



CHAPTER II

LITERATURE REVIEW

Biodiesel, which is monoalkyl esters of long chain fatty acids derived from renewable feed stocks for use in compression ignition engines (L.C. Meher *et al.*, 2006), plays an important role as an alternative fuel in recent years due to the increase in petroleum fuel prices and environmental concerns. Since biodiesel is an eco-friendly, non toxic, biodegradable, non flammable, and has significantly fewer emissions than petroleum-based diesel when burned, it has been gaining worldwide popularity as an alternative energy source (Bajpai *et al.*, 2006). Among the different possible resources, diesel fuels derived from the triglycerides of vegetable oils and animal fats have shown potential as substitutes for petroleum-based diesel fuels. However, the direct use of vegetable oils in a diesel engine can lead to a number of problems, such as poor fuel atomization, poor cold-engine start-up, oil ring stickening, and the formation of gum and other deposits. Consequently, considerable effort has been made to develop alternative diesel fuels that have the same properties and performance as the petroleum-based fuels, with the transesterification of triglycerides to fatty acid alkyl esters showing the most current promise (Jitputti *et al.*, 2006).

Vegetable oils are ester of glycerol called triglycerides or triacylglycerol. The main composition of fatty acids and iodine value are listed in Table 2.1. Some properties and heating values of vegetable oils were also shown in Table 2.2.

Table 2.1 Iodine values and main compositions of fatty acids in vegetable oils

Crude Oil	Iodine value	Main compositions of fatty acids						
		C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3
Palm oil	14.1-21.0	ND-0.5	0.5-2.0	39.3-47.5	3.5-6.0	36.0-44.0	9.0-12.0	ND-0.5
Palm olein	> 56	0.1-0.5	0.5-1.5	38.0-43.5	3.5-5.0	39.8-46.0	10.0-13.5	ND-0.6
Palm stearin	< 48	0.1-0.5	1.0-2.0	48.0-74.0	3.9-6.0	15.5-36.0	3.0-10.0	0.5
Palm Kernel oil	50.0-55.0	45.0-55.0	14.0-18.0	6.5-10.0	1.0-3.0	12.0-19.0	1.0-3.5	ND-0.2
Coconut oil	6.3-10.6	45.1-53.2	16.8-21.0	7.5-10.2	2.0-4.0	5.0-10.0	1.0-2.5	ND
Peanut	86-107	ND-0.1	ND-0.1	8.0-14.0	1.0-4.5	35.0-67.0	13.0-43.0	ND-0.3
Jatropha oil	101	ND	ND	14.9	6.0	41.2	37.4	ND
Rape seed oil	94-120	ND	ND-0.2	1.5-6.0	0.5-3.1	8.0-60.0	11.0-23.0	5.0-13.0
Soy bean oil	124-139	ND-0.1	ND-0.2	8.0-13.5	2.0-5.4	17.7-28.0	49.8-59.0	5.0-11.0

Ref.: Codex Alimentarius Commission, FAO/WHO, August 2000, ND: not found

Table 2.2 Properties and heating values of vegetable oils

Oil	Density 21°C (g/mL)	Viscosity 21°C (cp)	Heating value (kJ/kg)
Soy bean	0.918	57.2	39,350
Sunflower	0.918	60.0	39,490
Coconut	0.915	51.9	37,540
Peanut	0.914	67.1	39,470
Palm	0.898	88.6	39,550
Palm Kernel oil	0.904	66.3	39,720
Jatropha oil	0.915	36.9 ^{38°C}	39,000
Diesel	0.845	3.8	46,800

Ref: NAS. 1980

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except that alcohol is used instead of water. This process has been widely used to reduce the high viscosity of triglycerides and is commonly used to produce biodiesel. The transesterification reaction is represented in Figure 2.1.



Figure 2.1 General equation of transesterification.

If methanol is used in this process, it is called methanolysis. The methanolysis of triglycerides is represented in Figure 2.2 (L.C. Meher *et al.*, 2006). The stoichiometry requires 3 mol of alcohol and 1 mol of triglycerides to give 3 mols of fatty acid esters and 1 mol of glycerol. The overall process is a sequence of three consecutive reversible reactions where diglyceride and monoglyceride are intermediate products.

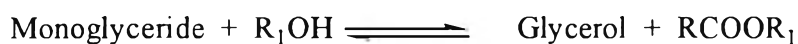
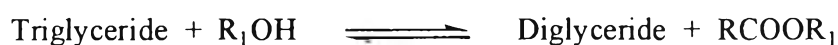
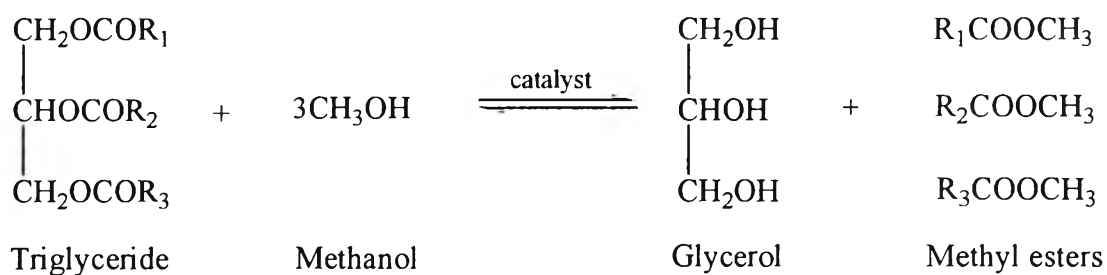


Figure 2.2 General equation for the transesterification of triglycerides.

The transesterification reaction can be catalyzed by both acid and alkaline catalysts, using a homogeneous or heterogeneous catalytic process. Sodium and potassium hydroxide are commonly used as industrial catalysts, since they are relatively cheap and also very active. On the other hand, their utilization in vegetable oil transesterification produces soaps by neutralizing the free fatty acid in the oil and by triglyceride saponification. The soap formation is an undesirable side-reaction because it partially consumes the catalyst, decreases the biodiesel yield, and complicates the separation and purification steps. The removal of these catalysts is technically difficult and brings extra cost to the final product. In addition, the difficulty for recycling and the generation of large amounts of waste make the traditional catalysts less favorable. Moreover, there was some research using an enzymatic catalyst for producing biodiesel since enzymes have shown good tolerance for the free fatty acid of the feedstock. However, the enzymes are expensive and are unable to provide the degree of reaction completion required to meet the ASTM fuel specification (Gerpen 2005). Thus, there has been an increasing development of new catalysts for biodiesel production.

Freedman *et al.* (1984) presented the results of a parametric study of the transesterification reaction variables that included temperature, molar ratio of alcohol-to-oil, type of catalyst, and the degree of refinement of the oil. They

observed that the reaction proceeded to completion in 1 h at 60°C, but took 4 h at 32°C and showed how the degree of reaction depends on the alcohol to oil ratio. They compared both crude and refined vegetable oils as feedstock and found that the yield of methyl esters was reduced from 93% to 67% for the refined oil, and from 98% to 86% for the crude oil.

Ma *et al.* (1998) studied the methanolysis of beef tallow with catalysts NaOH and NaOMe. The catalysts NaOH and NaOMe reached their maximum activity at 0.3 and 0.5% w/w of the beef tallow, respectively, implying that NaOH was significantly better than NaOMe.

Gryglewicz (1999) used basic alkaline-earth metal compounds in the transesterification of rapeseed oil for the production of fatty acid methyl esters. Sodium hydroxide exhibited the highest catalytic activity in this process. The degree to which the substrates were reacted reached 85% after 30 min of the process and 95% after 1.5 h, which represented a close value to the equilibrium. Barium hydroxide was slightly less active with a conversion of 75% after 30 min. Calcium methoxide was medially active with the degree to which the substrates were reacted being 55% after 30 min and 80% after 1 h. A state of reaction equilibrium (93%) was reached after 2.5 h. The rate of reaction was slowest when catalyzed by CaO. Magnesium oxide and calcium hydroxide showed no catalytic activity in rapeseed oil methanolysis.

Darnoko and Cheryan (2000) produced methyl esters by the transesterification of palm oil with methanol in the presence of 1% KOH. The rate of transesterification in a batch reactor increased with temperature up to 60°C. The kinetics of palm oil esterification in a batch reactor was investigated.

Tomasevic and Marinkovic (2003) used sodium hydroxide or potassium hydroxide as a catalyst in the process of alkaline methanolysis in concentration from 0.4 to 2% w/w of oil. Refined and crude oils with 1% either a sodium hydroxide or potassium hydroxide catalyst resulted in successful conversion. The best yields and viscosities of the esters obtained from the methanolysis of soybean oil with 1% potassium hydroxide.

Freedman and Pryde (1986) got a desirable product with 1 mol% of sulfuric acid with a molar ratio of 30:1 at 65°C and they got 99% conversion in 50 h, while

the butanolysis needed 117°C and the ethanolysis 78°C while the times should be 3 and 18 h, respectively.

Mohamad (2000) investigated the transesterification of waste vegetable oil by using acid catalysts. The reaction was conducted at four different catalyst concentrations (0.5, 1.0, 1.5 and 2.25 M HCl) in the presence of 100% excess alcohol. The result was compared with 2.25 M H₂SO₄, and a decrease in viscosity was observed. H₂SO₄ has superior catalytic activity in the range of 1.5–2.25 M concentration.

Although chemical transesterification using an alkaline catalysis process gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times, the reaction has several drawbacks: it is energy intensive, the recovery of glycerol is difficult; the acidic or alkaline catalyst has to be removed from the product; the alkaline wastewater requires treatment; and, free fatty acids and water interfere with the reaction. Attempts to use heterogeneous catalysts in the alcoholysis of triglycerides have been made in order to minimize the homogeneous process problems. The heterogeneous catalysts can be easily separated from the system at the end of the reaction and could also be reused. Moreover, the use of these catalysts does not produce soaps through free fatty acid neutralization or triglyceride saponification (Pinto *et al.*, 2005).

Monteiro and Cruz (2004) studied the transesterification of soybean oil using mixed oxides as catalysts. The reactions were carried out using a weight ratio of 4.5:6.0:0.3 (methanol:soybean oil:catalyst) at 70°C for 8 h. The following catalysts were investigated: ZrO₂-SiO₂; KOH/ZrO₂-SiO₂; Co₂O₃-SiO₂; Mo₂O₅-SiO₂; Na₂O-SiO₂; La₂O₃ (10%)-MCM-41; MgO (10%)-MCM-41; BaO (10%)-MCM-41; CaO; and MgO. The best results were obtained with La₂O₃ (10%)-MCM-41, Na₂O-SiO₂, and CaO, with conversions of 81%, 76%, and 67%, respectively.

Jitputti and coworkers (2006) reported on the preliminary results of using several acidic and basic solids, such as ZrO₂, ZnO, SO₄²⁻/SnO₂, SO₄²⁻/ZrO₂, KNO₃/KL zeolite, and KNO₃/ZrO₂ as heterogeneous catalysts for crude palm kernel oil (PKO) and crude coconut oil (CCO) transesterification with methanol. It was found that ZnO and SO₄²⁻/ZrO₂ exhibited the highest activity for both PKO and CCO transesterification. Only 1% wt of SO₄²⁻/ZrO₂ was needed to catalyze the reaction

and resulted in a fatty acid methyl ester content higher than 90%. Moreover, a study of the catalyst's recyclability indicated that the spent $\text{SO}_4^{2-}/\text{ZrO}_2$ cannot be directly reused for the transesterification. However, this spent catalyst can be easily regenerated and the same activity can be obtained.

Liu and coworkers (2007) synthesized a novel mesoporous solid base Na-ZrO₂ with a high thermal stability which was prepared by controlled sol-gel process. They found that Na-ZrO₂ exhibited a higher basic strength than conventional solid bases. As a result, the mesoporous framework and high specific area facilitated this solid base, showing a remarkable activity in the transesterification of methanol and propylene carbonate.

There are many analytical methods to identify biodiesel, such as thin layer chromatography (TLC), High performance liquid chromatography (HPLC) and gas chromatography (GC), and the most widely used technique is GC due to its generally higher accuracy in quantifying minor component (Knothe 2001). The original report on biodiesel GC analysis (Freedman et al., 1986) quantified mono-, di-, and triacylglycerols in methyl soyate on a short 100% dimethylpolysiloxane column (1.8 m x 0.32 mm i.d.). Mittelbach (1993) prepared the sample by mixing 100–500 µl rapeseed methyl ester (depending upon glycerol content) with 100 µl of 1,4-butanediol standard solution in N,Ndimethylformamide (approximately 0.1 mg 1,4-butanediol/mL) and 600–200 µl of DMF. Finally, 200 µl of bistrimethylsilyl trifluoroacetamide (BSTFA) was added to reach the final volume of 1 mL. The mixture was shaken vigorously for at least 10 min before injecting 2 µl of aliquots into the GC equipped with a capillary column with a dimension of 60 m x 0.25 mm, 0.25 mm containing DB-5 fused silica (J and W Scientific Inc.), whereas Boocock (2001) used a DB-1 fused silica capillary column with a dimension of 2 m x 0.25 mm i.d. coated with a 0.25 mm film of 100% polymethyl siloxane.

The yield of the transesterification reaction was determined by ¹H-NMR, as followed Gelbard and coworkers' work (1995). These authors used the protons of the methylene groups adjacent to the ester moiety in triglycerols and the protons in the alcohol moiety of the methyl ester product to monitor the yield. They used a simple equation, as shown below:

$$C = 100 \times \left(\frac{2A_{ME}}{3A_{\alpha-CH_2}} \right) \dots\dots\dots(2.1)$$

where

C = conversion of triacylglycerol feedstock (vegetable oil) to the corresponding methyl ester.

A_{ME} = integration value of the protons of the methyl esters (the strong singlet peak at 3.6 ppm)

$A_{\alpha-CH_2}$ = integration value of the methylene protons at 2.3 ppm

The factors 2 and 3 were derived from the fact that the methylene carbon had two protons and the alcohol (methanol-derived) carbon contained three attached proton.