



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Vegetable Oils and Animal Fats

The major components of vegetable oils and animal fats are triglyceride, which are tri-esters of glycerol (a triol) and free fatty acids (long alkyl chain carboxylic acids). Fat usually refers to the triglycerides, which are solid at room temperature while oils are liquid at room temperature. Chemically, triglycerides are the molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids differ by the length of carbon chains, the number, orientation, and position of double bonds in these chains. The triglyceride molecule has the chemical structure shown in Figure 2.1, where R_1 , R_2 , and R_3 represent long chain fatty acids (Ma and Hanna, 1999).

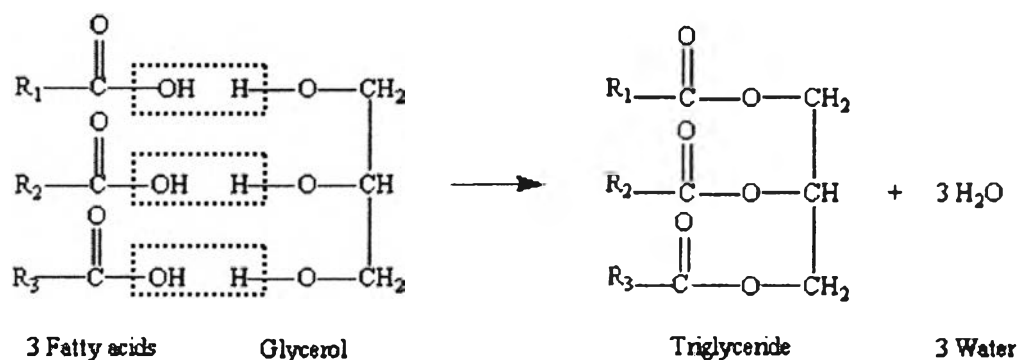


Figure 2.1 The formation and chemical structure of triglyceride (Ma and Hanna, 1999).

Molecules having three fatty acid chains are referred to as triglycerides, while those with two fatty acid chains are diglycerides, and those with one fatty acid chain are monoglycerides. The triglyceride of vegetable oils and animal fats typically contain several different fatty acids. Thus, different fatty acids can be attached to one glycerol backbone. The different fatty acids that are contained in the triglyceride comprise the fatty acids profile (or fatty acids composition) of the vegetable oil or

animal fat. Because different fatty acids have different physical and chemical properties, the fatty acids profile is probably the most important parameter influencing the corresponding properties of a vegetable oil or animal fat (Ma and Hanna., 1999).

Table 2.1 shows typical fatty acids found in oils and fats. The “Acronym” is a chemical abbreviation for the molecule. The first number refers to the number of carbon atoms in the chain, and the second number refers to the number of double bonds in the molecule. Thus, Linoleic acid, for example, is a fatty acid consisting of a chain of 18 carbon atoms, with two double bonds. Some fatty acids found in vegetable oils and animal fats are summarized in Table 2.2 and some chemical-physical properties of the vegetable oils are presented in Table 2.3.

Table 2.1 Chemical structure of common fatty acids (Srivastava and Prasad., 2000)

Fatty acid	Systematic name	Acronym	Formula
Lauric acid	Dodecanoic	12:0	C ₁₂ H ₂₄ O ₂
Myristic acid	Tetradecanoic	14:0	C ₁₄ H ₂₈ O ₂
Palmitic acid	Hexadecanoic	16:0	C ₁₆ H ₃₂ O ₂
Stearic acid	Octadecanoic	18:0	C ₁₈ H ₃₆ O ₂
Arachidic acid	Eicosanoic	20:0	C ₂₀ H ₄₀ O ₂
Behenic acid	Docosanoic	22:0	C ₂₂ H ₄₄ O ₂
Lignoceric	Tetracosanoic	24:0	C ₂₄ H ₄₈ O ₂
Oleic acid	cis-9-Octadecenoic	18:1	C ₁₈ H ₃₄ O ₂
Linoleic acid	cis-9,cis-12-Octadecadienoic	18:2	C ₁₈ H ₃₂ O ₂
Linolenic acid	cis-9,cis-12,cis-15-	18:3	C ₁₈ H ₃₀ O ₂
Erucic acid	cis-13-Docosenoic	22:1	C ₂₂ H ₄₂ O ₂

Table 2.2 Composition of vegetable oil biodiesel obtain from different sources
(Srivastava and Prasad., 2000)

Oil or Fat	Fatty acid composition (%wt)							
	Saturated				Mono unsaturated		Poly unsaturated	
	12:0	14:0	16:0	18:0	18:1	22:1	18:2	18:3
Babassu	44-45	15-17	5.8-9	2.5-5.5	12-16	1.4-3		
Canola			4-5	1-2	55-63	20-31	9-10	1-2
Coconut	44-51	13-18.5	7.7-10.5	1-3	5-8.2	1.0-2.6		
Corn			7-13	2.5-3	30.5-43	39-52	1	
Cottonseed		0.8-1.5	22-24	2.6-5	19	50-52.5		
Linseed			6	3.2-4	13-37	5-23	26-60	
Olive		1.3	7-18.3	1.4-3.3	55.5-84.5	4-19		
Palm		0.6-2.4	32-46.3	4-6.3	37-53	6-12		
Peanut		0.5	6-12.5	2.5-6	37-61	13-41		1
Rapeseed		1.5	1-4.7	1-3.5	13-38	9.5-22	1-10	40-64
Safflower			6.4-7.0	2.4-29	9.7-13.8	75.3-80.5		
Safflower (high oleic)			4-8	2.3-8	73.6-79	11-19		
Sesame			7.2-9.2	5.8-7.7	35-46	35-48		
Soybean			2.3-11	2.4-6	22-30.8	49-53	2-10.5	
Sunflower			3.5-6.5	1.3-5.6	14-43	44-68.7		
Tallow		3-6	25-37	14-29	26-50	1-2.5		

Table 2.3 Properties of the vegetable oils (Barnwal B.K. et al., 2005)

Vegetable oil	Kinematic viscosity at 38 °C (mm²/s)	Cetane No.	Heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)
Corn	34.9	37.6	39.5	-1.1	-40.0	277	0.9095
Cottonseed	33.5	41.8	39.5	1.7	-15.0	234	0.9148
Crambe	53.6	44.6	40.5	10.0	-12.2	274	0.9048
Linseed	27.2	34.6	39.3	1.7	-15.0	271	0.9236
Peanut	39.6	41.8	39.8	12.8	-6.7	271	0.9026
Rapeseed	37.0	37.6	39.7	-3.9	-31.7	246	0.9115
Safflower	31.3	41.3	39.5	18.3	-6.7	260	0.9144
Sesame	35.5	40.2	39.3	-3.9	-9.4	260	0.9133
Soya bean	32.6	37.9	39.6	-3.9	-12.2	254	0.9138
Sunflower	33.9	37.1	39.6	7.2	-15.0	274	0.9161
Palm	39.6	42.0	-	31.0	-	267	0.9180
Babassu	30.3	38.0	-	20.0	-	150	0.9460
Diesel	3.06	50	43.8	-	-16	76	0.8550

Often, the vegetable oils of choice for biodiesel production are those which occur abundantly in the region of testing. Therefore, rapeseed oil is the primary biodiesel source in Europe, while in the United States both rapeseed and soybean oils are used. Canola oil is a cultivated version of rapeseed oil, it contains very low erucic acid concentration and it is now widely produced in Western Canada. Therefore, raw canola oil was selected as feedstock for biodiesel production in this study. The fatty acid composition of canola oil is presented in Table 2.2.

2.2 Vegetable Oil Utilization as Engine Fuel

In the 1930s and 1940s, vegetable oils were used as emergency fuels in diesel engines by Shay, E.G., 1993. These oils contain no sulfur and have about 10% oxygen by weight. These tend to reduce their unburned hydrocarbons, sulfur dioxide, carbon monoxide, and particulate emissions compared with diesel fuel. Therefore, using vegetable oil based fuel may reduce air pollution. However, Ryan, T.W. et al., (1984) have reported that the use of vegetable oils directly in diesel engine is associated with many problems such as coking of injector nozzles, carbon deposits, oil ring sticking, lubricating oil contamination and poor fuel atomization. A key problem associated with the use of pure vegetable oils as fuels for diesel engines is caused by their high fuel viscosity. Conversion of the oils to their alkyl esters reduces the viscosity to near diesel fuel levels and produces a fuel with properties that are similar to petroleum based diesel fuel and therefore could be used in existing engines without modifications.

Three main processes have been investigated in attempts to overcome these drawbacks and allow vegetable oils and oil waste to be utilized as a viable alternative fuel: microemulsification, pyrolysis (thermal cracking), and transesterification. Among these, the transesterification is the most promising process for producing clean and environmentally safe fuel, so called biodiesel fuel, from vegetable oils (Schwab et al., 1987).

2.2.1 Microemulsification

Microemulsions are isotropic, clear or translucent thermodynamically stable dispersions of oil, water, surfactant, and often a small amphiphilic molecule, called a co surfactant (Schwab et al., 1983). Drop diameters in microemulsions typically range from 100 to 1000 Å (Srivastava and Prasad, 2000). Various investigators have studied microemulsification of vegetable oils with methanol, ethanol or 1-butanol (Pryde, 1984; Ziejewski et al., 1984; Schwab et al., 1987). They arrived at the conclusion that microemulsions of vegetable oils and alcohols cannot be recommended for long-term use in diesel engines for similar reasons as apply to neat vegetable oils. The fuels produced are prone to incomplete combustion, the

formation of carbon deposits, and an increase in the viscosity of the lubricating oil (Ziejewski et al., 1984). Moreover, microemulsions display considerably lower volumetric heating values as compared to hydrocarbon-based diesel fuel due to their high alcohol contents (Srivastava and Prasad, 2000), and they have been assessed insufficient in terms of cetane number and cold temperature behavior (Maurer, 1998).

2.2.2 Pyrolysis (Thermal Cracking)

Pyrolysis is the conversion of one substance into another by means of heat or by heat in the presence of a catalyst. It involves heating in the absence of air or oxygen (Sonntag, 1979b) and cleavage of chemical bonds to yield smaller molecules (Weisz et al., 1979).

This treatment results in a mixture of alkanes, alkenes, alkadienes, aromatics, and carboxylic acids, which is similar to hydrocarbon-based diesel fuels in many respects. The cetane number of plant oils is increased by pyrolysis, and the concentrations of sulfur, water and sediment in the resulting product are acceptable. However, according to modern standards, the viscosity of the fuel is considered as too high, ash, and carbon residue far exceed the values for fossil diesel, and the cold flow properties of pyrolyzed vegetable oils are poor (Schwab et al., 1983). Moreover, it is argued that the removal of oxygen during thermal decomposition eliminates one of the main ecological benefits of oxygenated fuels, namely more complete combustion due to higher oxygen availability in the combustion chamber (Ma and Hanna, 1999).

2.2.3 Transesterification

In organic chemistry, transesterification is the process of exchanging the alkoxy group of an ester compound by another alcohol. The reactions are often catalyzed by an acid or a base. Transesterification processes are crucial for producing biodiesel from biolipids. Transesterification of triglycerides produce fatty acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process

(Meher, L.C. et al., 2006). The details of the process of transesterification and biodiesel production are given in the following sections.

2.3 Biodiesel

The best way to use vegetable oil as fuel is to convert it into biodiesel. Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from renewable feed stocks, such as vegetable oil or animal fats, for use in compression ignition engine. It is formed from transesterification of vegetable oils with methanol, ethanol, or higher alcohols (Meher, L.C. et al., 2006).

Biodiesel has many merits as a renewable energy resource, thereby relieving reliance on petroleum fuel, and it is biodegradable and non-toxic. Further, compared to petroleum-based diesel, biodiesel has a more favorable combustion emission profile, such as low emissions of carbon monoxide, particulate matter, and unburned hydrocarbons (Al-Zuhair S., 2007).

2.4 Transesterification

The transesterification process is one useful method of reducing the high viscosity of triglyceride oils. In the reaction, a triglyceride molecule reacts with three alcohol molecules sequentially in the presence of a catalyst (acid or base) to produce first a diglyceride, then a monoglyceride, and finally a glycerol product and three molecules of monoester as can be seen in figure 2.2. All reaction steps are reversible with the net equilibrium favoring the formation of products. The reaction can use either a base or an acid catalyst. However, base catalysts are preferred because they give a faster reaction under milder reaction conditions (Freedman, B et al., 1986).

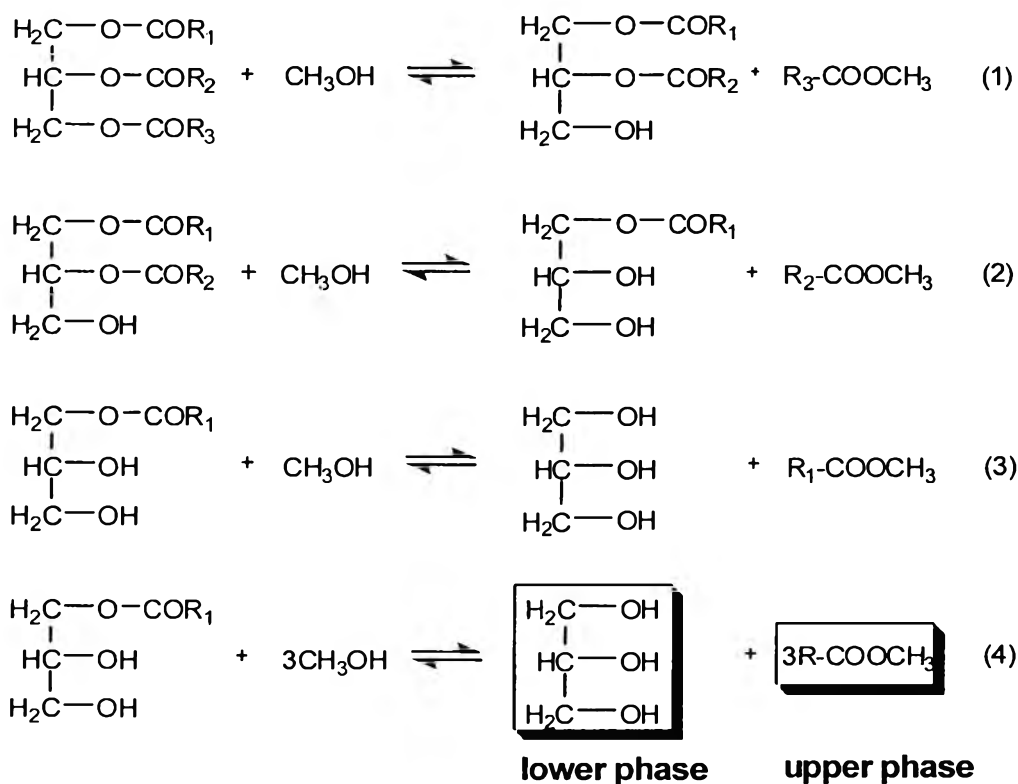


Figure 2.2 Reaction scheme for the transesterification of triglycerides with methanol (Mittelbach and Remschmidt, 2004).

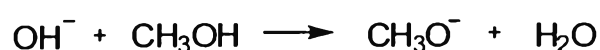
2.5 Catalysts for Biodiesel Production

The transesterification reaction can be catalyzed by both acid and base catalysts, using a homogeneous or heterogeneous catalytic process. Sodium and potassium hydroxide are commonly used as industrial catalysts, since they are relatively cheap and very active. The base-catalyzed transesterification reaction is much faster than the acid-catalyzed transesterification and it is most often used commercially (Freedman, B et al., 1986). Therefore, this work will be focused on the base-catalyzed transesterification.

2.5.1 Homogeneous Base-Catalyzed Transesterification

Among the most commonly used homogeneous base catalysts in biodiesel industry are potassium hydroxide (KOH) and sodium hydroxide (NaOH)

flakes, which are inexpensive, easy to handle in transportation and storage, and are preferred by small producers. Alkyl oxide solutions of sodium methoxide (NaOCH₃) or potassium methoxide (KOCH₃) in methanol, which are now commercially available, are the preferred catalysts for large continuous-flow production processes. In transesterification, the effective species of catalysis is the methoxide radicals (CH₃O⁻). For sodium or potassium hydroxide, methoxide ion is prepared *in situ* by reacting hydroxide and methanol as follow:



This reaction also yields water that remains in the system. Hydrolysis of triglycerides and alkyl esters may occur due to the presence of water, which further leads to the formation of free fatty acids and thus to undesired soap. The water problem can be avoided if sodium and potassium methoxide solutions, which can be prepared water-free, are applied. Additionally, although the use of methoxides cannot avoid soap formation if the feedstock contains free fatty acids, which is also true for use of KOH or NaOH, but very little saponification of triglycerides occurs because methoxides behave as weak Lewis base (Singh, A. et al, 2006).

In this work, sodium methoxide solution 30% in methanol was chosen to be a representative of industrial catalyst. Sodium methoxide solution 30% in methanol is a colorless viscous liquid with an alcohol-like odor. The physical properties are shown in the following table:

Table 2.4 Properties of sodium methoxide solution 30% in methanol (data from Degussa AG/Germany)

Property	Value Unit	Method
Boiling point at 1013 hPa	92 °C	DIN 51751
Flash point	32 °C	EN 22719
Density (20 °C)	0.97 g/cm ³	DIN 51757
Viscosity	60-62 mPas s	

Even though the base-catalyzed process seems operator friendly and economically possible, it suffers from a key limitation: only refined oils and pretreated fats with low concentrations of free fatty acids (FFAs) can be used to produce biodiesel using homogeneous base catalysts. FFAs can react with the base catalyst giving rise to saponification as shown in Figure 2.4(a). The presence of soaps causes an increase in viscosity and the formation of gels, which complicates the glycerol-monoalkyl ester separation process. Water also contributes to soap production since water can react with the monoalkyl ester product to form FFAs as shown in Figure 2.4(b).

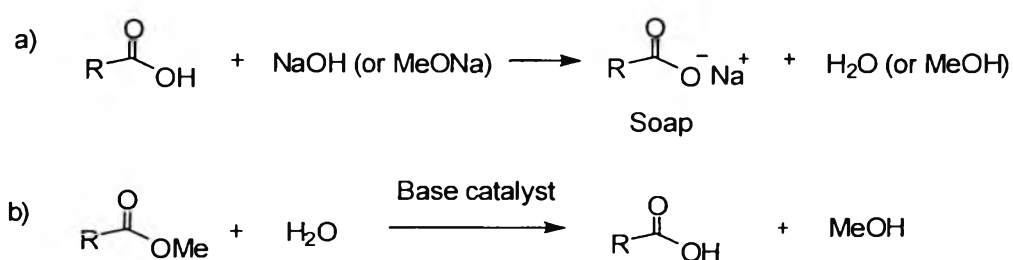


Figure 2.4 (a) Reaction of the base catalyst with FFAs to produce soap and water, both undesirable by-products. (b) Ester hydrolysis due to reaction with water forming FFAs (Schuchard et al., 1998).

Currently, nearly all biodiesel is produced via homogeneous catalysis. The use of homogeneous catalysts allows carrying out the transesterification of lipid feedstock with small alcohols under mild conditions. However, additional separation procedures are required. Residual catalyst must be removed and catalyst loss is inherent, raising the overall cost of production. In contrast, processes using heterogeneous catalysts need higher temperatures to be as effective as homogeneous catalysts in a reasonable reaction time. On the other hand, products do not necessitate complex separation procedures and, in most cases, heterogeneous catalysts can be recycled and reused for long periods of time.

2.5.2 Heterogeneous Base-Catalyzed Transesterification

Presently, many researchers are attempting to use heterogeneous catalysts to replace homogeneous catalysts. Claire S. MacLeod et al. (2007) have evaluated the activity of a series of alkali-doped metal oxide catalysts such as LiNO_3/CaO , NaNO_3/CaO , KNO_3/CaO and LiNO_3/MgO . The research findings indicate that these catalysts exhibited $> 90\%$ conversion in a standard 3 h test and the best catalyst is LiNO_3/MgO . The reuse characteristics of these catalysts are good. The conversion activity does not drop significantly after 5 cycles. However, there is some degree of catalyst leaching, and this leaching creates some homogeneous catalytic activity. This problem should be minimized and the catalysts would have a reasonable lifetime in an industrial setting.

Yang and Xie. (2007) have evaluated the efficiency of some heterogeneous catalysts in terms of the conversion of soybean oil to methyl esters. They have shown that the highest catalytic activity was obtained with ZnO loaded with 2.5 mmol $\text{Sr}(\text{NO}_3)_2/\text{g}$ which gave a conversion of 94.7% within 4 hours of reaction time.

Xuejun Liu et al. (2007) presented results for using SrO as a solid base catalyst and proposed the reaction mechanism of this catalyst. The results showed that the yield of biodiesel produced with SrO as a catalyst was in excess of 95% at temperatures below 70 °C within 30 min of reaction time. The SrO catalyst maintained sustained activity even after being used for 10 cycles. It has basic sites stronger than $\text{H}_\ominus = 26.5$ and is insoluble in methanol, vegetable oils, and fatty acid methyl ester. The results proved that transesterification of soybean oil to biodiesel using SrO as a catalyst is a commercially viable process to decrease the costs of biodiesel production. Catalytic reactions take place on the surface of solid base catalysts as shown in Figure 2.5. The mechanism of the reaction is as follows. In the first step, surface O^{2-} extracts H^+ from CH_3OH to form surface CH_3O^- which is strongly basic and has high catalytic activity in the transesterification reaction. In the second step, the carbonyl carbon atom of the triglyceride molecule attracts a methoxide anion from the surface of the SrO to form a tetrahedral intermediate, where R_1 represents the long chain alkyl group. In the third step, the tetrahedral intermediate picks up H^+ from the surface of the SrO. The tetrahedral intermediate

also can react with methanol to generate methoxide anions. In the last step, rearrangement of the tetrahedral intermediate results in the formation of biodiesel.

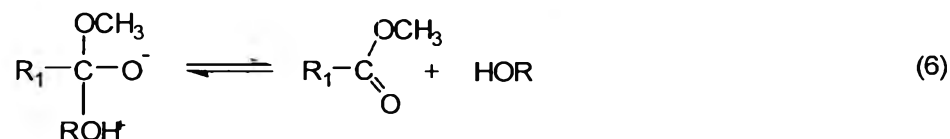
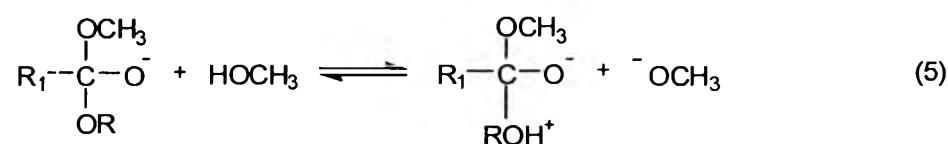
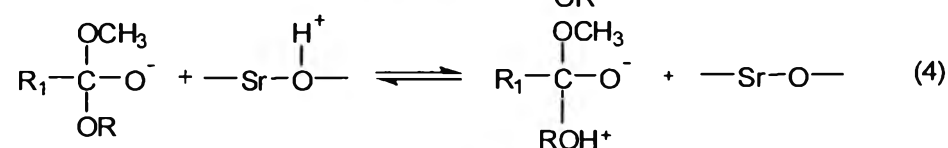
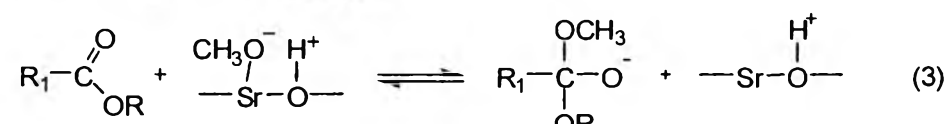


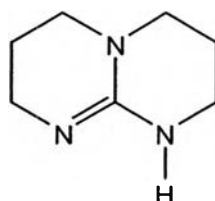
Figure 2.5 SrO catalyzed reaction mechanism for the transesterification of triglycerides (Liu et al., 2007).

Xie and Li. (2006) reported that the catalysts, which were prepared by loading alkali metal compounds such as KI on alumina followed by calcinations at 773K for 3h, gave the highest basicity and the best catalytic activity for the transesterification of soybean oil. A conversion of 96% was achieved.

2.5.3 Non-ionic Base-Catalyzed Transesterification

While a large body of work has been carried out on ionic base catalysts for transesterification of vegetable oil to methyl ester, less research efforts have been directed to the use of non-ionic nitrogen bases. However, since they are easy to handle and can be used under mild conditions, non-ionic nitrogen bases could be employed as base catalysts. In this regard, TBD or 1,5,7-triazabicyclo[4.4.0]dec-5-ene and its methyl derivative MTBD are strong organic bases, their use as basic

catalysts seemed especially interesting for synthesis purposes (Simoni D. et al., 2000). TBD is a strong guanidine base ($pK_b = 25$) widely utilized as acid scavenger and homogeneous catalyst, i.e. for transesterification reactions (Ballini R. et al., 2002). Figure 2.6 shows the chemical structure of TBD



1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)

Figure 2.6 The structure of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (Schuchardt *et al.*, 1998).

In order to obtain milder reaction conditions and to simplify manipulations, a great number of organic bases have been developed. The activity and efficiency of such non-ionic bases as catalysts for the transesterification of vegetable oils were studied. In a first series of studies, it was observed that TBD, even if applied at only 1 mol%, produces more than 90% of methyl esters after 1 h when compared to other bases such as the amidines DBU and DBN, and the triamino(imino)phosphoranes BEMP and Me_7P .

In 1995, Schuchardt *et al.* studied the transesterification of rapeseed oil with methanol in the presence of eight substituted cyclic and acyclic guanidines and compared them with unsubstituted guanidines. They found that the best catalyst was 1,5,7-triazabicyclo[4.4.0]dec-5-ene which, when used at 1 mol%, produces a 90% yield of methyl esters with 1 h reaction time.

The advantage of using guanidines in the transesterification of vegetable oils is the possibility of heterogenized them on organic polymers. Schuchardt *et al.* 1995, also reported results on the heterogenization of these guanidines on different types of chloromethylated poly(styrene/divinylbenzene) and linear polystyrene with the use of a “spacer-arm”. They found that the guanidines heterogenized on gel-type poly(styrene/divinylbenzene) with 1 meq Cl/g showed a

slightly lower activity than their homogeneous analogous but reached the same high conversions after a prolonged reaction time. However, they slowly leached from the polymers, allowing only nine catalytic cycles. On the other hand, a significant advantage to using the TBD catalyst is a clean transesterification process, even if unrefined oils are used, with an easy phase separation of the glycerin, as the guanidium salts of the fatty acids, present in small amounts in the oil, are soluble in the reaction mixture and do not form soaps or emulsions (Schuchardt U. et al., 1995).

In recent years, the food industry generates huge amounts of egg shell and animal shell waste. Lea, F.M. (1990) found that eggshell consists of several mutually growing layers of CaCO_3 , the innermost layer-maxillary layer (=100 μm) grows on the outermost egg membrane and creates the base on which palisade layer constitutes the thickest part (=200 μm) of the eggshell. The top layer is a vertical layer (=5.8 μm) covered by the organic cuticle. The chemical composition (by weight) of by-product eggshell has been reported by Stadelman (2000) as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%). Since eggshell and animal shell has base properties it can be used as the combination of a basic heterogeneous catalyst to generate the multiple basic catalytic sites in the transesterification reaction. However, the synergistic effect of heterogeneous catalyst combinations on the transesterification should be evaluated. Therefore, it is interesting to study these combinations.

2.6 Determination of Biodiesel Yield by Using ^1H NMR

The first report on the use of ^1H NMR spectroscopy to monitor the progress and yield of the transesterification reaction was presented by Gelbard G. *et al.*, 1995. These authors used the protons of the methylene group adjacent to the ester moiety in triglycerides, which appears at 2.30 ppm and the protons in the alcohol moiety of the product methyl esters, which appears at 3.70 ppm to monitor the reaction yield. A simple equation (Eq. 1) given by the authors is as follows.

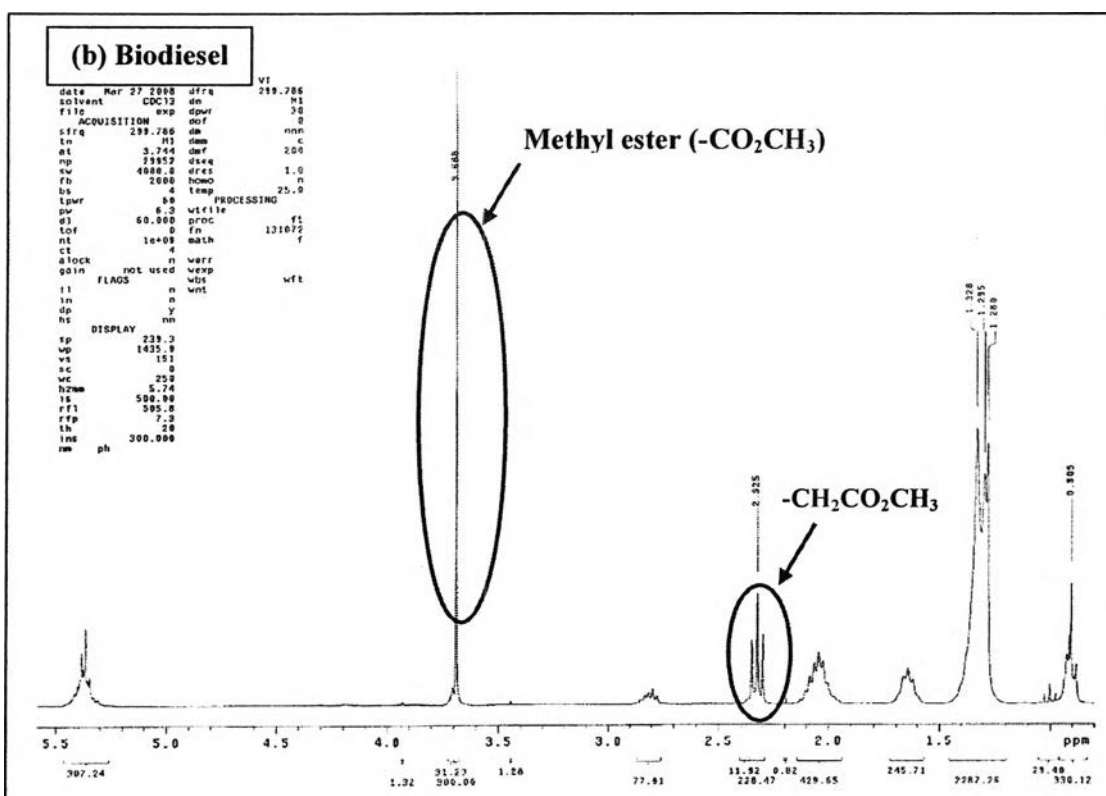
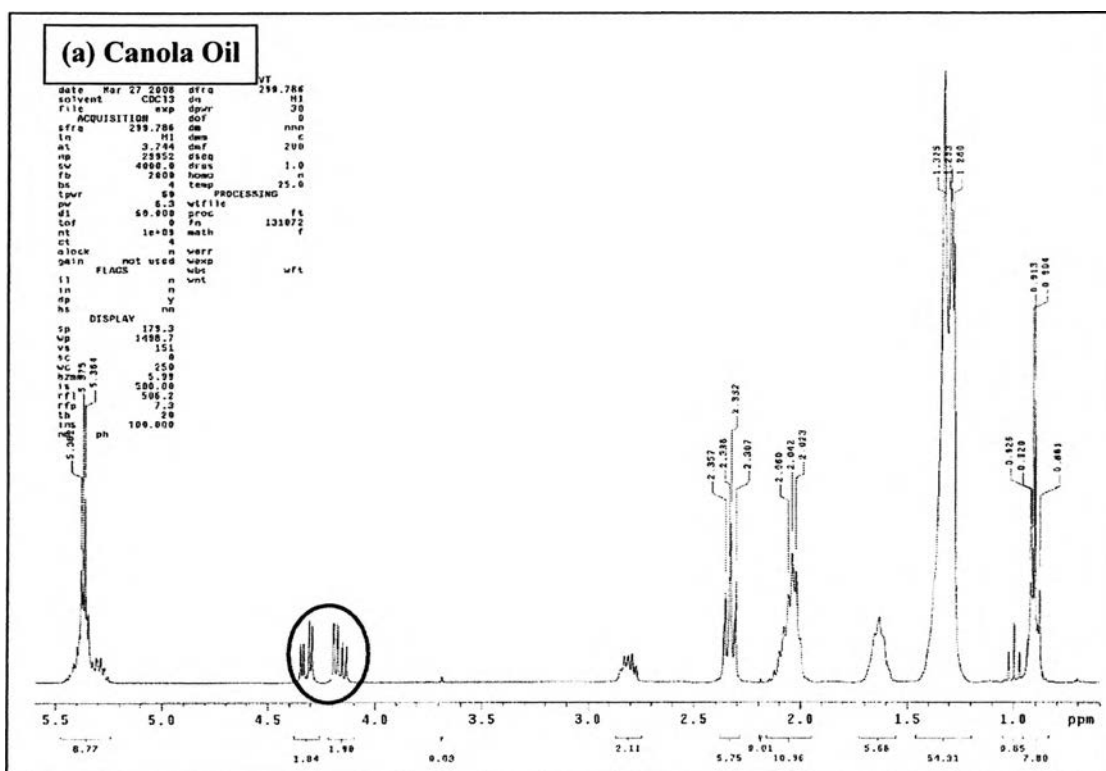


Figure 2.8 ¹H-NMR spectrum of a progressing transesterification reaction for (a) canola oil and (b) biodiesel.

This research will evaluate the optimum condition for the transesterification of raw canola oil by using homogeneous and heterogeneous catalysts. The progress of the reaction is monitored by ^1H NMR spectroscopy. Catalysts efficiency is examined based on the conversion of canola oil to methyl esters. The quality of the biodiesel produced is evaluated through the determination of soap content. This evaluation is conducted at Laboratory bench scale. The ultimate goal of this research is to establish the optimum reaction conditions for the production of high biodiesel yield as a function of catalyst type and concentration, excess reagent, temperature, and biodiesel quality.