CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Properties of Zinc Oxide

ZnO is a II-VI compound semiconductor of which the ionicity resides at the borderline between covalent and ionic semiconductor. ZnO appears in three types of crystal structure, i.e. wurtzite, zinc blende, and rocksalt, as schematically shown in Figure 2.1. In ambient conditions, the thermodynamically stable phase is wurtzite. The zinc-blende structure can be formed only by the growth of ZnO on cubic substrate. The rocksalt structure may be obtained at relatively high pressure.
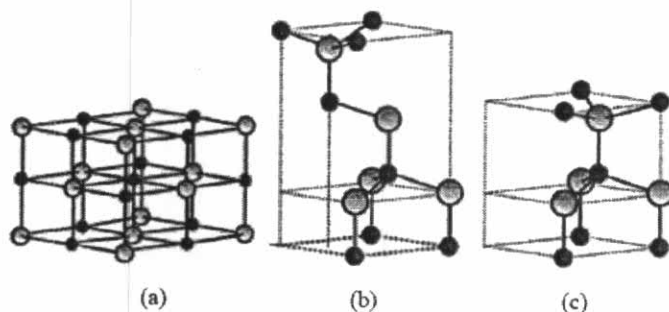

(a)   (b)   (c)

Figure 2.1 Stick and ball representation of ZnO crystal structures: (a) cubic rocksalt, (b) cubic zinc blende, and (c) hexagonal wurtzite. The shaded gray and black spheres denote Zn and O atoms, respectively.

ZnO is an n-type semiconductor with a band gap of 3.37 eV and the free exciton energy of 60 meV, which gives it very high potential for room temperature light emission. This also gives ZnO strong resistance to high temperature electronic degradation during operation. Therefore, it is attractive for many optoelectronic applications in the range of blue and violet light as well as UV devices for wide range of technological applications. ZnO also exhibits dual semiconducting and piezoelectric properties. The other properties of ZnO are given in Table 2.1.

Table 2.1 Properties of wurtzite ZnO

Property	Value
Lattice parameters at 300 K	
a	0.32495 nm
c	0.52069 nm
a/c	1.602 (ideal hexagonal structure is 1.633)
Density	5.606 g/cm^3
Melting point	1975 ^{o}C
Thermal conductivity	130 W/m.K
Linear expansion coefficient (/ ^{o}C)	a: 6.5 x 10-6
	c: 3.0 x 10-6
Static dielectric constant	8.656

2.2 Solvothermal Technique

Solvothermal method has been developed to synthesize metal oxide and binary metal oxide via the decomposition of metal-alkoxide precursor in organic solvent. It is principally similar to hydrothermal method which employs water as the reaction medium. The use of solvent instead of water produces different form of intermediates, of which the stability is not so strong. Instability of the intermediate gives large driving force for the formation of product. Therefore, the synthesis can be accomplished at a relatively low temperature and pressure in a closed system, which can be easily controlled. Moreover, it has been applied to successfully synthesize nanocrystalline zinc oxide with high crystallinity in one step.

Kunjara et al. [11] synthesized ZnO with various aspect ratios using various types organic solvent (alcohols, glycols, n-alkanes and aromatics) at 250-300°C for 2 hours. All products were ZnO in the hexagonal wurtzite structure. The aspect ratio of ZnO primary particles depended upon the solvent employed, such that the aspect ratio increased when the solvent employed had low dielectric constant. The products synthesized in glycols consisted of polyhedral crystals with the lowest aspect ratio, whereas those synthesized in alcohols had moderate aspect ratio and the products

obtained using n-alkane or aromatic compounds as solvent were ZnO nanorods with extremely high aspect ratio.

Tonto et al. [12] prepared ZnO nanorods by solvothermal reaction of zinc acetate in various alcohols and aromatic compounds, e.g.1-butanol, 1-hexanol, 1-octanol, 1-decanol, benzene, toluene and xylene, at 250-300°C for 2 hours. All products were ZnO having the hexagonal wurtzite structure. No impurity or secondary phase was observed. The product from the synthesis in alcohol was ZnO nanorods and the length of the rods increased and diameter of the rods decreased when alcohol with longer molecule was employed. It was found that both average diameter and length of ZnO nanorods increased with an increase in either initial concentration of precursor or reaction temperature. The linear relationship between boiling points of organic solvent and aspect ratios of ZnO particles was also reported.

2.3 Biodiesel

Biodiesel is an alternative fuel for diesel engines. It is comprised of mono-alkyl esters of long chain fatty acids. Biodiesel is one of the renewable fuels currently available, which is also non-toxic and biodegradable. Biodiesel can be used as B100 (neat) or blended with petroleum diesel. A blend of 5% biodiesel with 95% petrodiesel, by volume, is termed "B5". The well-known advantages of biodiesel, comparing to petro-diesel, are: (1) lower dependence on foreign crude oil, (2) renewable resource, (3) limitted on greenhouse gas emissions because of the closed CO_2 cycle, (4) lower combustion emission profile (especially SOx) , (5) potential improvement of rural economics, (6) biodegradability, (7) can be used without engine modifications, (8) good engine performance, (9) improved combustion because of its oxygen content, (10) low toxicity, and (11) ability to be blended in any proportion with regular petroleum-based diesel fuel [13].

Biodiesel is produced by chemical reaction between fat or oil with alcohol. The product of the reaction is a mixture of methyl esters and this process is called transesterification. Transesterification is extremely important for biodiesel production. Biodiesel, as it is defined today, is obtained by transesterification of triglycerides with methanol, since the base-catalyzed formation of methyl ester is relatively easy,

comparing to that of ethyl esters. Moreover, the formation of stable emulsion during ethanolysis is also a problem. Methanol and ethanol are not miscible with triglycerides at ambient temperature, and the reaction mixtures are usually mechanically stirred to enhance mass transfer. During the course of the reaction, emulsions are usually formed. In the case of methanolysis, these emulsions quickly and easily break down to form immiscible glycerol-rich layer and upper methyl ester-rich layer. On the other hand, for ethanolysis, emulsions are more stable and severely complicate the separation and purification of esters [14]. Nevertheless, for the reaction to occur within a reasonable time, a catalyst must be added to the mixture of the vegetable oil and methanol.

Ester is a group of organic compounds with general formula RCO2R' (where R and R' are alkyl groups or aryl groups) that are formed by the reaction between an alcohol and an acid. For example, when ethanol and acetic acid react, ethyl acetate (an ester) and water are formed. The reaction is called esterification. Ethyl acetate is used as a solvent. Methyl acetate, formed by the reaction between methanol and acetic acid, is a sweet-smelling liquid used in perfumes extracts, and lacquers. Esters react with water (i.e. hydrolysis) under basic conditions to form an alcohol and an acid. When heated with a hydroxide, certain esters decompose to yield soap and glycerol. This process is called saponification. Common fats and oils are mixtures of various esters, such as stearin, palmitin, and linolein, formed from glycerol, which is an alcohol, and fatty acids. Naturally occurring esters of organic acids in fruits and flowers give them their distinctive odors.

Glycerol, glycerine, or 1,2,3-propantriol propantriol, $CH_2OHCHOHCH_2OH$, which is colorless, odorless, sweet-tasting, syrupy liquid, is a trihydric alcohol. It melts at $17.8^{\circ}C$; boils with decomposition at $290\ ^{\circ}C$; and is miscible with water and ethanol. It is hygroscopic (i.e. it absorbs moisture form the air), which makes it valuable as a moistener in cosmetics. It is obtained commercially as a byproduct when fats and oils are hydrolyzed to yield fatty acids or their metals salts (soaps). It is also synthesized on a commercial scale from propylene (obtained by cracking petroleum). It can also be obtained during the fermentation of sugars if sodium bisulfite is added together with yeast. Glycerol is widely used as a solvent; used as a sweetener; used in the manufacture of dynamite, cosmetics, liquid soaps, candy, liqueurs, inks, and

lubricants; used to keep fabrics pliable; used as a component of antifreeze mixtures; used as a source of nutrients for fermentation cultures in the production of antibiotics; and in medicine. Besides the aforementioned applications, it also has many other uses.

Fatty Acid is the organic carboxylic acids present in fats and oils. Molecular weights of fatty acids vary over a wide range. The carbon skeleton of any fatty acid is unbranched. Some fatty acids are saturated, i.e., each carbon atom is connected to its carbon atom neighbors by single bonds, while some fatty acids are unsaturated, i.e. they contain at least one carbon-carbon double bond. When fats and oils are hydrolyzed with an alkali, the fatty acids are liberated as their metal salts, which are called soaps.

Vegetable oils are esters of glycerol called glycerides or acylglycerols. Mono-, di-, triglycerides are possible configurations since glycerol has three hydroxyl groups. Generally, vegetable oils are triglycerides (or triacylglycerols), and are generally formed as follows.
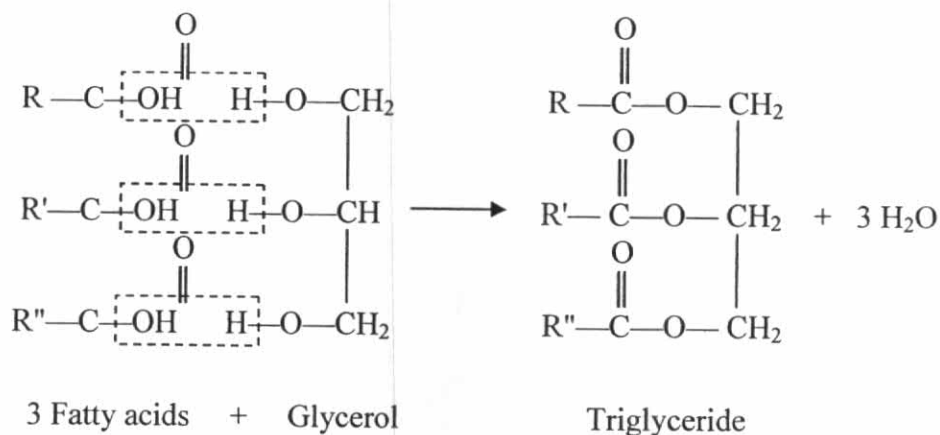

Figure 2.2 Formation of triglyceride [15]

Table 2.2 Common fatty acids in nature [16]

Acids	Common Name	Structure
C_{12}	Lauric	$CH_3(CH_2)_{10}COOH$
C_{14}	Myristic	$CH_3(CH_2)_{12}COOH$
C_{16}	Palmitic	$CH_3(CH_2)_{14}COOH$
	Palmitoleic	$CH_3(CH_2)_5CH=CH-CH_2(CH_2)_6COOH$
C_{18}	Stearic	$CH_3(CH_2)_{16}COOH$
	Oleic	$CH_3(CH_2)_7CH=CH-CH_2(CH_2)_6COOH$
	Linoleic	$CH_3(CH_2)_4(CH=CH-CH_2)_2(CH_2)_6COOH$
	Linolenic	$CH_3CH_2(CH=CH-CH_2)_2(CH_2)_6COOH$
	Ricinoleic	$CH_3(CH_2)_5CH(OH)CH_2CH=CH(CH_2)_7COOH$

In a simple triglyceride such as palmitin or stearin, all three fatty-acid groups are identical. In a mixed triglyceride, two or even three different fatty-acid group are present. Most fats and oils contain mixed triglyceride.

2.3.1 Properties of Triglycerides as Fuels

A large number of research has gone into examining Diesel's dream of using raw vegetable oils as fuels. When one speaks of growing crops for liquid fuels, it is often assumed that the oil will be used after only basic extraction and filtering. Experience has shown that the use of unsaturated triglyceride oils as a fuel may cause significant problems that can affect the viability of their fuel use. The main problem encountered has due to high viscosity of the triglyceride oils and their chemical instability. These can cause difficult starting in cold condition, the gumming of injectors and the coking-up of valves and exhaust. However, this is not always the case and in many circumstance these problems can either be dealt with or are acceptable to the user.

In the last years, great attention has been paid on the use of straight or modified vegetable oils as fuel in diesel engines, in developed countries mainly to reduce the enormous of subsidies spent for agricultural over-production, while in underdeveloped countries to become less dependent on fossil oil imports. In Europe, the route of transforming vegetable oils into fatty acid methyl esters is intensively

followed. Austria is one of the leading countries in that field, which can be demonstrated by the existence of two industrial plants and several decentralized plants for the production of rape seed oil methyl esters (RME) with a total capacity of about 30,000 tons per year. As vegetable oils are still not economically competitive with mineral based products, the use of old cooking oils as starting materials seems very attractive.

2.3.2 Direct Use and Blending of Vegetable Oils as Fuels

Direct use of vegetable oils and/or the use of blends of the oils have generally been considered to be not satisfactory and impractical for both direct and indirect engines. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems and the potential solutions are shown in Table 2.3.

Table 2.3 Known problems, probable causes and potential solutions for using straight vegetable oil in diesels [17]

Problem	Probable cause	Potential solution
Short-term		
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 filters, lines and in injectors	Natural gums (phosphatides) in vegetable oil. Other 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. Use higher compression engines. Preheat prior to injection. Chemically alter fuel to an ester

Table2.3 (Continued)

Problem	Probable cause	Potential solution
Long-term		
4. Coking of injectors on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils.	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester.
5. Carbon deposits on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils.	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester.
6. Excessive engine wear	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part loads with vegetable oils. 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 fuel when operation at part loads. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation
7. Failure of engine lubricant	Collection of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation

2.4 Transesterification Reaction

Transesterification or alcoholysis is the displacement of alkyl group in an ester by another alkyl group from alcohol, in a process similar to hydrolysis, except than alcohol is used instead of water. This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by the general equation shown in Figure 2.2. If methanol is used in this process, it is called methanolysis. Methanolysis of triglyceride is represented in Figure 2.3. Transesterification is reversible and the presence of a catalyst (a strong acid or base) accelerates the conversion.
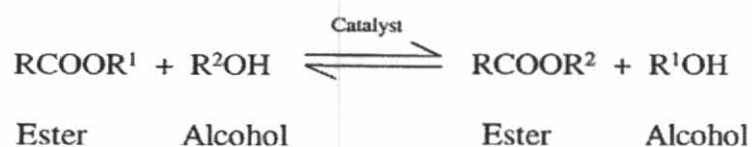
$$RCOOR^1 + R^2OH \xrightleftharpoons{Catalyst} RCOOR^2 + R^1OH$$

Ester   Alcohol   Ester   Alcohol

Figure 2.3 General equation of transesterification.

$$
\begin{array}{l}
CH_2-OCOR^1 \\
| \\
CH-OCOR^2 \\
| \\
CH_2-OCOR^3
\end{array}
+ 3CH_3OH \xrightleftharpoons{Catalyst}
\begin{array}{l}
CH_2OH \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
+
\begin{array}{l}
R^1COOCH_3 \\
R^2COOCH_3 \\
R^3COOCH_3
\end{array}
$$

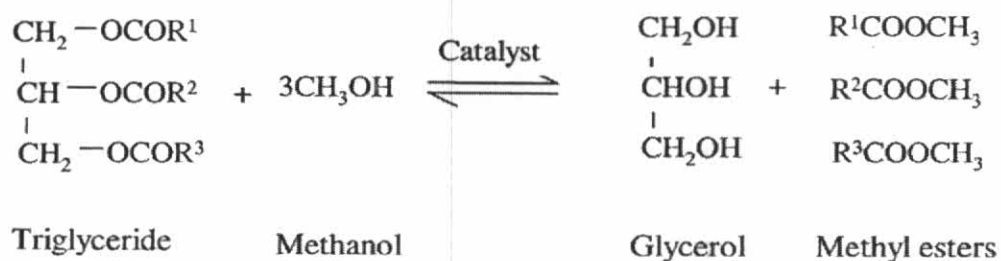Triglyceride   Methanol   Glycerol   Methyl esters

Figure 2.4 General equation of transesterification of triglycerides.

2.4.1 Transesterification Kinetics and Mechanism

Transesterification of triglycerides produces fatty acid alkyl esters and glycerol. Diglycerides and monoglycerides are the intermediates in this process. The mechanism of transesterification is described in Figure 2.4.
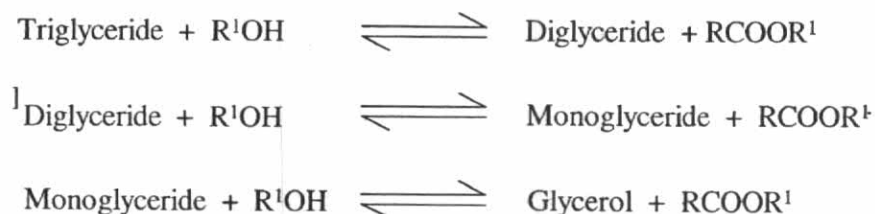
$$Triglyceride + R^1OH \rightleftharpoons Diglyceride + RCOOR^1$$

$$Diglyceride + R^1OH \rightleftharpoons Monoglyceride + RCOOR^1$$

$$Monoglyceride + R^1OH \rightleftharpoons Glycerol + RCOOR^1$$

Figure 2.5 General equation of transesterification of triglycerides.

The step-wise reactions are reversible and slight excess of alcohol is used to shift the equilibrium toward the formation of esters. In the presence of excess alcohol, the forward reaction is pseudo-first order and the reverse reaction is found to be second order. It has also been observed that transesterification is faster when it is catalyzed by alkali. The mechanism of alkali-catalyzed transesterification is described in Figure 2.5. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule, which results in the formation of a tetrahedral intermediate. The reaction of this intermediate with alcohol produces alkoxide ion in the second step. In the last step, the rearrangement of the tetrahedral intermediate gives rise to an ester and a diglyceride [18].
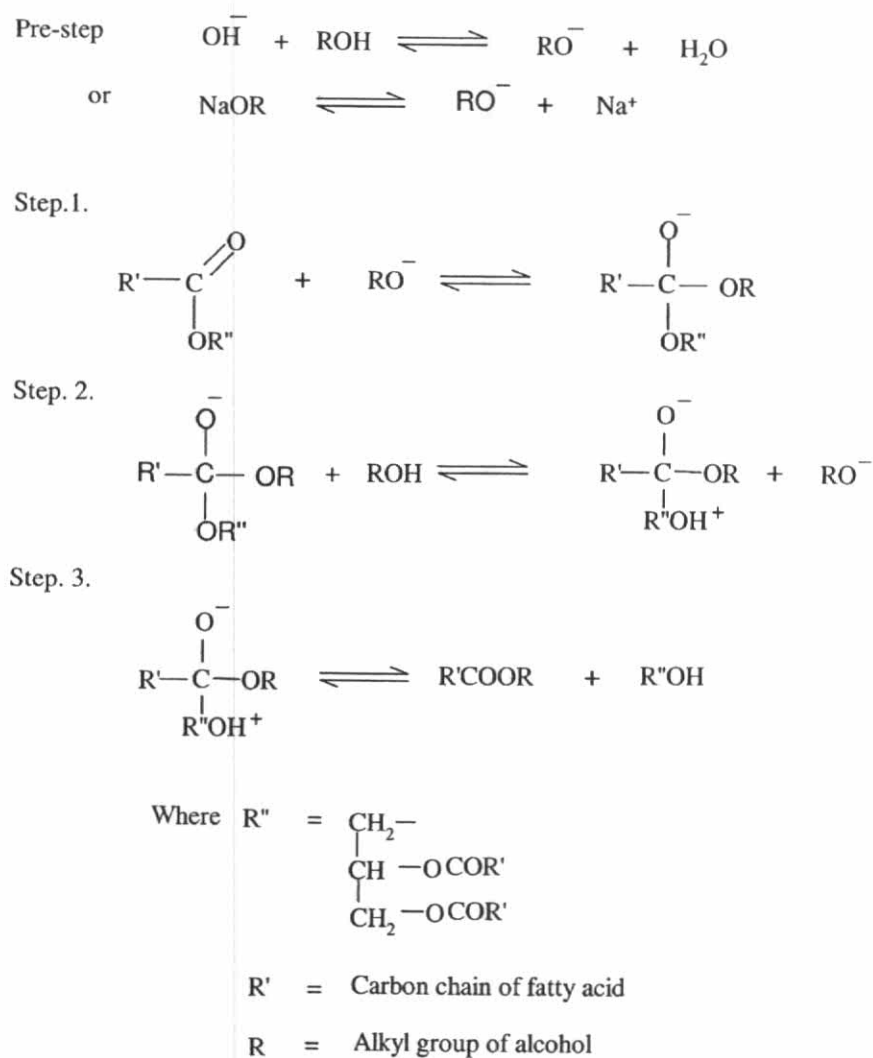
Pre-step $\overline{OH}$ + ROH $\rightleftharpoons$ RO^- + H_2O

   or   NaOR $\rightleftharpoons$ RO^- + Na^+

Step.1.

$$R'-\overset{\displaystyle \overset{O}{\parallel}}{\underset{\displaystyle \underset{OR''}{|}}{C}} \quad + \quad RO^- \quad \rightleftharpoons \quad R'-\overset{\displaystyle \overset{O^-}{|}}{\underset{\displaystyle \underset{OR''}{|}}{C}}-OR$$

Step. 2.

$$R'-\overset{\displaystyle \overset{\overline{O}}{|}}{\underset{\displaystyle \underset{OR''}{|}}{C}}-OR \; + \; ROH \rightleftharpoons \quad R'-\overset{\displaystyle \overset{O^-}{|}}{\underset{\displaystyle \underset{R''OH^+}{|}}{C}}-OR \; + \; RO^-$$

Step. 3.

$$R'-\overset{\displaystyle \overset{O^-}{|}}{\underset{\displaystyle \underset{R''OH^+}{|}}{C}}-OR \quad \rightleftharpoons \quad R'COOR \quad + \quad R''OH$$

Where R" = $\overset{\displaystyle CH_2-}{\underset{\displaystyle \underset{CH_2-OCOR'}{\overset{|}{CH}-OCOR'}}{|}}$

R' = Carbon chain of fatty acid

R = Alkyl group of alcohol

Figure 2.6 General equation for transesterification of triglycerides: mechanism of base catalyzed transesterification.

Transesterification can be catalyzed by Brownsted acids, preferably by sulfonic or sulfuric acids. These catalysts give very high yields in alkyl esters but the reactions are slow, requiring typical temperature above 100 °C and more than 3 h to complete the conversion. The mechanism of acid catalyzed transesterification of vegetable oil (for a monoglyceride) is shown in Figure 2.6. However, it can be extended to di-and tri-glycerides. The protonation of carbonyl group of the ester leads to the carbonation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst.
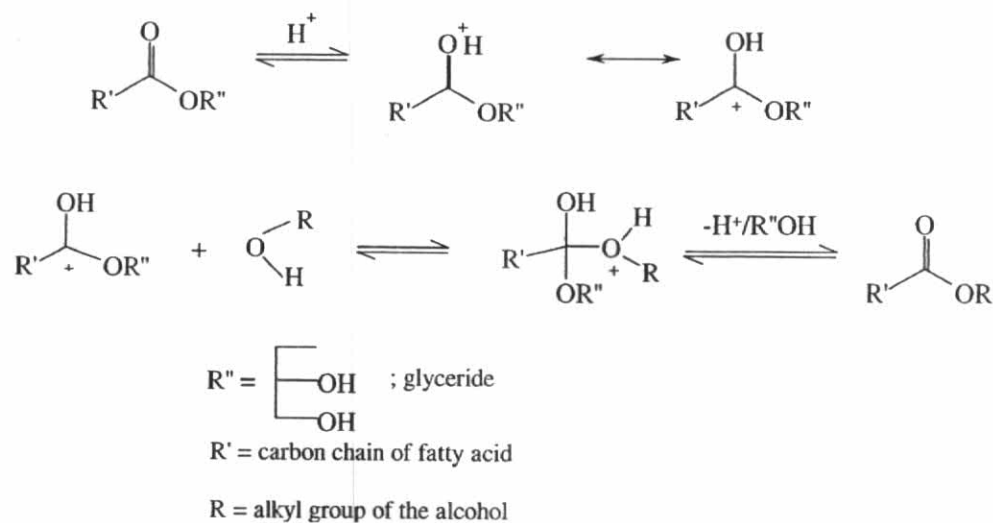
$$R'' = \begin{array}{c} \text{—OH} \\ \text{—OH} \end{array} \quad ; \text{glyceride}$$

R' = carbon chain of fatty acid

R = alkyl group of the alcohol

Figure 2.7 General equation for transesterification of triglycerides: mechanism of acid catalyzed transesterification.

2.4.2 Transesterification using Heterogeneous Catalysts

Several attempts have been done using heterogeneous catalysts on the transesterification of vegetable oils. Peterson et al. [19] led the first study. They discovered that the CaO/MgO catalyst has activity comparable to sodium methoxide-catalyzed transesterification with 95% methyl ester yield. However, the catalyst produces substantial amount of saponified products thereby rendering the effectiveness of this heterogeneous catalyst.

Gryglewicz [20] found out that the basic alkaline earth metal compounds could effectively catalyze the transesterification of rapeseed oil. Though the results were not the same as sodium hydroxide, the activity increased in the following order: $CaO < Ca(CH_3O)_2 < Ba(OH)_2$. In spite of the high activity of $Ba(OH)_2$, it is much more soluble in methanol than the other alkaline earth metal compounds.

Leclercq et al. [21] investigated basic zeolites and solid catalysts in the transesterification of rapeseed oil. They found that magnesium oxide with a high surface area over 300 m^2/g is far more active than cesium-exchanged NaX faujasites and hydrotalcites. They also examined that calcination of barium hydroxide overnight

at 473 K under reduced pressure increases the activity with 96% methyl ester fraction, which is close to the conversion obtained using homogeneous catalysts.

Experiments conducted by Suppes et al. [22] indicated that $CaCO_3$ may be suitable as a heterogeneous catalyst. The alcoholysis were conducted in a batch reactor and flow-reactor studies using beef tallow or soybean oil as the triglyceride source and diethylene glycol as the alcohol. Reaction times of 18 min provided essentially complete conversion. Khan [23] attempted to verify these results but thay have failed to replicate those results. Their only difference was the source of the $CaCO_3$.

In addition, Zajdlewicz [24] reported that there were five commercially available catalysts that were active for transesterification of soybean oil. The most active of these catalysts was Valfor (alumina silicate) followed by ZSM5, Beta zeolite, MCM-41, and then zeolite Y. This information needs further verification since his results were just only based on the peak height obtained from gas chromatography. Khan [23] tried to use Valfor as a heterogeneous catalyst and he confirmed that it has still not considered as a possible candidate.

Most patents dealing with the heterogeneous transesterification of vegetable oils are carried out in temperature between 200 and 250 °C and a pressure that is less than 60 bars. Gheorghiu [25] patented a process for the preparation of methyl fatty acid esters from natural oil in the presence of an organotitanate base catalyst specifically tetrabutyl organotitanate. Stern et al. [26] obtained their patent of making esters in the presence of a catalyst that is selected from zinc oxide, mixture of zinc oxide and aluminum oxide and zinc aluminate. Recently, Kaita et al. [27] received their patent on their catalyst for transesterification that is a phosphate of a metal selected from the group consisting of aluminum, gallium and iron.

Sanjib et al. [28] prepared biodiesel from non-edible oil of Pongamia pinnata by transesterification with methanol in the presence of KOH as catalyst. A maximum conversion of 92% (oil to ester) was achieved using 1:10 molar ratio of oil-to-methanol at 60 °C. Tetrahydrofuran (THF), used as a co-solvent, increased the

conversion to 95%. Solid acid catalysts viz. Hb-Zeolite, Montmorillonite K-10 and ZnO were also used for this transesterification.

Wenlei et al. [7] studied a process for the transesterification of soybean oil to methyl esters using alumina loaded with potassium as a solid base catalyst in a heterogeneous manner. The 35 wt% of KNO_3 loaded on Al_2O_3, after being calcined at 773 K for 5 h, was found to be the optimum catalyst, which gave the highest basicity and the best catalytic activity for this reaction. The effects of various reaction variables such as the catalyst loading, oil-to-methanol ratio, reaction time and temperature on the conversion of soybean oil were investigated. The results indicated that K_2O derived from the calcinations of KNO_3 at high temperature and the Al–O–K groups were, probably, the main reasons for the catalytic activity towards the reaction. The catalyst activity was correlated closely with its basicity as determined by Hammett method.

Wenlei et al. [8] synthesized NaX zeolites loaded with KOH as a solid base catalyst for the transesterification of soybean oil with methanol. The best result was obtained with NaX zeolite loaded with 10% KOH, followed by heating at 393 K for 3 h. When the transesterification reaction was carried out at reflux of methanol (338 K), with a 10:1 molar ratio of methanol-to-soybean oil, a reaction time of 8 h and a catalyst amount of 3 wt. %, the conversion of soybean oil was 85.6%.

Wenlei et al. [9] studied a heterogeneous transesterification of soybean oil with methanol, using alumina loaded with potassium iodide as a solid base catalyst. After loading of 35 wt. %KI on alumina followed by calcination at 773K for 3 h, the catalyst gave the highest basicity and the best catalytic activity for this reaction. Moreover, the dependence of the conversion of soybean oil on the reaction variables such as the catalyst loading, the molar ratio of methanol-to-oil and the reaction time was studied. The conversion of 96% was achieved under the optimum reaction conditions. Besides, a correlation of the catalyst activity for the transesterification reaction with its basicity was proposed.

Zhenqiang et al. [10] reported on the preliminary results of using alkaline earth metal-doped zinc oxide as a heterogeneous catalyst for transesterification of soybean oil. The highest catalytic activity was obtained with 1 g of ZnO loaded with 2.5 mmol $Sr(NO_3)_2$, followed by calcination at 873 K for 5 h. When the transesterification reaction was carried out at reflux of methanol (338 K), with a 12:1 molar ratio of methanol-to-soybean oil and a catalyst amount of 5 %wt., the conversion of soybean oil was 94.7%. Besides, tetrahydrofuran (THF), used as a co-solvent, could increase the conversion up to 96.8%. However, the recovered catalyst exhibited the lower catalytic activity with a conversion of soybean oil of 15.4%.

Xuejun et al. [29] used SrO as a solid base catalyst for the transesterification of soybean oil to biodiesel. The reaction mechanism was proposed and the separate effects of reaction temperature, molar ratio of methanol-to-oil, mass ratio of catalyst-to-oil and repeated experiments were investigated. The results showed that the yield of biodiesel produced with SrO as a catalyst was about 95% at temperatures below 70 ^{0}C within 30 min. SrO had a long catalyst lifetime and could maintain sustained activity even after being repeatedly used for 10 cycles.

2.5 Analysis of Methyl Esters

Biodiesel can be significantly contaminated with glycerol, mono-, di-, and triglycerides due to incomplete transesterification and insufficient purification. A sensitive and reliable analytical method is needed to monitor the purity of the methyl esters. Various chromatographic techniques such as GC, TLC and HPLC are now being employed.

Plank [30] applied capillary gas chromatography (GC) equipped with flame ionization detector (FID) in determining the glycerol, mono-, di- and triglycerides in methyl esters in a single run. However, this method is less convenient because derivatization such as transmethylsilylation before analysis is needed for the free hydroxyl groups in the mono-, di- and triglycerides. Furthermore, Holcapek et al. [31] mentioned that the derivatization step is unessential when high temperature (approximately 350°C) and a short capillary column with good temperature stability is employed.

Meanwhile Marquardt [32] improved the separation of saturated methyl esters ranging from C12 to C22 by utilizing the reversed-phase thin layer chromatography (TLC) which employs silver nitrate in a mobile phase containing acetonitrile/1, 4-dioxane/acetic acid. Freedman et al. [33], Karaosmanoglu et al. [34] and Diasakou et al. [35] also used TLC equipped with FID in the analysis of their ester product.

Furthermore, De Filippis et al. [36] had developed a simple and quick analytical method for the evaluation of methyl esters in the transesterification products. A correlation with viscosity is applied in a defined range of weight fractions. This correlation was tested on a wide range of samples with various methyl ester content and the results were in agreement with the values measured by GC analysis.