reaction, and that above 6:1 methanol/oil molar ratio makes the separation of glycerol difficult, since the excess methanol hindered the decantation by gravity so that the apparent yield of esters decreased because part of the glycerol remained in the biodiesel phase (Freedman et al., 1984).

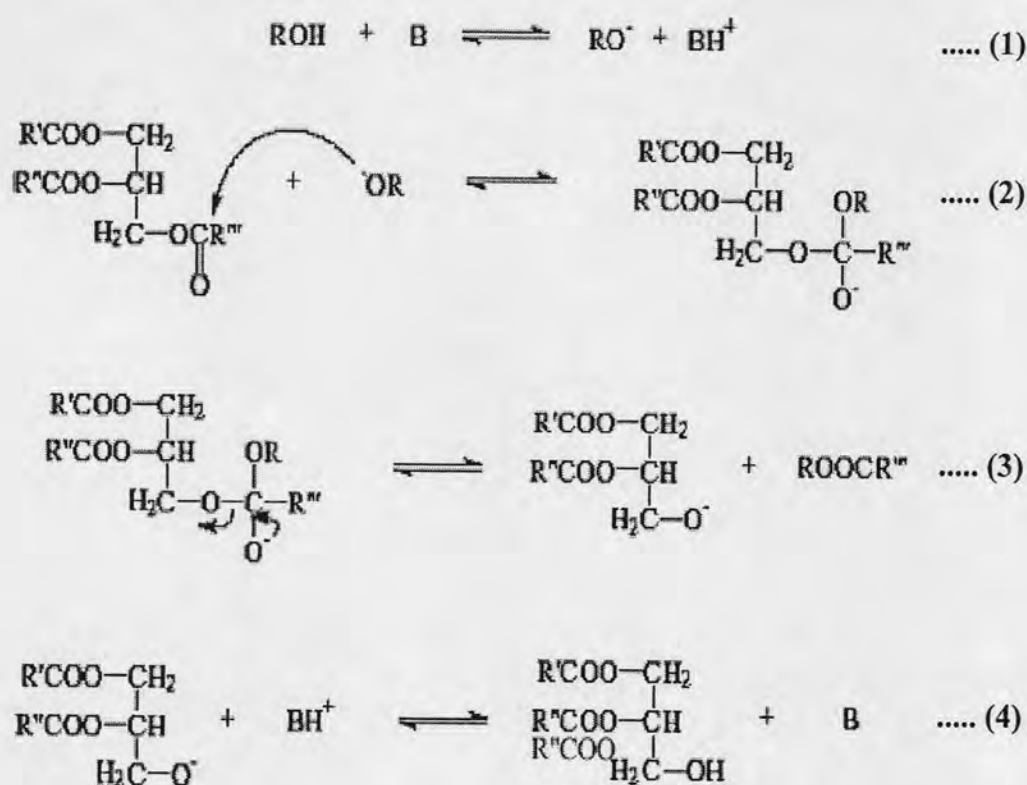


Figure 2.4 Mechanism of the alkali-catalyzed transesterification of vegetable oils (Demirbas, 2005)

The mechanisms of alkaline catalyzed transesterification are depicted in Figure 2.4. The first step equation 1 is the reaction of the base with 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 in equation 4 which is now able to react with a second molecule of the alcohol, starting another catalyst cycle. 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 minute, 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 2.5. However, when the vegetable oil contain high FFA (about 5 %), alkali-catalyst ineffective because reaction want more alkali-catalyst for neutralization and the excess catalyze can react with FFA to form soap (Figure 2.6). The soap increases the viscosity or formation of gel or emulsion and interfered with separation of ester and glycerol (Freedman et al., 1984). Although the alkali catalyzed process has short reaction time and high conversion, the process has several problems such as difficult recovery of glycerol due to the soap production from FFA and the catalyst. In addition, the alkaline catalyst has to be removed from the product by washing with water, thus alkaline waste water is generated. Thus, for oil with high content of FFA, an acid catalyst, such as sulfuric acid, can be used to esterify the FFA to methyl esters.

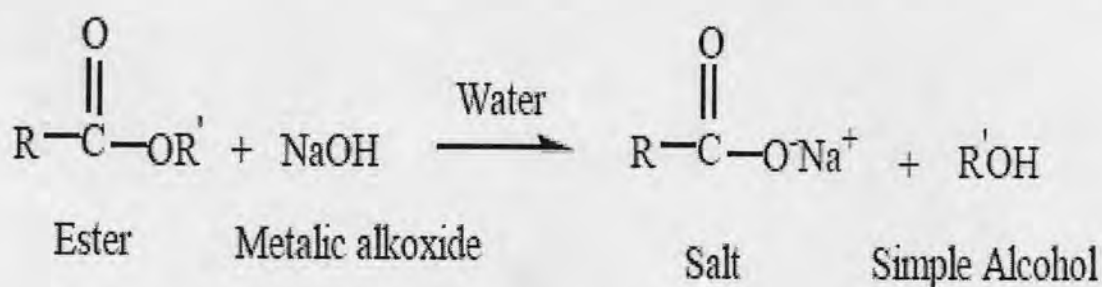


Figure 2.5 Saponification from ester

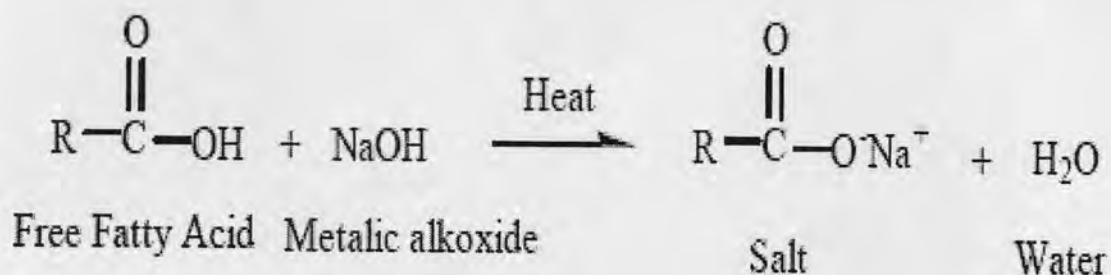


Figure 2.6 Saponification from FFA

Acid-catalyzed process

Most of the biodiesel is currently made from edible oils by using methanol and alkaline catalyst. However, one limitation in the alkali-catalyzed process is its sensitivity to the purity of reactants, especially to both water and FFA. The FFA and water make the use of an alkaline catalyst difficult, because of soap formation and then difficulty in product separation. Therefore, acid catalyst can be used for transesterification. Thus acid catalyzed process can reduce biodiesel production cost as low cost feedstock (waste frying oil) with high FFA can be used as a raw material. The transesterification process can be catalyzed by acids such as sulfuric or hydrochloric acids. 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. Transesterification 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 important factors that influence transesterification. An excess of the alcohol assists the formation of the products. On the other hand, an excessive amount of alcohol 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 2.7 for a mono-triglyceride. However, it can be extended to diglyceride and triglycerides. The protonation of the carbonyl group of the ester leads

to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III. Elimination of glycerol from the new ester IV, and regenerates the catalyst H^+ . According to this mechanism, carboxylic acids can be formed by 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.

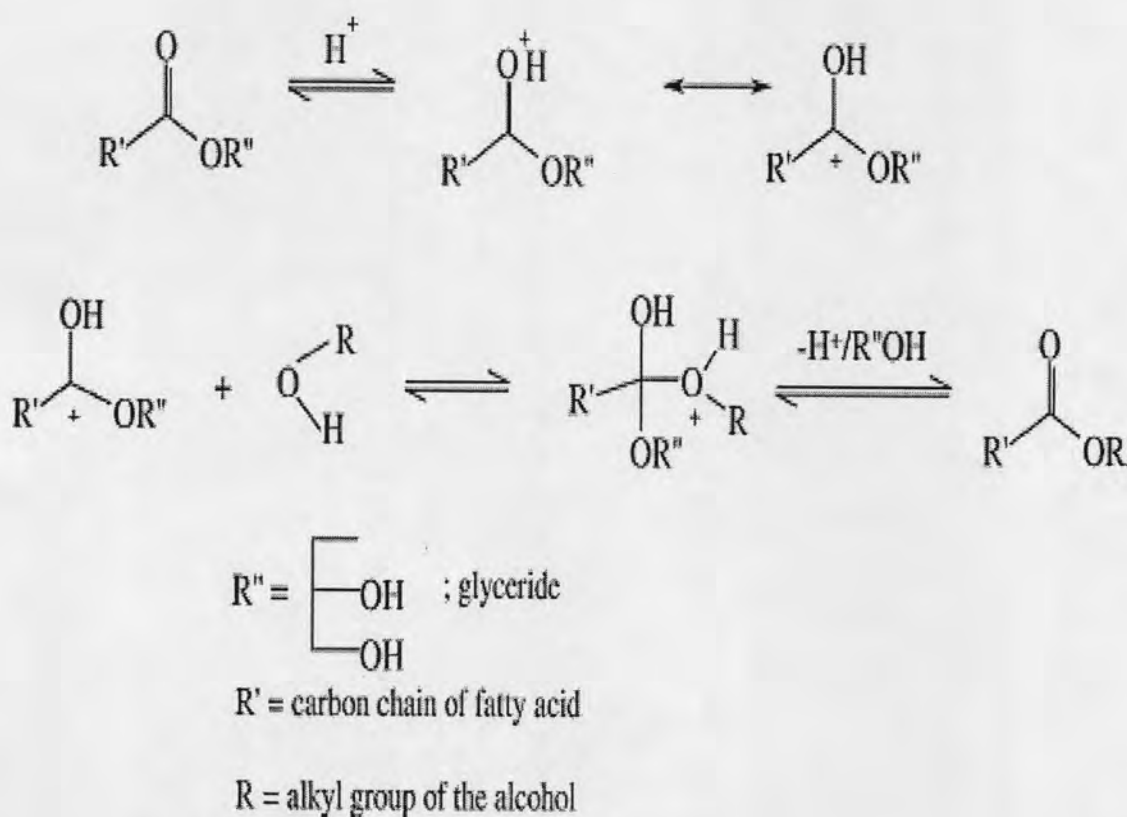


Figure 2.7 Mechanism of acid catalyzed transesterification (Meher et al., 2006)

Acid- and Alkali-catalysed two-step transesterification

Two step transesterification in which the first acid catalyzed step was followed by the second alkali catalyzed step was developed for the production of biodiesel from oil with high FFA content. Initially, acid catalyst can be used to convert FFA to the esters and to decrease the FFA level. In the second step, alkali catalyst can be performed for the transesterification of oil (two-step). The technique overcomes the problem of a slow reaction rate with acid catalyst and the formation of soap with an

alkaline catalyst and increases the ester yield. However, the problem with the removal of the catalysts is still a big issue for the two-step method (Kulkarni et al., 2006).

Heterogeneous catalysts process

Although homogeneous catalyzed biodiesel processes are relatively fast and gives high conversions with minimal side reaction, they still have several problems such as (1) the catalyst cannot be recovered and must be neutralized at the end of the reaction, (2) there is limited use of continuous process, and (3) the processes are very sensitive to the presence of water and FFA which give rise to competing hydrolysis and saponification reactions. Nowadays, heterogeneous reaction is being considered in which the liquid catalyst is replaced by solid catalysts. This process could potentially lead to cheaper production costs because it is possible to reuse the catalysts and to carry out both transesterification and esterification simultaneously (Lopez et al., 2005).

Enzymatic transesterification

Chemical (acid or alkali)-catalyzed transesterification of vegetable oils have problems, such as pretreatment of reactants, recovery of glycerol, removal of the catalyst, and the energy-intensive nature of the process (high stirring speed, and temperature required for good conversions). Enzyme (such as lipase)-catalyzed reactions have advantages over conventional chemical-catalyzed reactions, such as the generation of no byproducts, easy product recovery, mild reaction conditions, and catalyst recycling. Moreover, enzymatic reactions are insensible to FFA and water content in vegetable oil (Wu et al., 1999; Hsu et al., 2004). The major problem with this process however is the enzyme stability and recovery. Therefore, immobilization is the most widely used method for achieving favorable stability of lipases and to make them more attractive for reaction (Cowan, 1996; Clark, 1994). However, the production of biodiesel fuel by enzymatic method has not often been used in industry because of the high cost of enzyme catalyst. An alternative process such as non-catalyzed transesterification is considered.

2.2.4.2 Non-Catalytic transesterification method (Supercritical Methanol)

Novel alcoholysis processes are developed for the synthesis of biodiesel from vegetable oils and fats using any catalyst. Kusdiana and Saka (2001) studied the biodiesel production in supercritical methanol. They demonstrated that rapeseed oil could be converted to methyl ester in 240 s by supercritical methyl transesterification at 350 °C, 45 MPa and a molar ratio of methanol to rapeseed oil of 42 to 1. Although 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.

In the case of a supercritical fluid process, the pressure and temperature of reactor are manipulated to influence the thermophysical properties of solvent (alcohol), such as dielectric constant, viscosity, specific gravity, and polarity. When a fluid is subjected to temperatures and pressures in excess of its critical point, there are a number of unusual properties exhibited. Firstly, there no longer is a distinct liquid and vapor phase, but a single, fluid phase present. Secondly, solvents containing a hydroxyl group, such as water or primary alcohols, take on the properties of superacids. For this reason, transesterification in supercritical alcohol can be achieved without use of catalyst for production of biodiesel. In addition, alcohol used in biodiesel production such as methyl or ethyl alcohol are polar solvents and have hydrogen bonding between hydroxyl oxygen and hydroxyl hydrogen to which normally form clusters of these molecules, separating them from other nonpolar compounds such as glyceride. However, because the degree of hydrogen bonding decreases with increasing temperature, the polarity of the alcohol would decrease in supercritical state, thus supercritical alcohol has a hydrophobic nature with the lower dielectric constant. As a result, non-polar triglycerides can dissolve in the supercritical alcohol to form a single phase of vegetable oil/methanol mixture (Kusdiana and Saka, 2001).

Although the supercritical methanol method has all the above advantages, it has some serious disadvantages. These include the requirement of high temperature (350 °C) and high pressure (45 MPa). In addition, this method requires a large amount of methanol (1:42 molar ratio of oil to alcohol). Therefore, to apply this method on an industrial scale, further investigations of the production process, such as continuous operation and scaling up, as well as economic evaluations, are needed.

2.2.5 Esterification

The formation of ester occurs through a condensation reaction known as esterification. This requires two reactants, carboxylic acids (fatty acids) and alcohol. Esterification reactions 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. The equation for esterification reaction can be seen in Figure. 2.8.

Esterification can also be carried out non catalyst in supercritical condition. Similar to the supercritical transesterification, the advantages of carrying out the methyl esterification is the rapid reaction and the ease of product separation.

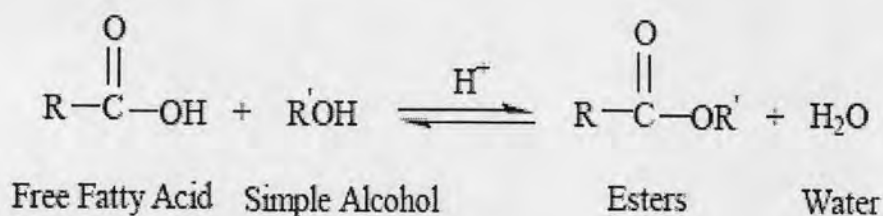


Figure 2.8 Esterification reaction

2.3 Variables affecting transesterification and esterification

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

2.3.1 Ratio of alcohol to oil or fatty acids

It is generally known that one of the most important variables affecting the yield of ester is molar ratio of alcohol to triglyceride. For transesterification, the stoichiometric ratio 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. The molar ratio is associated with the type of catalyst used.

For alkali-catalyzed reaction, the maximum conversion to the alkyl ester was a molar ratio of 6:1. While acid catalyzed reaction required a molar ratio of 30:1 to achieve the same yield (Freedman et al., 1986). 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 one mole of the fatty acid and alcohol to yield one mole of fatty acid alkyl ester and water. Furthermore, no glycerol is produced. As a result, it is expected that lower alcohol to fatty acids molar ratio would be needed compared with triglyceride transesterification.

2.3.2 Reaction temperatures

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 (45 MPa) and high temperature (above 300 °C).

2.3.3 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.

2.3.4 Use of organic co-solvent

An improved process was investigated by Krisnangkura and Simamaharnnop (1992) for continuous transmethylation of palm oil at 70 °C in an organic co-solvent

with sodium methoxide as a catalyst. It was found that the optimum ratio of toluene to palm oil is 1:1 (v/v). When the methanol to oil molar ratio was 13:1, transmethylation was 96% complete within 60 s. At higher molar ratio of methanol to oil (17:1), transmethylation was 99 % complete in 15 s. For lower molar ratios of methanol to oil (9:1 and 5.8:1), yields of palm oil methyl esters were 84 and 58 %, respectively. Moreover, benzene was a good co-solvent for transmethylation, but the yield of palm oil methyl ester was slightly lower than toluene. Tetrahydrofuran did not accelerate transmethylation. The co-solvent increases 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.

2.3.5 Purity of reactant

Impurities present in the oil also affect conversion levels. Under the same condition, 65 to 84 % conversion into ester using crude vegetable oils can be obtained, compared with 94 to 97 % when using refined oils under the same reaction conditions. The FFA in the original oils interfere with catalyst, however, under conditions of high temperature and pressure this problem can be overcome (Freedman et al., 1984).

2.3.6 Catalyst type and concentration

Catalysts used for transesterification of triglyceride are classified as alkaline, acid, enzyme or heterogeneous catalyst, among which alkaline are the most effective transesterification catalyst compared to acidic 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 has found to yields 94-99 % (Freedman et al., 1984). 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 2.25 M HCl in presence of 100 % excess alcohol and result was compared with 2.25 M H₂SO₄ and it was observed that decrease in viscosity. H₂SO₄ was found to have superior catalyst activity in the range of 1.5-2.25

M concentration (Mohamad, 2002). For heterogeneous catalyst, the several acidic and basic solid catalysts such as ZrO_2 , ZnO , SO_4^{2-}/SnO_2 , SO_4^{2-}/ZrO_2 , KNO_3/KL zeolite and KNO_3/ZrO_2 were investigated with vegetable oils and fatty acids. SO_4^{2-}/SnO_2 and SO_4^{2-}/ZrO_2 were found to be the most appropriate for the biodiesel production (Jitputti et al., 2006). The amount of solid catalyst in range of 1 to 3 % by weight was found to have high catalytic activity (Jitputti et al., 2006).

2.3.7 Presence of water

In biodiesel production, it is well known that the vegetable oils used as raw material for the transesterification should be water free since water has a negative effect on the reaction. Water can consume the catalyst and reduce catalyst efficiency and it is believed that the presence of water has a greater negative effect than that of the FFA. Therefore, 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 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, Vicente et al. (2004) used different alkali catalysts (sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide) for homogeneous 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 homogeneous alkali process is that of Meher et al. (2006), in which the transesterification of karanja oil with methanol was carried out in a batch type reactor at 65 °C, at a molar ratio of 1:6 of the karanja oil to methanol, using KOH as catalyst. The 97 % conversion to methyl esters was obtained after 3 h. 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 FFA

(<0.5 %). The presence of minor amount of FFA and moisture in the reaction mixture produces soap, which lowers the yield of ester as the separation of ester and glycerol by washing with water is 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. (2002) studied transesterification of waste palm oil with ethanol at different excess levels using acid catalysts (H_2SO_4 and HCl) under various conditions concentrations. In this study, was also used. The higher catalyst concentrations were found to give biodiesel with lower specific gravity in much shorter reaction time. Furthermore, H_2SO_4 was shown to perform better than HCl , resulting in biodiesel with lower specific gravity in about 3 h. Moreover, a 100 % excess alcohol resulted in significant reductions in reaction time and lower specific gravity. Zheng et al. (2006) studied the reaction kinetics of acid catalyzed (H_2SO_4) transesterification of waste frying oil in excess methanol to form fatty acid methyl esters 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 esters (FAMES), and as a result of the large excess of methanol, the reaction completed (99 ± 1 % conversion) in 4 h. Since no soap is produced, acid catalyzed process is more suitable than alkali process for use with low cost raw materials such as oil that contains high content of FFA. This is the main advantage of acid catalyzed process since the price of feed stock is considered most significant factor affecting the economic viability of biodiesel manufacturing (Zhang et al., 2003), and it has indeed been reported that approximately 70–95 % of the total biodiesel production cost arises from the cost of raw material (Krawczyk et al., 1996). Chongkhong et al. (2007) investigated the production of biodiesel from palm fatty acid distillate (PFAD) having high FFA by esterification process in a continuous stirred tank reactor (CSTR) under atmospheric pressure. The optimum condition was 60 min reaction at 70 °C and 8:1 molar ratio of methanol to PFAD, using 1.834 wt % of H_2SO_4 . The amount of FFA was reduced from 93 wt % to less than 2 wt % at the end of the reaction. Bhatti et al. (2008) investigated waste tallow as low cost sustainable potential feedstock for biodiesel production. The optimal conditions for processing 5 g of tallow were 50 °C, oil/methanol molar ratio 1:30, 1.25 g of H_2SO_4 for chicken tallow; and 60 °C, oil/methanol molar ratio 1:30, 2.5 g of H_2SO_4 for mutton tallow. The yields of biodiesel under optimized conditions were 99.01 ± 0.71 % and 93.21 ± 5.07 % in case of chicken tallow and mutton tallow,

respectively. Although acid catalyzed process does have advantages such as reduced purification costs, the reaction is much slower. Ramadhas et al. (2005) has proposed a two-step process developed, in which the high FFA oil was first converted to its mono-ester in the first step via acid catalyzed esterification. In this step, the FFA content of the oil was reduced to less than 2 %. In the second step, alkaline catalyzed transesterification was then used to convert the product from the first step into 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., 2007).

Acid and base catalyzed process may also be carried out heterogeneously using solid catalysts. These processes reduce the problems of product separation (Gorzawski et al., 1999). Furuta et al. (2004) studied transesterification of soybean oil and the esterification of n-octanoic acid with three types of solid superacid catalysis such as sulfated tin and zirconium oxides and tungstated zirconia in a fixed bed reactor. Of these solid superacid catalysts, tungstated zirconia-alumina was found the most promising catalyst for the production of biodiesel and the conversions over 90 % were obtained for both the transesterification and the esterification of soybean oil. Baba et al. (2005) studied transesterification of triolein with methanol and glycerolysis of triolein with glycerol using alkali metal salt-loaded alumina catalysts. A K_2CO_3 -loaded alumina catalyst prepared by evacuation at 823 K added to the reaction at 333 K in 1 h gave the highest yields of methyl oleate and glycerol of 94 and 89 %, respectively. This catalyst also effectively catalyzes the glycerolysis of triolein with glycerol to give dioleoyl glycerol at 71 % yield at 453 K in 5 h. Lopez et al. (2005) investigated the use of different solid catalysts for the transesterification of triacetin with methanol. Reaction was carried out at 60 °C in a batch reactor with a variety of solid and liquid, acid and base catalysts. Amberlyst-15, Nafion NR50, sulfated zirconia, and ETS-10 (Na, K) showed reasonable activities, suggesting that they could be suitable alternatives to liquid catalysts. Furthermore, sulfated zirconia and tungstated zirconia were found to have comparable turnover frequencies as H_2SO_4 . Kiss et al. (2006) studied several solid acids (zeolites, ion-exchange resins, and mixed metal oxides) as catalysts for the esterification of dodecanoic acid with 2-ethylhexanol, 1-propanol and methanol at 130–180 °C. In this study, sulfated zirconia

was shown to be the most suitable catalyst. The high conversions (~90 %) can be reached even at 140 °C provided that an increased amount of catalyst is used. Jitputti et al. (2006) investigated six types of acidic and basic solid catalysts (ZrO_2 , ZnO , SO_4^{2-}/SnO_2 , SO_4^{2-}/ZrO_2 , KNO_3/CL zeolite and KNO_3/ZrO_2) as heterogeneous catalysts for crude palm oil and crude coconut oil transesterification with methanol. They found that SO_4^{2-}/ZrO_2 exhibited the highest activity for both crude palm oil and crude coconut oil transesterification. Only 1 wt % of SO_4^{2-}/ZrO_2 was needed to catalyze the reaction, and resulted in FAMEs content higher than 90 %. Despite these positive examples, there still appear to be some problems with this technique such as incomplete reaction. Finding a suitable catalyst that is active, selective and stable under the process conditions is still the major challenge (Kiss et al., 2006).

Besides alkali and acid catalyzed process, enzyme catalyzed process is also being considered for the production of biodiesel. Wang 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. Furthermore, there was no obvious loss in lipase activity even after 120 cycles of repeated use. The highest biodiesel yield of 97 % could be achieved with 3 °A molecular sieve as the adsorbent for water adsorption however. The production of biodiesel fuel by enzymatic method has not been adopted industrially, 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 to 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 esters and that, although the prepared methyl esters were basically the same as those of the common method with a basic catalyst, the yield of methyl esters by the former was found to be higher than that by the latter. Moreover, Kudiana and Saka (2003) studied the effect of FFA and water content in rapeseed oil on biodiesel fuel production by conventional alkali, acid, and in supercritical transesterification. They found that, unlike in acids and alkali catalyzed process, FFA and water did not lower the conversion of methyl ester when transesterification was carried out under supercritical conditions. In addition, the reaction by supercritical methanol has advantages such as the process could use the low cost feedstock (high FFA content), glycerides and FFA are reacted with shorter reaction time, the homogeneous phase eliminates diffusive problem and the catalyst removal step is eliminated. However, some disadvantages of supercritical methanol are the high temperature, high pressure and high methanol:oil ratio. Then, it results in high cost of product and energy consumption.

To reduce the disadvantages of mentioned above, it is probable that addition of an appropriate solid catalyst which would allow the supercritical reaction to be carried out under milder conditions. Demirbas (2007) investigated the transesterification reaction of sunflower oil in supercritical methanol with calcium oxide (CaO) which was found to considerably improve the transesterification reaction of sunflower oil. With 3 wt % CaO, the reaction was essentially completed within 6 min, at 525 K and 41:1 methanol/oil molar ratio. Several solid catalysts have been investigated for transesterification and esterification reactions (Furuta et al., 2004; Baba et al., 2005; Lo'pez et al., 2005; Kiss et al., 2006; Jitputti et al., 2006). Of these solid catalyst, sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) have been shown to give high activity and selectivity for the transesterification and esterification of vegetable oils and fatty acids with a variety of alcohols (Lo'pez et al., 2005; Kiss et al., 2006; Jitputti et al., 2006). Although this catalyst is already of interest in several industrial processes, such as hydrocarbon isomerization, alkylation and esterification (Tanabe and Holderich, 1999), the study on the use of this catalyst for the production of biodiesel is limited.

Table 2.2 Review studies production of biodiesel by alkali, acid or enzyme catalyzed methods

Reference	Material	Method	Temp. (°C)	Pressure	Condition Molar ratio (MeOH:Oil)	Time (hr)	Volume reactor (ml)	Analysis	Objective
Aracil et al. (2004)	sunflower oil methanol NaOH KOH Na(CH ₃ O) K(CH ₃ O)	Conventional (base catalyst)	65	-	6:1	4	100	GC	To compare different basic catalysts for transesterification of sunflower oil
Meher et al. (2006)	karanja oil methanol KOH	Conventional (base catalyst)	65	-	6:1	3	-	GC	To investigated the reaction variables affecting the transesterification such as concentration of catalyst, oil/alcohol ratio, temperature
Xie et al. (2006)	soybean oil methanol NaX zeolites KOH	Conventional (base catalyst)	65	-	2:1-16:1	8	-	GC NMR	To develop base catalyzed reactions involved in the production of different chemicals, the KOH/NaX catalyst was adopted for the production of biodiesel from soybean oil

Reference	Material	Method	Temp. (°C)	Pressure	Condition			Analysis	Objective
					Molar ratio (MeOH:Oil)	Time (hr)	Volume reactor (ml)		
Mohamad et al. (2003)	waste palm oil ethanol H ₂ SO ₄ HCl	Conventional (acid catalyst)	90-100	-	6:1	-	-	GC	To investigated the reaction variables affecting the trans-esterification such as concentration of catalyst, temperature and compare concentration of acid catalyst
Zheng et al. (2006)	waste frying oil methanol H ₂ SO ₄	Conventional (acid catalyst)	70	-	6:1-24:1	1-3	-	HPLC HNMR	To investigated the reaction variables affecting the trans-esterification such as concentration of catalyst, oil/alcohol ratio, temperature
Ramadhas et al. (2005)	rubber seed oil methanol H ₂ SO ₄ NaOH	Conventional (two-step catalyst)	40-50	-	3:1-15:1	0.83-1	-	GC	To develop a process for producing biodiesel from a low cost feedstock like crude rubber seed oil

Reference	Material	Method	Temp. (°C)	Pressure	Condition Molar ratio (MeOH:Oil)	Time (hr)	Volume reactor (ml)	Analysis	Objective
Wang et al. (2007)	KOH ferric sulfate waste cooking oil	Conventional (two-step catalyst)	65, 95	-	3:1-10:1	8	-	GC NMR	To develop base-catalyzed reactions involved in the production of different chemicals, the KOH/NaX catalyst was adopted for the production of biodiesel from soybean oil
Iso et al. (2001)	triolein safflower oil methanol ethanol 1-propanol 1-butanol lipase AK, PS, M, AY, newlase F	Conventional (lipase catalyst)	40-70	-	1:1-48:1	25	100	GC	To studied trans-esterification of triglycerides and short chain alcohol using immobilized lipase obtained by effective method employing an inorganic porous partical as a carrier in non-aqueous condition

Reference	Material	Method	Temp. (°C)	Pressure	Condition Molar ratio (MeOH:Oil)	Time (hr)	Volume reactor (ml)	Analysis	Objective
Liu et al. (2006)	SODD methanol Novozym 435 Lipozyme TL IM molecular sieve <i>tert</i> -butanol	Conventional (lipase catalyst)	40	-	3.9:1	12	50	GC	To studied Lipase-catalyzed alcoholysis of soybean oil deodorizer distillate (SODD) for biodiesel production
Talukder et al. (2006)	<i>C. Antarctica</i> lipase palm oil acetone hexane isopropanol methanol pentane heptane acetonitrile THF	Conventional (lipase catalyst)	40	-	0.5:1-3:1	1-40	80	GC	To optimize the methanolysis of palm oil catalyzed by immobilized <i>C. antarctica</i> lipase for production of biodiesel and to provide a method suitable for overcoming methanol

Table 2.3 Review studies production of biodiesel by solid catalyzed methods

Reference	Material	Method	Temp. (°C)	Pressure	Condition Molar ratio (MeOH:Oil)	Time (hr)	wt % cat	Analysis	Objective
Furata et al. (2004)	soybean oil n-octanoic acid SZA WZA STO	Conventional (solid catalyst)	200-300 175-200	- -	40:1 4.5:1	20 20	4g 4g	GC	To apply these superacid catalyst to the transesterification of soybean oil with methanol
Kitiyanan et al. (2006)	crude palm-kernel oil crude coconut-oil	Conventional (solid catalyst)	200	-	6:1	0-4	0.5-6	GC	To investigate the production of biodiesel using heterogeneous catalyst for the transesterification of crude palm oil and crude coconut oil
Xie et al. (2007)	soybean oil KOH/NaX	Conventional (solid catalyst)	65	-	4:1-16:1	2-12	1-6	GC	To investigate the KOH/NaX catalyst was adopted for the production of biodiesel from soybean oil

Reference	Material	Method	Temp. (°C)	Pressure	Condition Molar ratio (MeOH:Oil)	Time (hr)	wt % cat	Analysis	Objective
Kawashima et al. (2007)	rapeseed oil CaTiO ₃ CaMnO ₃ Ca ₂ Fe ₂ O ₅ CaZrO ₃ BaTiO ₃ BaZrO ₃ BaCeO ₃ MgTiO ₃ MgZrO ₃ MgCeO ₃ LaZrO ₃ LaCeO ₃	Conventional (solid catalyst)	60	-	6:1	10	10	GC	To investigate the catalytic activity and durability for the transesterification of oil to fatty acid methyl ester
Liu et al. (2007)	soybean oil Ca(OCH ₃) ₂	Conventional (solid catalyst)	40-65	-	0.134:1-2:1v/v	0.25-3	0.5-4	GC	To investigate the physical and Chemicals characterization of calcium methoxide solid base catalyst with some instrumental methods and effect of various reaction condition on the biodiesel yields

Reference	Material	Method	Temp. (°C)	Pressure	Condition Molar ratio (MeOH:Oil)	Time (hr)	wt % cat	Analysis	Objective
Liu et al. (2007)	soybean oil CaO	Conventional (solid catalyst)	50-80	-	3:1-18:1	0-3	1-12	GC	To investigate the effect of the reaction condition and the catalyst lifetime using CaO as a solid base catalyst to produce biodiesel
Liu et al. (2007)	soybean oil SrO	Conventional (solid catalyst)	55-70	-	6:1-18:1	5-30min	0.5-3	GC	To investigate the reaction mechanism and the optimum reaction condition using SrO as a solid base catalyst to produce biodiesel

Table 2.4 Review studies production of biodiesel in supercritical alcohol methods

Reference	Material	Method	Temp. (°C)	Pressure	Condition Molar ratio (MeOH:Oil)	Time	Volume reactor (ml)	Analysis	Objective
Saka and Kusdiana (2001)	rapeseed oil methanol	SC-MeOH	400	-	42:1	4-45min	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)	rapeseed oil methanol	SC-MeOH	300-450	-	42:1	10-240s	5	HPLC	To study effect of free fatty acids and water in triglycerides on biodiesel fuel production
Cao et al. (2005)	soybean oil methanol	SC-MeOH	200-310	-	6:1-42:1	5-30min	250	GC	To study the transesterification of soybean Oil in methanol under supercritical condition in the presence of propane as co-solvent

Reference	Material	Method	Temp. (°C)	Pressure	Condition Molar ratio (MeOH:Oil)	Time	Volume reactor (ml)	Analysis	Objective
Zhu et al. (2007)	soybean oil methanol n-hexane butanol molecular sieve	Continuous (SC-MeOH)	240-340	10-40MPa	6:1-80:1	12.5-50min	75	GC	To study a new continuous production process of biodiesel production from vegetable oil with supercritical methanol by using a tubular reactor