



CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Vegetable Oil and Animal Fat

Vegetable oil and animal fat contain triglyceride as the major component. The word “fat” usually refers to the triglycerides, which are solid at room temperature; while “oil” is liquid at room temperature. Chemically, triglycerides are molecules containing three long chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids are differentiated by the length of carbon chains, the number, orientation, and position of double bonds between the carbon atoms in these chains. The number of double bonds in the triglyceride molecules allows to categorize the type of oil based on saturation, which can be classified as saturated triglycerides when there are no double bonds within the molecules and unsaturated triglycerides when the molecules have at least one position of double bond within the molecules. The chemical structure of the triglyceride molecule is shown in Figure 2.1, where R_1 , R_2 , and, R_3 represent the long chain fatty acids (Ma and Hanna., 1999).

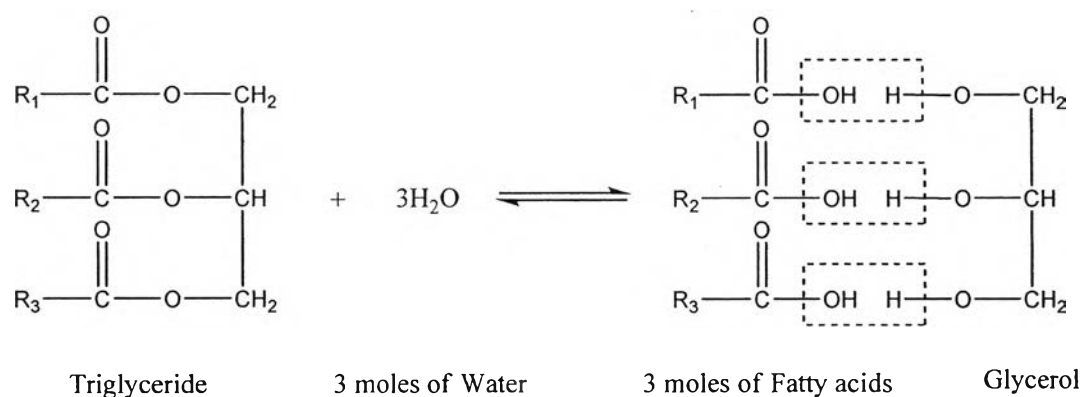


Figure 2.1 The chemical structure of triglyceride and the hydrolysis products (Ma and Hanna., 1999).

Molecules having three chains of fatty acid are referred to as triglycerides, while those with two fatty acid chains are diglycerides, and those with one fatty acid chain are monoglycerides. Vegetable oil and animal fat typically contain several

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

Table 2.1 shows typical fatty acids found in oil and fat. 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, Oleic acid, for example, is a fatty acid consisting of a chain of 18 carbon atoms, with one double bond. Some fatty acids found in vegetable oil and animal fat are summarized in Table 2.2 and some properties of the vegetable oil 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	$C_{18}H_{36}O_2$
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-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Arachidic acid	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic acid	Docosanoic	22:0	$C_{22}H_{44}O_2$
Erucic acid	cis-13-Docosenoic	22:1	$C_{22}H_{42}O_2$
Lignoceric acid	Tetracosanoic	24:0	$C_{24}H_{48}O_2$

Table 2.2 Composition of vegetable oil biodiesel obtained 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 (beef)		3-6	25-37	14-29	26-50	1-2.5		

Table 2.3 Properties of the vegetable oil (Barnwal *et al.*, 2005)

Vegetable oil	Kinematic viscosity at 38 °C (mm ² /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	50.0	43.8	-	-16.0	760	0.8550

2.2 Use of Vegetable Oil as Engine Fuel

Shay (1993) stated that back in the 1930s and 1940s, vegetable oil were used as emergency fuels in diesel engines. The main advantages of using vegetable oil as fuels are that they do not contain sulfur and have about 10% oxygen by weight. These tend to reduce the unburned hydrocarbons, sulfur dioxide, carbon monoxide, and particulate emissions compared with conventional diesel fuel. Therefore, the use of vegetable oil based fuel may reduce air pollution. However, the use of vegetable oil directly in diesel engines causes several problems such as coking of injector nozzles, carbon deposits, oil ring sticking, contamination and degradation of lubricating oil, and poor fuel atomization (Ryan *et al.*, 1984). A key problem associated with the use of pure vegetable oil as fuels for compression ignition engines is caused by their high viscosity. Conversion of the oil to their alkyl esters reduces their viscosity to near fossil based diesel fuel levels and produces a fuel with

properties that are similar to the petroleum based diesel fuel. Therefore, alkyl esters (chemically modified vegetable oil) could be used in existing diesel engines without major modifications.

Three main processes have been investigated to overcome the drawbacks of the direct use of virgin vegetable oil or waste cooking oil as viable alternative fuels: 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 oil (Ma and Hanna., 1999).

2.3 Biodiesel

The best process to overcome the drawbacks of the use of vegetable oil as automotive fuel is the chemical conversion of vegetable oil into biodiesel. Biodiesel is defined as the mono or di alkyl esters of long chain fatty acids of the alcohol used during the transesterification, that is derived from renewable feedstocks, such as vegetable oil or animal fat, for use in compression ignition engines also known as diesel engine. It is formed from the transesterification of vegetable oil with methanol, ethanol, or higher molecular weight alcohols. Table 2.4 presents some methyl esters derived from fatty acid , with their corresponding name, molecular weight, and molecular formula.

Table 2.4 Methyl esters derived from fatty acid (Knothe, G., 2005)

Fatty acid	Ester names	Molecular weight (g/mole)	Formula
Palmitic acid	Methyl palmitate	270.46	C ₁₇ H ₃₄ O ₂
Palmitoleic acid	Methyl palmitoleate	268.44	C ₁₇ H ₃₂ O ₂
Stearic acid	Methyl stearate	298.51	C ₁₉ H ₃₈ O ₂
Oleic acid	Methyl oleate	296.49	C ₁₉ H ₃₈ O ₂
Linoleic acid	Methyl linoleate	294.47	C ₁₉ H ₃₄ O ₂
Linolenic acid	Methyl linolelaidate	292.47	C ₁₉ H ₃₂ O ₂
Arachidic acid	Methyl arachidonate	318.50	C ₂₁ H ₄₂ O ₂
Behenic acid	Methyl behenate	354.61	C ₂₃ H ₄₆ O ₂
Erucic acid	Methyl erucate	352.60	C ₂₃ H ₄₄ O ₂
Lignoceric acid	Methyl lignocerate	382.67	C ₂₅ H ₅₀ O ₂
Nervonic acid	Methyl nervonate	380.65	C ₂₅ H ₄₈ O ₂

Biodiesel has many merits as a renewable energy resource, thereby it has the potential to relieve the current reliance on petroleum fuel, in addition to its biodegradable and non-toxic properties. 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 as previously indicated (Al-Zuhair., 2007).

2.4 Transesterification

The transesterification process allows 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. 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 mild reaction conditions (Freedman *et al.*, 1986). Figure 2.2 illustrates the overall transesterification reaction.

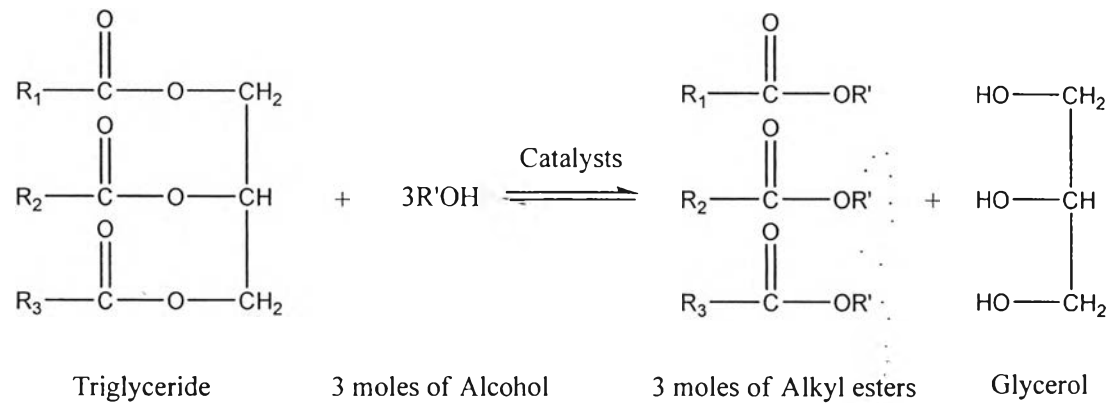


Figure 2.2 The transesterification reaction. R_i is a mixture of various fatty acid chains. The alcohol used for producing biodiesel is usually methanol, thus R' is CH_3 (Freedman *et al.*, 1986).

2.5 Catalysts for Biodiesel Production

The transesterification reaction can be catalyzed by both acid and basic catalysts, using a homogeneous or heterogeneous catalytic process. Sodium and potassium hydroxide are commonly used as industrial homogeneous basic catalysts, because they are relatively cheap and active. The base-catalyzed transesterification reaction is much faster than the acid-catalyzed transesterification and it is most often used commercially.

2.5.1 Homogeneous Base-catalyzed Transesterification

The mechanism of the base-catalyzed transesterification of vegetable oil is shown in Figure 2.3. The sequence of steps can be summarized as follows: first, the base catalyst reacts with alcohol producing the catalytically active species, RO^- . Second, a tetrahedral intermediate is formed by nucleophilic attack on a carbonyl carbon in the triglyceride. Third, the tetrahedral intermediate breaks down into a fatty

acid ester and a diglyceride anion. The latter step is the deprotonation of the catalyst, thus regenerating the active species, which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. This sequence is then repeated twice to yield first a monoglyceride intermediate and finally the glycerol product and biodiesel (Schuchardta *et al.*, 1998).

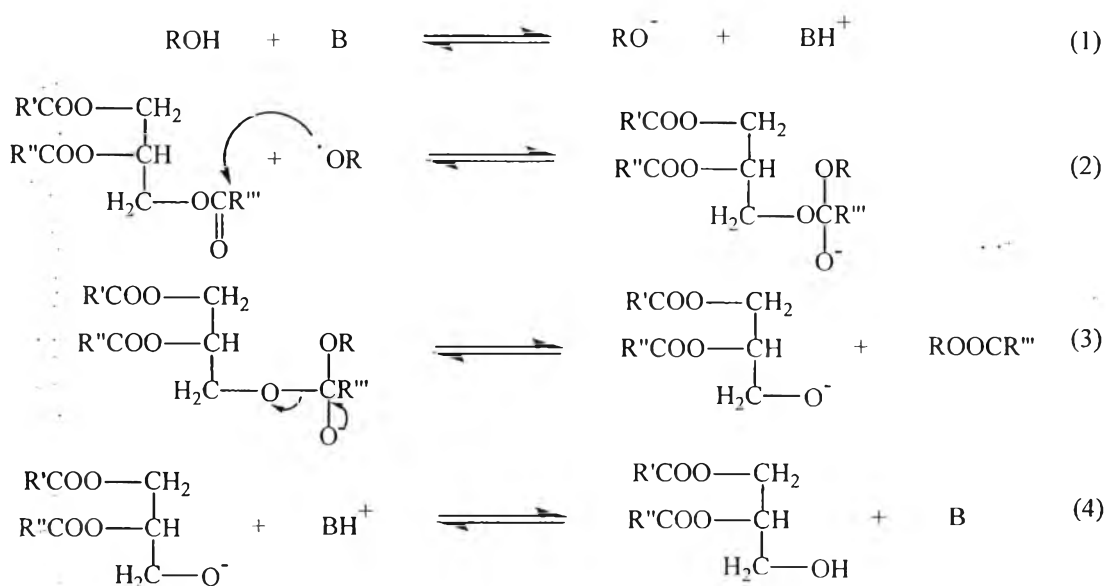


Figure 2.3 Homogeneous base-catalyzed reaction mechanism for the transesterification of triglycerides (Schuchardt *et al.*, 1997).

Even though the base-catalyzed process seems operator friendly and economically possible, it suffers from a key limitation: only refined oil and pretreated fat 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 shown in figure 2.4(b). To solve this problem, starting vegetable oil must be dried (moisture level less than 0.06% w/w), free fatty acid content must be less than 0.5%

by weight and both alcohol and catalyst must be essentially anhydrous (Ma and Hanna., 1999).

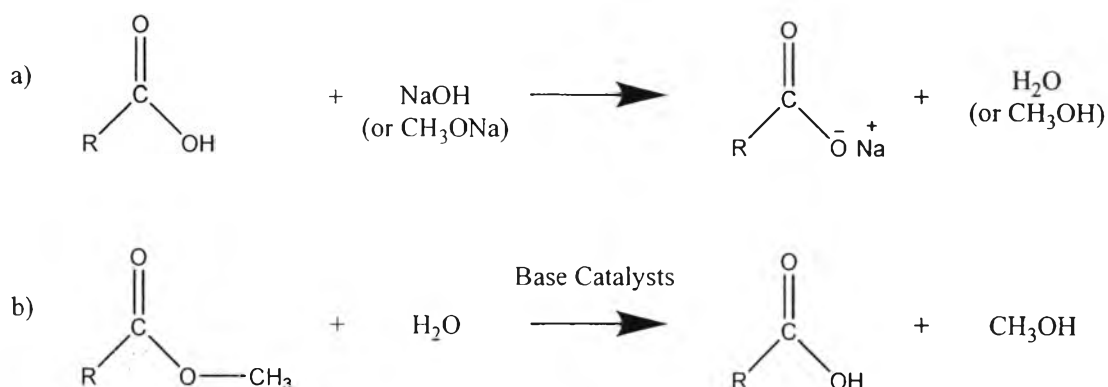


Figure 2.4 (a) Reaction of the base catalyst with FFAs to produce soap and water, both undesirable by-products. (b) Ester hydrolysis due to reaction with water forming FFAs (Schuchard *et al.*, 1998).

Currently, nearly all biodiesel is produced via homogeneous catalysts. The use of homogeneous catalysts allows carrying out the transesterification of lipid feedstock with short chain alcohols (low carbon number) under mild reaction 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. Some of the advantages of using heterogeneous catalysts are as follows. The reaction products do not require complex separation procedures and, in most cases, catalysts can be recycled and reused for long periods of time.

2.5.2 Homogeneous Acid-catalyzed Transesterification

Normally, the basic-catalyzed or alkali-catalyzed transesterification of oils proceeds faster than the acid-catalyzed transesterification especially when refined oils which have low acid value and high cost are used. In the other hand unrefined oils or waste grease, which has high acid value and low cost, can be

successfully used to produce biodiesel by acid catalysis (Canakci and Van Gerpen, 2001). The deactivation of the alkali catalyst by the high free fatty acid contents of the oil, leading to lower biodiesel yields, has been observed (Goff *et al.*, 2004). The effectiveness of various acid catalysts (sulfuric, hydrochloric, nitric, acetic, and phosphoric acids) (5%, v/v) in the esterification of the feedstock with a feedstock to methanol molar ratio of 1:20 was investigated by Ting *et al.*, (2008). Strong acids (sulfuric, hydrochloric, or nitric acid) exhibited higher catalytic activity as compared to weak acids (phosphoric or acetic acid). The highest biodiesel conversion obtained was of 86% in presence of sulfuric acid after 1 hour of reaction at 50°C. However, the results of their study revealed that the strength of the acid alone is not the best indicator to screen a suitable acid as catalyst for transesterification. Goff *et al.*, (2004) reported similar findings on the catalytic activity of various acids for transesterification of soybean oil.

Homogeneous acid-catalyzed transesterification is more suitable for waste or unrefined oil which contain more free fatty acids that cause some trouble for basic-catalyzed transesterification. High amounts of free fatty acids (FFA) result in extensive soap formation as shown in the Figure 2.4(a), which is a common occurrence when sodium hydroxide (NaOH) or potassium hydroxide (KOH) are used as the basic catalysts. This side reaction consumes some of the catalyst and results in lower biodiesel yield. Soap renders biodiesel purification and catalyst removal even more challenging due to the formation of a stable emulsion generating a significant amount of waste water. In fact, studies have indicated that the amount of free fatty acids (FFA) in the feedstock for biodiesel production should not be higher than 0.5% in order to reach the ASTM biodiesel standard. The acid catalyzed-process has not gained as much attention as the base-catalyzed transesterification because of the slower reaction rate and the very high methanol to oil molar ratio requirements. The two-step biodiesel process address this issue by using an acid catalyst followed by a normal base-catalyzed transesterification. The first step involve the esterification reaction between the methanol and free fatty acids (FFA) to produce the corresponding fatty acid methyl ester (FAME) and reduce the amount of free fatty

acid in the reaction mixture. Finally, the basic catalyst is used to achieve higher yield with shorter reaction time (Marchetti *et al.*, 2007).

2.5.3 Heterogeneous Base-catalyzed Transesterification

Currently, research and development are focused on attempting the development and use of heterogeneous catalysts to replace homogeneous catalysts. Ngamcharussrivichai, Totarat, and Bunyakiat (2008) have used a mixture of calcium and zinc oxide (CaO and ZnO) as heterogeneous catalysts for the transesterification of palm kernel oil with methanol. They found that a mixture ratio 1:4 of CaO and ZnO catalyst can render more than 94% yield of methyl ester at a reaction temperature of 60°C, 1 hour of reaction time, and methanol-to-oil molar ratio equal to 30. The catalyst concentration used in this experiment was 10% by weight of the oil used. In addition, this catalyst can be regenerated by washing with a mixture of methanol and ammonium hydroxide (NH₄OH). The experimental results demonstrated that the recycled catalyst renders a methyl ester yield higher than 90% up to 3 recycle times. Further research is being conducted using different mixtures of these types of metal oxide catalysts for the transesterification of different vegetable oil, as well as research and development of catalyst regenerating methods.

In 2007, Xuejun Liu and his coworkers presented the results for using SrO as a solid base catalyst and proposed the reaction mechanism of this catalyst as shown in the Figure 2.5. 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 minutes of reaction time. The SrO catalyst maintained sustained activity even after being used for 10 cycles. It 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. The mechanism of the reaction is as follows. In the first step shown in Figure 2.5(a), surface O²⁻ extracts H⁺ from CH₃OH to form surface CH₃O⁻ which is strongly basic and has high catalytic activity in the transesterification reaction. In the second step shown in Figure 2.5(b), the carbonyl carbon atom of the triglyceride molecule attracts a methoxide anion from the surface of the SrO to form a tetrahedral

intermediate, where R1 represents the long chain alkyl group. In the third step shown in Figure 2.5(c), the tetrahedral intermediate picks up H⁺ from the surface of the SrO. The tetrahedral intermediate also can react with methanol to generate methoxide anions as shown in Figure 2.5(d). In the last step shown in Figure 2.5(e), rearrangement of the tetrahedral intermediate results in the formation of methyl ester.

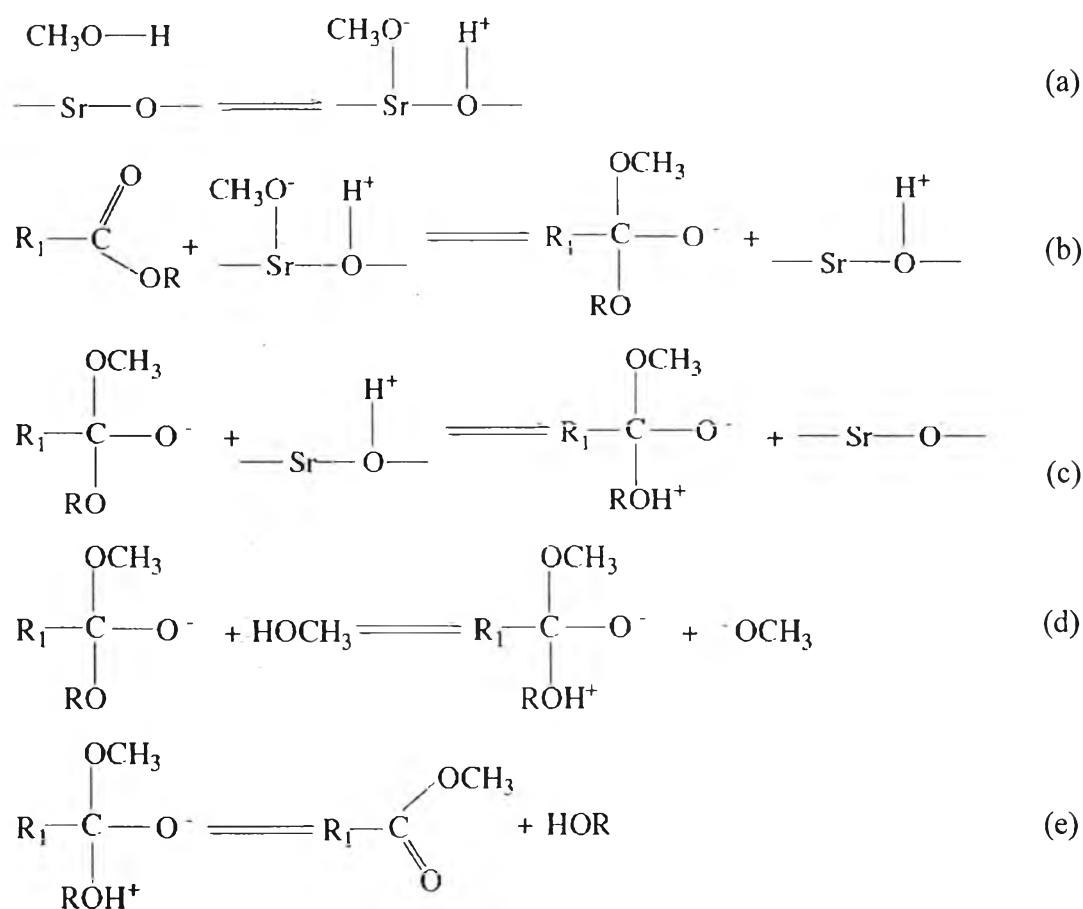


Figure 2.5 Transesterification mechanism of triglycerides and methanol by using SrO as a catalyst (Liu *et al.*, 2007).

In addition, a series of alkali-doped metal oxide catalysts such as lithium nitrate loaded on calcium oxide (LiNO₃/CaO), sodium nitrate loaded on calcium oxide (NaNO₃/CaO), potassium nitrate loaded on calcium oxide (KNO₃/CaO), and lithium nitrate loaded on magnesium oxide (LiNO₃/MgO) have been evaluated by Macleod *et al.*, (2008). The researchers indicated that these catalysts could reach more

than 90% yield in 3 hours reaction time and found that the best catalyst is “LiNO₃/MgO”. The reusability of these catalysts could last long up to 5 runs. However, some degree of catalyst leaching was observed and this caused homogeneous catalytic activity which could improve the yield but reduce the lifetime of the catalyst.

2.5.4 Heterogeneous Acid-catalyzed Transesterification

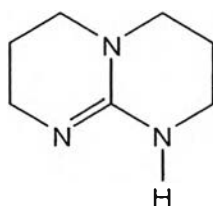
The effect of the catalytic properties on the esterification of FFA to FAME was examined using WO₃/ZrO₂ catalysts in a batch reactor by Park *et al.*, (2008). The free fatty acid conversion was compared with those of the SO₄²⁻ / ZrO₂ and Amberlyst-15 catalysts under optimized reaction conditions. All catalysts showed approximately 93% FFA conversion. However, SO₄²⁻ / ZrO₂ and Amberlyst-15 exhibited some structural problems. The main concern with the SO₄²⁻ / ZrO₂ catalyst was the potential loss of SO₄²⁻. On the other hand, the structure of the Amberlyst-15 catalyst might be decomposed at reaction temperatures over 180°C. Increasing the WO₃ loading favored the crystallization of triclinic phase WO₃ and generation of the tetragonal phase of zirconia. Among the WO₃/ZrO₂ catalysts with WO₃ loading amount from 10 to 30 wt%, 20 wt% WO₃/ZrO₂ showed the highest catalytic activity. And TPD analysis indicated that the 20 wt% WO₃/ZrO₂ catalyst had higher acidity than the other samples, as evidenced by the existence of a high temperature desorption peak at 750°C. Therefore, it can be concluded that the strong acidity of the catalyst is thought to be one of the reasons for the highest catalytic activity of the 20 wt% WO₃/ZrO₂ catalyst.

The drawbacks for this kind of catalyst are longer reaction times or higher reaction temperatures. These conditions will lead to higher biodiesel production cost.

2.5.5 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 *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 *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 Me₇P.

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 hour 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 *et al.*, 1995).

2.6 Natural Materials as Catalysts for Transesterification

Boey *et al.*, (2009) used crab shell from crab aquaculture as a source of calcium oxide to transesterify palm olein into methyl esters (biodiesel). Characterization results revealed that the main component of the shell is calcium carbonate which is transformed into calcium oxide when activated above 700°C for 2 hours. The optimal conditions for this catalyst were found to be methanol/oil mass ratio, 0.5:1; catalyst amount, 5 wt%; reaction temperature, 65°C; and a stirring rate of 500 rpm. The waste catalyst performs equally well as synthetic CaO, thus creating another low-cost catalyst source for biodiesel production. Reusability results confirmed that the prepared catalyst is able to be used up to 11 times.

In addition, the possibility to use eggshell, golden apple snail shell, and meretrix venus shell as sources for calcium oxide was investigated by Viriyempikul *et al.*, (2010). They found that the CaO catalysts derived from eggshell, golden apple snail shell, and meretrix venus shell were elucidated to become active in heterogeneous transesterification for biodiesel production. The descending order of the catalytic activity over the shell-derived catalysts was as follows: eggshell > golden apple snail shell > meretrix venus shell. After simple calcination at 800 °C, all shell-derived catalysts mainly consisted of CaO phase with high crystallinity as confirmed by XRD. Among three raw materials, the catalyst synthesized from eggshell showed the highest Ca content and highest surface area with smallest particle size, which could be the reasons of highest biodiesel yield.

In recent years, the food industry generates huge amounts of egg shell and animal shell waste. Lea (1990) found that egg shell consists of several mutually growing layers of CaCO_3 , the innermost layer-maxillary layer ($\approx 100 \mu\text{m}$) grows on the outermost egg membrane and creates the base on which palisade layer constitutes the thickest part ($\approx 200 \mu\text{m}$) of the eggshell. The top layer is a vertical layer ($\approx 5.8 \mu\text{m}$) 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 have base properties, they 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 of interest to study these combinations.

2.7 Determination of Biodiesel Yield by $^1\text{H-NMR}$ Spectroscopy

The first report on the use of $^1\text{H-NMR}$ spectroscopy to monitor the progress and yield of the transesterification reaction was presented by Gelbard *et al.*, (1995). These authors used the protons of the methylene group adjacent to the ester moiety in triglycerides, which appears at 2.3 ppm and the protons in the alcohol moiety of the product methyl esters, which appear at 3.7 ppm to monitor the reaction yield. A simple equation given by the authors is as follows.

$$C = 100 \times \left(\frac{2A_{ME}}{3A_{\alpha-CH_2}} \right) \quad (1)$$

Where C is the percentage conversion of triglycerides to the corresponding methyl ester, A_{ME} is the integration value of the protons of methyl esters (the strong singlet), and $A_{\alpha-CH_2}$ is the integration value of the methylene protons. The factors 2 and 3 are derived from the fact that the methylene carbon possesses two protons and the alcohol (methanol-derived) carbon has three attached protons, and in equation 1, the

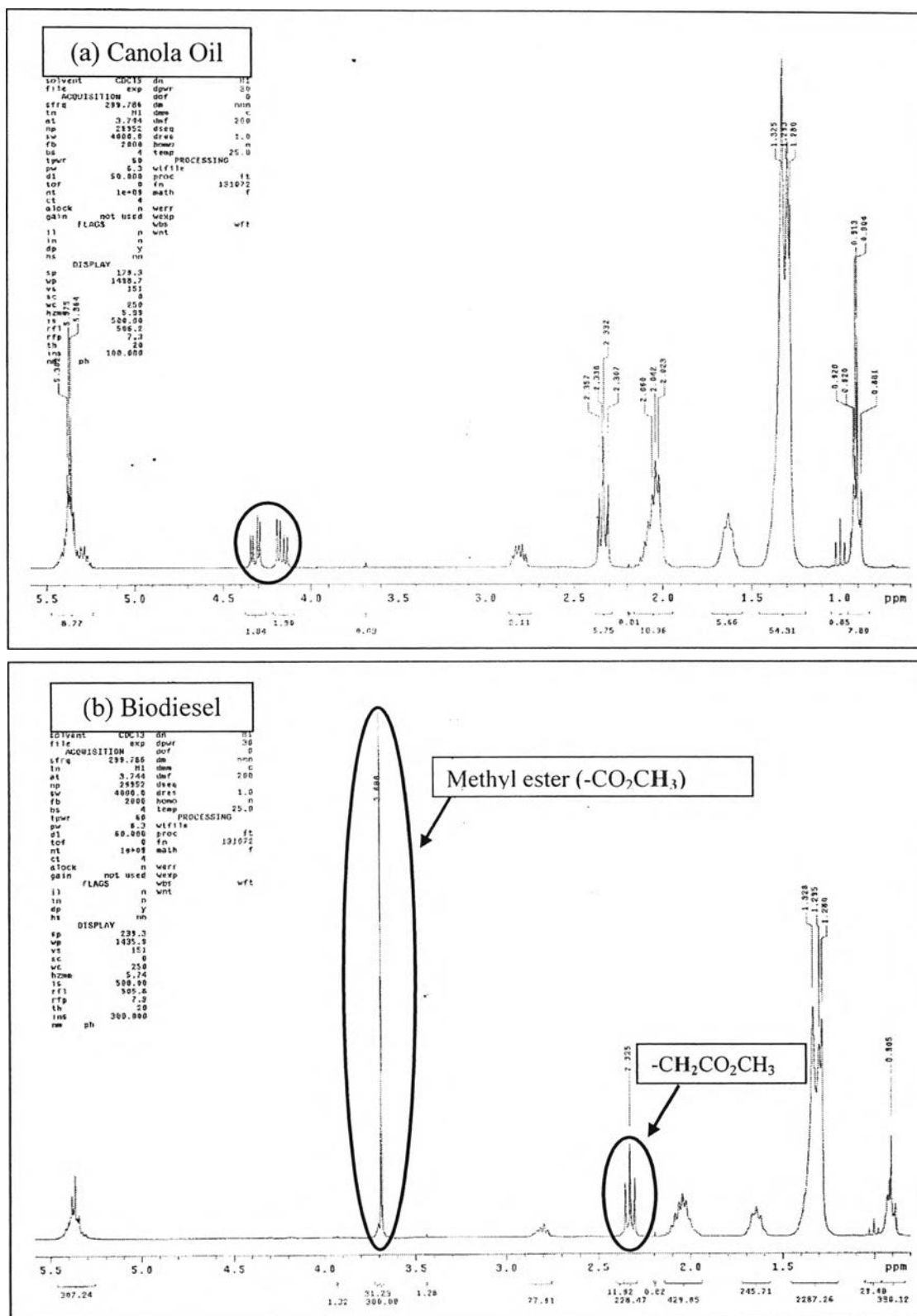


Figure 2.8 $^1\text{H-NMR}$ spectrum of a progressing transesterification reaction for (a) canola oil and (b) biodiesel.

The overall objective of this research is the development of formulations of heterogeneous catalysts for the efficient transesterification of vegetable oils and methanol at mild reaction conditions. Consequently, the optimum reaction conditions for the most efficient catalyst formulations were determined. The progress of the reaction was monitored by $^1\text{H-NMR}$ spectroscopy. The catalytic efficiency was examined based on the conversion of canola oil to methyl esters. This evaluation was conducted at laboratory bench scale. The ultimate goal of this research was to identify and develop formulations of heterogeneous catalysts that demonstrate high catalytic activity under mild reaction conditions feasible for commercial applications.