# CHAPTER II

THEORY AND LITERATURE REVIEWS

This chapter concern with the literature reviews of the transesterification of vegetable oils with alcohol. The literatures are divided into four sections. The properties of vegetable oils are in the first section. The second section describes the transesterification reaction of vegetable oils using homogeneous catalysts. Acid and alkaline-catalyzed in transesterification are described in this section. The third section describes the transesterification reaction of vegetable oils using heterogeneous catalysts and the last section describes the transesterification reaction of vegetable oils using heterogeneous modified with metal catalysts.

2.1 Vegetable oils

Vegetable oils used in this studied were palm olein oil and coconut oil. The basic component of vegetable oils is triglycerides. Vegetable oils comprise 90 to 98 % triglycerides and small amount of mono- and diglycerides. They also contain free fatty acids (generally 1 to 5 %) and trace amount of water. Triglycerides are esters which are produced from three fatty acids and one glycerol. Generally, triglycerides can be formed as follow.

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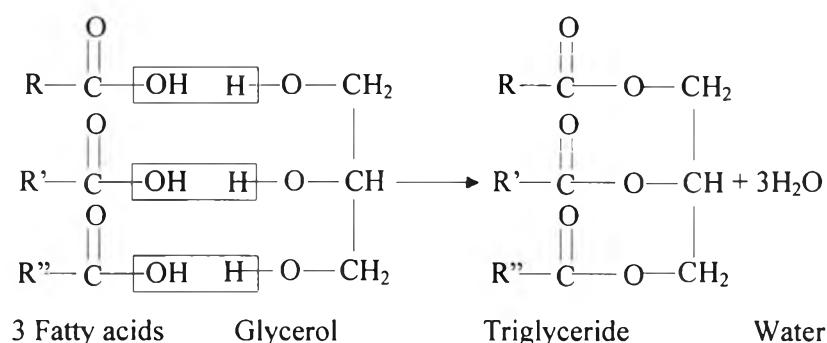
Figure 2.1 Formation of Triglyceride

Differences in vegetable oils result from differences in fatty acid which glycerol may be combined with Table 2.1 shows the names and structures of common fatty acids. Table 2.2 summarizes the fatty acids of some vegetable oils. The fatty acids which are commonly found in vegetable oils are stearic, palmitic, oleic, linoleic and linolenic.

Table 2.1 Chemical structure of common fatty acids (Srivastava et al. 2000)

Fatty acid	Systematic name	Structure[a]	Fomula
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Bcchenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$
Oleic	Cis-9- Octadecanoic	18:1	$C_{18}H_{34}O_2$
Linoleic	Cis-9,cis-12- Octadecanoic	18:2	$C_{18}H_{32}O_2$
Linolenic	Cis-9,cis-12,cis-15- Octadecanoic	18:3	$C_{18}H_{30}O_2$
Erucic	Cis-13- Docosenoic	21:1	$C_{22}H_{42}O_2$

[a]xx:y indicates x carbon in fatty acid chain with y double bonds.

2.1.1 Palm olein oil and coconut oil

Palm olein and coconut oil are the liquid fraction of palm oil and coconut oil, like all oils and fats, is made up mostly of glyceridic materials with some nonglyceridic materials in small or trace qualities. Triglycerides from the major component and bulk of the glyceridic material present in palm olein oil and coconut oil with small amounts of monoglycerides and diglycerides. The fatty acid chains present in the palm olein and coconut oil triglycerides could vary in the number of carbons present in the chain (chain length) and in structure (presence of double bonds, i.e., unsaturation). It is the variations in the structure and number of carbons in these fatty acid chains that largely define the chemical and physical properties of palm olein and coconut oil. The chain length of the fatty acids present in triglycerides of palm olein oil and coconut oil fall within a very narrow from 12 to 20 carbons as shown in Table 2.2.

Table 2.2 Chemical composition of vegetable oils (Srivastava et al. 2000)

Vegetable	Fatty acids composition, wt.%								
oil	8:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2	18:3
Palm	-	-	-	1.0	44.2	4.5	39.3	9.6	0.3
Jatropha	-	-	-	-	14.0	8.0	34.0	43.0	-
Coconut	8.30	5.80	48.70	18.00	8.60	2.60	6.50	-	-
Rapeseed	-	-	-	-	4.0	1.7	58.6	21.8	10.8
Soybean	-	-	-	-	10.3	3.8	24.3	52.7	7.9
Sunflower	-	-	-	-	6.7	3.7	19.0	69.9	0.7

2.1.2 The properties of palm olein oil and coconut oil

Free fatty acid value

Free fatty acid value is a measure of free fatty acid concentration, which indicates number of carbons in the chain and structure (presence of double bonds, i.e., unsaturation). Free fatty acids are present in vegetable oils and are removed in the refining process. Removing the free fatty acids is performed by conditioning the oil with sulfuric acid to optimise precipitation of gums solution is mixed with the conditioned oil which neutralises the acid as well as reacting with the free fatty acids in the oil and forming soap (Frank et al, 2001). The soap and precipitated materials agglomerate and are separated out from the neutralised oil. The quantity of free fatty acids is an important parameter in the refining process of vegetable oils. The refining process can be optimised by reducing the chemical costs in removing gums solution which provides improved product quality. Each of oils was refined that free fatty acid value was lower than 3% (Meher et al. 2006).

Acid value

Acid value or acid number is a measure of acid strength. It is defined as the milligrams of potassium hydroxide required for the neutralisation of the free carboxyl groups in one gram of the sample (Frank et al. 2001). The test procedure involves the dissolution of a sample of known weight in suitable solvent, usually neutralized 95% ethanol in the case of fatty acids and dimer acids, or neutralized mixture of toluene and isopropyl alcohol (1:1, v/v) if the sample contains other glyceridic components. The solution is the titrated against standardized aqueous 0.1 N potassium hydroxide or sodium hydroxide using 1% phenolphthalein as an indicator (EN 14104).
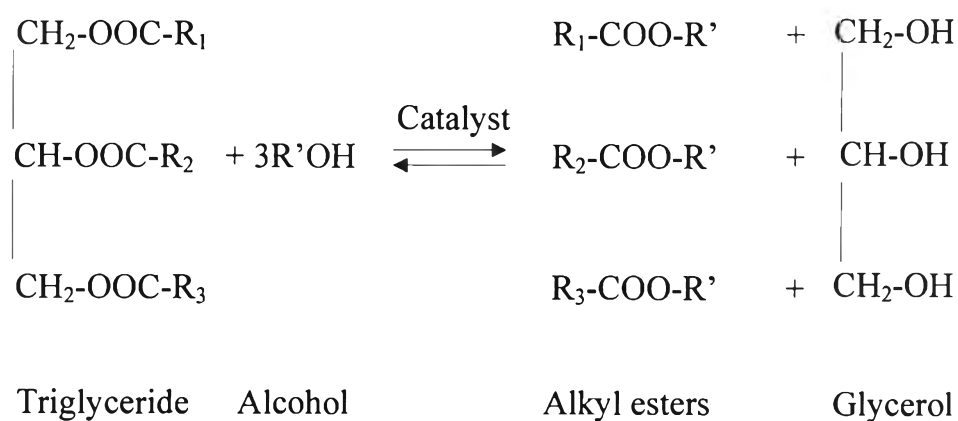
Saponification value

The saponification value (SV) or saponification number is a measure of alkali reactive groups in oleochemicals and their derivatives. It is expressed as the number of milligrams of potassium hydroxide needed to hydrolyse (saponify) one gram of the sample (Frank et al. 2001). The used of alcoholic potassium hydroxide at the reflux temperature, as specified in the analysis method, results in both the neutralization of the fatty acid and saponification of ester groups that might be present as other alkyl esters. It is determined by heating under flux a suitable weight of fatty material with a known volume of standard ethanolic potassium hydroxide and back titration of the excess hydroxide with standard mineral acid to the phenolphthalein end-point. The back titration should be carried out without any delay after the heating stage as the saponified solution can absorb carbon dioxide from the atmosphere and this will affect the titration result.

Iodine value

Iodine value is a measure of total unsaturation within a mixture of fatty, regardless of the relative shares of mono-, di-, tri- and poly unsaturated compounds. When formally adding iodine to the double bonds. Another idea behind the use of the iodine value is that it indicates the propensity of the oil or fat. It is expressed in grams of iodine which react with 100 g of the respective sample (Frank et al. 2001). Iodine number is limited to less than 120 g I_2/100 g of oil in the European standard, (EN 14111). The iodine value of a vegetable oil or animal fat is almost identical to that of the corresponding methyl esters.

2.2 Transesterification of vegetable oils

Transesterification can be used to reduce the viscosity of vegetable oils by reacting with alcohol using a catalyst. The general equation of transesterification is shown in Figure 2.2. Based on the stoichiometry of the transesterification reaction, it requires 3 moles of alcohol per one mole of triglyceride to yield 3 moles of fatty acid alkyl esters and 1 mole of glycerol. The first step is the conversion of triglyceride to diglyceride, following by the conversion of diglyceride to monoglyceride, and finally monoglyceride to methyl esters. The conventional catalysts for this reaction are homogeneous alkali catalysts or acid catalysts.

$$
\begin{array}{llll}
CH_2\text{-}OOC\text{-}R_1 & & R_1\text{-}COO\text{-}R' & + \quad CH_2\text{-}OH \\
& & & \\
| & & & | \\
CH\text{-}OOC\text{-}R_2 & +\,3R'OH \xrightarrow[\ ]{\text{Catalyst}} & R_2\text{-}COO\text{-}R' & + \quad CH\text{-}OH \\
| & & & | \\
CH_2\text{-}OOC\text{-}R_3 & & R_3\text{-}COO\text{-}R' & + \quad CH_2\text{-}OH
\end{array}
$$

Triglyceride   Alcohol   Alkyl esters   Glycerol

Figure 2.2 General equation of transesterification reaction (Mether, 2004)
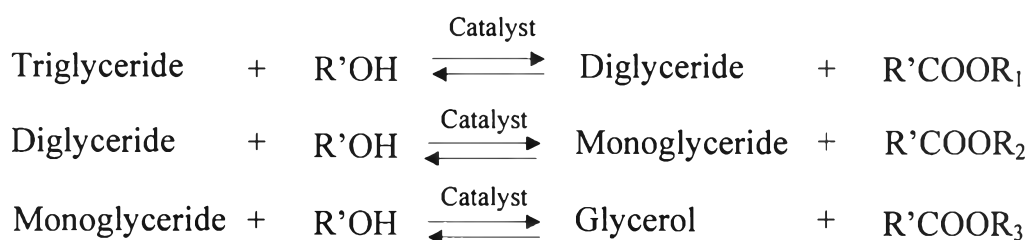
Catalysts for transesterification reaction

Transesterification can be catalyzed by many types of catalysts including:
1. Acidic catalysts
2. Basic catalysts
3. Solid catalysts (heterogeneous catalysts)

2.3 Transesterification of vegetable oils using homogeneous catalysts

Transesterification is the reaction of a triglyceride with an alcohol to form esters and a by-product, glycerol. It is in principle the action of one alcohol displacing another from an ester, the term alcoholysis (cleavage by an alcohol). The reaction, as shown in Figure 2.2 is reversible and thus an excess of alcohol is usually used to force the equilibrium to the product side (Mether et al. 2004). The stoichiometry for the reaction is 3:1 alcohol to triglycerides; however in practice this is usually increased to 6:1 to increase product yield. If methanol is used in this process, it is called methanolysis of triglycerides. The step reaction is shown in Figure 2.3. The first step is the conversion of triglycerides, which is followed by the conversion of diglycerides to monoglycerides and of monoglycerides to glycerol.

$$\text{Triglyceride} + \text{R'OH} \underset{}{\overset{\text{Catalyst}}{\rightleftarrows}} \text{Diglyceride} + \text{R'COOR}_1$$

$$\text{Diglyceride} + \text{R'OH} \underset{}{\overset{\text{Catalyst}}{\rightleftarrows}} \text{Monoglyceride} + \text{R'COOR}_2$$

$$\text{Monoglyceride} + \text{R'OH} \underset{}{\overset{\text{Catalyst}}{\rightleftarrows}} \text{Glycerol} + \text{R'COOR}_3$$

Figure 2.3 Transesterification of triglycerides: three consecutive and reversible reactions. R1, R2, R3 and R' represent alkyl groups (Fukuda et al. 2001)

The transesterification of vegetable oil can be performed using alkaline, acidic and solid catalyst, depending on the undesirable compound (especially FFA and water) each catalyst has its own an advantages and disadvantages.

2.3.1 Acid-catalyzed transesterification

One limitation in the alkalini-catalyzed process is its sensitivity to the purity of reactants, especially to both water and free fatty acids. The free fatty acids and water make the use of an alkaline catalyst difficult, because of soap formation and then difficulty in product separation. The only disadvantage of an acidic catalyst is slower reaction rate. Transesterification can be catalyzed by Bronsted acids, such as sulfonic acid, sulfuric and hydrochloric acids. The mechanism of acid catalyzed transesterification of vegetable oil. However, it can be extended to di- and tri glycerides. The protonation of carbonyl group of the ester leads to the carbocation, 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.

Cana ki and Van Gerpen (1999) studied the reagent molar ratio affected reaction rates and product yield in the transmethylation of soybean oil by sulfuric acid. Five different molar ratios, from 3.3:1 to 30:1, were studied. Their results indicated that ester formation increased with increasing molar ratio, reaching its highest value, 98.4%, at the highest molar ratio used, 30:1. However, the benefits from higher alcohol to triglycerides molar ratios became limited with increasing ratio, ester formation increase sharply from 77% at 3.3:1 to 87.8% at 6:1 and ultimately reaching a plateau value of 94.8% at 30:1.

Crabbe et al. (2001) investigated acid catalyzed (sulfuric acid) production of methyl esters from crude palm oil. The reactions were carried out at the temperature of 95°C. They determined the effect of molar ratio with in the range of 3:1 to 40:1, the effect of amount of catalyst with in the range of 1 to 5% H_2SO_4 (vol/%wt) and temperature reaction. The optimized variables, 40:1 methanol/oil (mol/mol) with 5% H_2SO_4 (vol/%wt) reacted at the temperature of 95°C for 9 hours, gave a maximum ester yield of 97%.

Widyan et al. (2002) studied a comparison of the catalytic activities of HCL and H_2SO_4 for the transesterification of waste palm oil. Compared to HCL, H_2SO_4 was as a better catalyst. The use of excess alcohol can reduce the longer reaction time that is required for the acid-catalyzed reaction. Thus, Bronsted acid catalyst transesterification requires high catalyst concentration and a higher molar ratio to reduce the reaction time. Lewis acids can also act as a catalyst for the transesterification of vegetable oil.

Mohamad et al. (2003) studied transesterification reaction of waste palm oil using acid catalyst was under various conditions such as different H_2SO_4 and HCl concentrations. In this study, ethanol at different excess levels was also used. They found that higher catalyst concentrations produced biodiesel with lower specific gravity, in much shorter reaction time than lower concentrations. The H_2SO_4 performed better than HCl as it results in diesel with lower specific gravity in about 3 h. Moreover, a 100% excess alcohol resulted in significant reductions in reaction time and lower specific gravity.

Diserio et al. (2005) studied a method for the simultaneous esterification and transesterification of waste oils using homogeneous Lewis acids base on carboxylic salts of the metal (Cd, Mn, Pb, Zn). Catalytic activities of these catalysts are related to the Lewis acid strength of the metals (which must have an optimum value) and to the molecular structure of the anion. Acetates and stearates of calcium, barium, magnesium, cadmium, manganese, lead, zinc, cobalt, and nickel were tested for their catalytic activity for the transesterification of waste oil at a molar ratio of oil to alcohol of 1:12 and temperature of 200°C for 200 min. The influence of water and free fatty acids on the catalyst activity has been studied. Stearates showed better performance than acetates, because of better solubility in the oil. This catalyst showed better performance than the Bronsted acid at lower catalyst concentration and a lower molar ratio of oil to alcohol. Homogeneous acid catalysts are good for the transesterification of vegetable oil with high free fatty acids content. However,

it has slow reaction rate, and the requirement of high catalyst concentration and high temperature.

Zheng et al. (2006) studied the reaction kinetic of acid catalyzed (H_2SO_4) transesterification of waste frying oil in excess methanol to from fatty acid methyl esters for possible use as biodiesel. The oil:methanol:acid molar ratios and temperature were the most significant factors affecting the yield of fatty acid methyl esters at 70°C with oil:methanol:acid molar ratios of 1:245:3.8 and at 80°C with oil to methanol to acid molar ratios in range 1:74:1.9 to 1:245:3.8. As a result of the large excess of methanol, the reaction completed (99±1% conversion) in 4 h. Although acid catalyzed process does have advantages such as reduced purification costs, the reaction is much slower.

Transesterification using acid catalysts is normally done with sulfuric, phosphoric, hydrochloric or organic sulfonic acids. In fact, transesterification using an acid catalyst is much slower than using an alkali catalyst, but it is suitable for glycerides that have high free acid contents and water. Acid catalysts can catalyze the reaction without any disturbances from those presences. Although acid catalysts can be used for transesterification they are too slow for industrial processing. Moreover, scaling up an acid-catalyzed system requires to using a corrosive resistant material which is costly.

2.3.2 Alkaline-catalyzed transesterification

Common alkaline catalysts are well know for the transesterification reaction of edible oil. The rate of alkaline–catalyzed transesterification reaction is reported that the rate could be a high as 400 times compared to that used acid catalysts (Fukuda, 2001). Nonetheless, from a chemical standpoint the active spicies with both types of catalyst are methoxide ions. Methoxide ions form methanol reacts with hydroxyl ions from added alkaline hydroxides

in the second situation. Once formed, the methoxide ions are strong nucleophiles and attack the carbonyl moiety in glyceride molecules to produce the alkyl esters.

The application of an alkaline catalyst in the transesterification of vegetable oil is show that limited because the FFA in vegetable oil or ester reacts with alkaline catalyst (KOH, NaOH) and forms soap.

Tomasevic et al. (2003) studied the transesterification reaction of used sunflower oil with methanol, using alkaline catalysts such as KOH and NaOH and different molar ratios of methanol to oil (4.5:1, 6:1, 9:1). The effects of various parameters such as the variation in oil quality, the molar ratio of methanol to oil, the type and amount of alkaline catalyst, the time and temperature of reaction on the yield, and the properties of esters were studied. The optimum conditions developed for the production of good-quality biodiesel from used sunflower oil were as follows: molar ratio of methanol to oil, 6:1, with 1 %wt of KOH; reaction temperature 25°C, and reaction time 30 min. It was observe that, under the optimal conditions of methanolysis, the quality of the used frying oil did not have an essential effect on the quanlity of methyl esters produced. An increase in the quantity of catalyst and molar ratio of methanol to oil did not change the yield or quality of the esters. Of the two catalysts NaOH and KOH, 1% KOH has given the best yields and viscosities of esters.

Aracil et al. (2004) studied different basic catalysts (sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide) for transesterification of sunflower oil. The biodiesel purity near 100 %wt was obtained for all catalysts. However, biodiesel yields near 100 %wt were only obtained with the methoxide catalysts. Although all the transesterification reactions were quite rapid and the product achieved nearly 100% methyl esters concentrations, the reactions using sodium hydroxide turned out the fastest.

Dorado et al. (2004) studied a comparison of the catalytic activities of KOH and NaOH for the transesterification of wast cooking oil with an FFA content of 2.76 %wt. According to this study, the KOH-catalyzed transesterification proceeds quicker than NaOH-catalyzed reaction. The optimization of other reaction parameters (such as temperature, molar ratio of oil to alcohol, reaction time and stirring) is also reported.

Encinar et al. (2005) studied a comparison of the catalytic activities of NaOH, KOH, sodium methoxide, and potassium methoxide for the transesterification of used frying oil with methanol. The effects of operation variables such as the molar ratio of alcohol to oil (3:1 to 9:1), the catalyst concentration (0.1 %wt to 1.5 %wt of oil), the temperature of 25 to 65°C, and the catalyst type on the ester yield were studied. The biodiesel with the best properties was obtained using a methanol/oil molar ratio of 6:1 potassium hydroxide as the catalyst (1 %wt of oil), and temperature of 65°C. Two-stage transesterification with a separation of glycerol after the first stage was determined to be better than a one-stage process.

Felizardo et al. (2005) studied the transesterification reaction of waste cooking oil that has an acid value in the range of 0.42 to 2.07, using NaOH as acatalyst. The effects of the molar ratio of alcohol to oil (3.6 to 5.4), the acid value (0.4 to 2.07) and the sodium hydroxide to frying oil mass ratio (0.2 to 1.0) on the percentages of esters yield were studied. Oils with an acid value of 4.2 mg KOH/g gave a maximum yield of esters at methanol to oil molar ratio of 4.8 and a catalyst to oil ratio of 0.6.

Meher et al. (2006) studied the transesterification reaction of karanja oil with methanol was carried out using alkaline catalyst in a batch type reactor. At 65°C, with a molar ratio of 1:6 of the karanja oil to methanol, using KOH as catalyst, the 97% conversion to methyl esters was obtained after 3 h. Although high purity and yield of biodiesel can be achieved in a short time with the alkali process. However, it is very sensitive to the purity of reactants. For example,

the starting material (oil or fat) must be dried (moisture level less than 0.06%) and free of free fatty acid less than 0.5%. The presence of minor amount of FFA and moisture in the reaction mixture produces soap, which lower the yield of ester and renders the separation of ester and glycerol by water washing difficult. FFA also consumed the catalyst and reduced catalyst efficiency.

In transesterification with alkali catalyst, sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide can be used. Alkali catalysts in transesterification make process response faster than acidic catalysts by about 4000 times (Ma and Hanna. 1999). Therefore, the alkali catalysts are the most popular and used widely in commercial scale. An important factor in the transesterification with alkali catalysts is the moisture because it can react with the fatty acid and following the saponification reaction, produce soap. The soap consumes the catalyst, reduces the efficiency of the process, increases the viscosity and makes it difficult to separate glycerol. Hence, the free fatty acid should be reduced to lower than 0.5 % and oils should be dried to get rid of moisture.

2.4 Transesterification of vegetable oils using heterogeneous catalysts

Homogeneous catalysts, although effective, lead to serious contamination problems that make essential the implementation of good separation and product purification protocols, which translate in to higher production cost. The synthesis of fatty acid methyl esters need to involve continuous processing in a flow system, have as few reaction steps as possible, limit the number of separation processes, and ideally use a robust heterogeneous catalyst (such as metal oxides). The appropriate solid catalysts could be easily incorporated into a packed bed continuous flow reactor, simplifying product separation and purification and reducing waste generation.

Therefore, it is of interest to investigate the possibility to replace the homogeneous catalyst by solid catalysts in transesterification reactions.

The two conventional catalysts mentioned above need to use a large amount of water during the catalyst separation and product cleaning. This process generates a large amount of waste water that requires treatment before discharging to the environment. The treatment adds an extra cost to the total production cost. Moreover, the presence of water in vegetable oils leads to the hydrolysis of ester and the result is soap. The formation of soap reduces the biodiesel yield. Therefore, heterogeneous catalysts such as Nickel, palladium, Calcium carbonate and Calcium oxide are new catalysts to lower the cost of production and reduce the amount of waste water. These heterogeneous or solid catalysts can be removed easily by filtration and can be used in a large-scale production. Moreover, they can be reused, recycled and regenerated making the production cost more efficient. On the other hand, homogeneous catalysts cannot be reused because they are dissolved in methanol. Many heterogeneous catalysts have been developed for transesterification of vegetable oil with methanol as shown in the part of literature reviews. The strong basic sites of calcium methoxide can catalyze the reaction with high methyl esters yield of 91%. The mechanism of calcium methoxide as base heterogeneous catalyst in transesterification

Although the heterogeneous catalysts have many advantages, lower methyl esters content and yield is still a problem. For this reason, improving the methyl esters content and yield in this catalytic system is of interest. In this study, the optimum condition of methyl esters content and yield was examined. Then the catalyst was investigated for the possibilities of the recycling and regeneration.
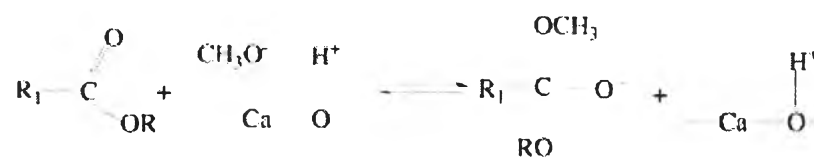
The mechanism of transesterification of glyceride to methyl esters in the presence of methoxide anion is as shown in Figures 2.5. In the first step, the methoxide anion attaches to the carbonyl carbon atom of the triglyceride

molecule to form a tetrahedral intermediate (step 1a and 1b). In the second step, the tetrahedral intermediate picks up an H^+ atom from the surface of CaO (step 2). The tetrahedral intermediate also can react with methanol to generate methoxide anion (step 3). In the last step, the rearrangement of the tetrahedral intermediate results in the formation of biodiesel and glycerol (step 4).
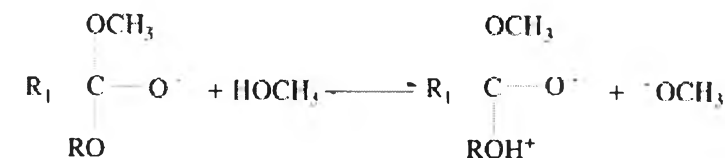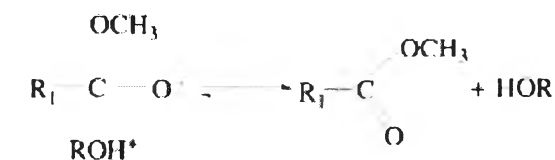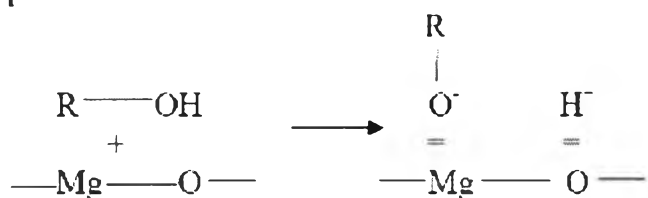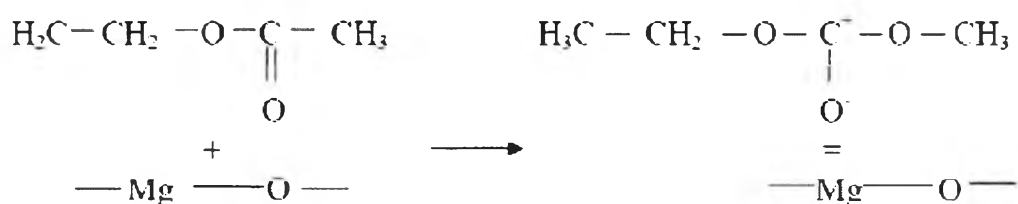
Step 1-a

Step 1-b

Step 2

Step 3

Step 4

Figure 2.4 Reaction mechanisms of transesterification reaction over CaO by Xuejin et al. (2007)

Step 1-a

R——OH
+
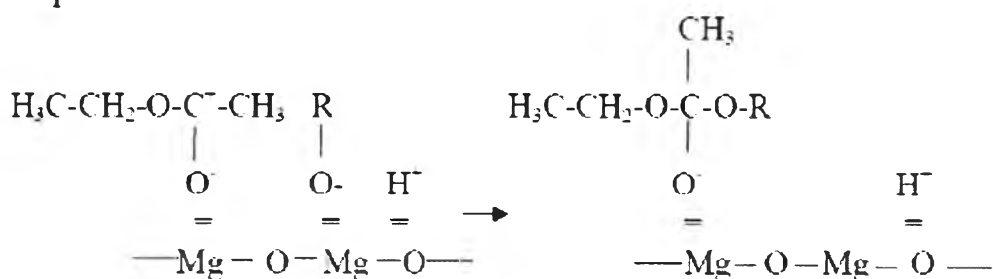—Mg——O—

$\longrightarrow$

R
|
O⁻   H⁻
=   =
—Mg—— O—

Step 1-b

H₂C−CH₂ −O−C− CH₃
          ‖
          O
+
— Mg ——O —

$\longrightarrow$

H₃C − CH₂ −O− C⁻ −O −CH₃
              |
              O⁻
              =
             —Mg——O—

Step 2

H₃C-CH₂-O-C⁻-CH₃   R
        | |
        O⁻   O- H⁻
        =   =   =
       —Mg − O⁻Mg −O—

$\longrightarrow$

            CH₃
            |
H₃C-CH₂-O-C-O-R
            |
            O⁻   H⁻
            =   =
           —Mg− O −Mg− O —

Step 3

        CH3
        |
H₃C-CH₂-O-C-O-R
        |
        O⁻   H⁺
        =   =
       —Mg −O−Mg−O—

$\longrightarrow$

        H₃C − C- R
              ‖
              O

H₃C-CH₂-O-   H⁻
        =   =
       —Mg−O −Mg −O —

Step 4

H₃C —CH₂—O⁻   H⁺
        =   =
       —Mg− O −Mg −O —

$\longrightarrow$

H₃C —CH₂ —OH
+
—Mg —— O —
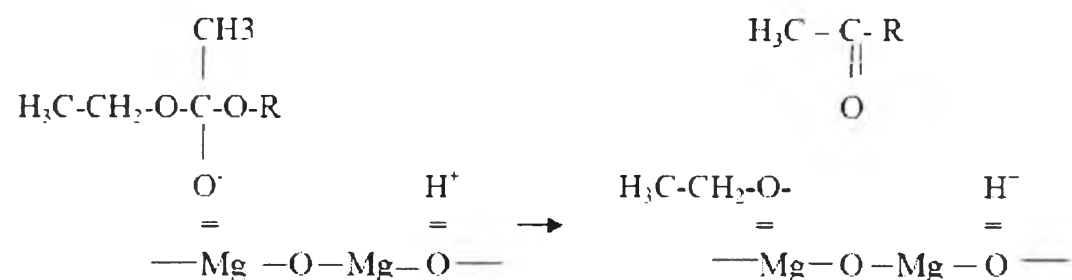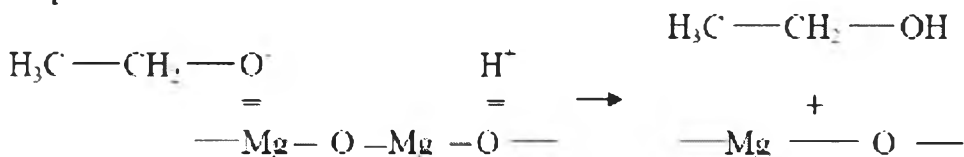
Figure 2.5 Reaction mechanisms for the transesterification of ethyl acetate
with alcohol catalyzed by solid catalyst proposed by Dossin et al. (2005)

The proposed reaction mechanism consists of four steps as shown in Figures 2.6. The first two steps (step 1a and 1b) describe the adsorbtion of alcohol and ethyl acetate on two neighboring free catalytic sites. The two adsorbed species then react to form a sureface intermediate (step 2) that further decomposes to methyl acetate and adsorbed ethanol (step 3) that finally desorbed (step 4).

Vicente et al. (1998) studied the reaction of refined sunflower oil and methanol was carried out over different types (acid and basic, homogeneous and heterogeneous catalyst) of catalyst (NaOH, Amberlyst A26, Amberlyst A27, Amberlyst 15, MELCat XZO682/01 (Sulfate doped zirconium hydroxide), MELCat XZO645/01 (Silica doped zirconium hydroxide), TIS (Titanium silicate), TISCOM STC (Titanium chelate), $SnCl2$, MgO, USY-929 and Novozym 435 (Immobilized lipase). The temperature chosen for the reaction was 60°C. The reaction time for all experiments was 8 hours. The 1% (wt/wt of oil) concentration of catalyst is chosen. The resulted that that the activity of sodium hydroxide was found to be much larger than that for all the other catalysts (80% conversion at 5 min.). The only other catalyst that showed significant activity was MgO, but even yield obtained for this catalyst was about ten times lower than that measured for sodium hydroxide. The strong cation-exchange resin gave a slightly higher yield than the anion-exchange ion samples. However, none of the yields obtained for the ion exchangers exceed 1%. The worst behavior was observed for the zirconium-based catalysts and immobilized lipase which did not product any methyl esters.

Gryglewicz (1999) studied the transesterification of rapeseed oil by methyl alcohol can be catalyzed effectively by basic alkaline-earth metal compound: calcium oxide, calcium methoxide and barium hydroxide. Though, the results were less active than sodium hydroxide. The activity increase in the order: $CaO < Ca(CH_3O)_2 < Ba(OH)_2$. Unfortunately, barium hydroxide is much more soluble in methanol than the other alkaline earth metal compound

and highly toxic. Therefore barium hydroxide cannot serve as a catalyst investigated process. Calcium methoxide which can form on the surface of calcium oxide, is the real catalyst of the methanolysis of triglycerides. Because of its slight methanol-solubility calcium methoxide acts mainly as a heterogeneous catalyst.

Exconde et al. (2003) studied the transesterification reaction of crude coconut oil with methanol using heterogeneous catalysts (Na_2CO_3, K_2CO_3, $CaCO_3$, ZrO_2, ZnO, Beta zeolite, NaX zeolyte, NaY zeolite, Al_2O_3 and S. SnO_2 (supper acid stannous oxide). Two conditions were used in this studied: the temperature was 65 to 70°C, atmospheric pressure, 20:1 methanol to oil molar ratio, and a reaction time of 10 hours. The temperature was 200°C at 50 bars, 20:1 methanol to oil molar ratio, and a reaction time of 4 hours. The resulted showed that, K_2CO_3 and ZnO showed high activities (99.34% and 54.27% methyl esters content) in transesterification of crude coconut oil at temperature of 60 to 70°C, atmospheric pressure, 20:1 methanol to oil molar ratio, and a reaction time of 10 hours. All catalyst except Al_2O_3 showed high activities (more than 80% methyl esters content) at temperature of 200°C, pressure of 50 bars, 20:1 methanol to oil molar ratio, and a reaction time of 4 hours.

Xuejun Liu et al. (2006) studied physical and chemical characterizations of calcium methoxide were investigated to assess its performance as an excellent solid base catalyst using some instrumental methods, such as BET surface area measurement, scanning electron micrographs and particle size distribution. Then, it was used to catalyze transesterification of soybean oil to biodiesel with methanol. The effects of various factors such as mass ratio of catalyst to oil, reaction temperature and volume ratio of methanol to oil were studied to optimize the reaction conditions. The results showed that calcium methoxide has strong basicity and high catalytic activity as a heterogeneous solid base catalyst and it was obtained a 98% biodiesel yield within 2 h in this reaction. Besides, the recycling experiment results showed it had a long

catalyst lifetime and could maintain activity even after being reused for 20 cycles.

Ayhan Demirbas (2007) studied the sunflower seed oil was subjected to the transesterification reaction with calcium oxide (CaO) in supercritical methanol for obtaining biodiesel. Methanol is used most frequently as the alcohol in the transesterification process. Calcium oxide (CaO) can considerably improve the transesterification reaction of sunflower seed oil in supercritical methanol. The variables affecting the methyl esters yield during the transesterification reaction, such as the catalyst content, reaction temperature and the molar ratio of soybean oil to alcohol, were investigated and compared with those of non-catalyst runs. The catalytic transesterification ability of CaO is quite weak under ambient temperature. At a temperature of $62^{\circ}C$, the yield of methyl esters is only about 5% in 3 h. When CaO was added from 1.0% to 3.0%, the transesterification speed increased evidently, while the catalyst content was further enhanced to 5%, the yield of methyl esters slowly reached to a plateau. It was observed that increasing the reaction temperature had a favorable influence on the methyl esters yield. In addition, for molar ratios ranging from 1 to 41, as the higher molar ratios of methanol to oil were charged, the greater transesterification speed was obtained. When the temperature was increased to $50^{\circ}C$, the transesterification reaction was essentially completed within 6 min with 3 wt% CaO and 41:1 methanol/oil molar ratio.

Arzamendi et al. (2008) studied the catalytic activity and selectivity of several compounds of the alkaline and alkaline-earth metals in the transesterification with methanol at $50^{\circ}C$ of refined sunflower oil have been evaluated. Catalytic runs were conducted with a molar methanol to oil ratio of 12:1 in a batch reactor. The considered catalysts were Li, Na, K, Rb, Cs and Ca hydroxides, Na, K, Ca and Mg carbonates, Na and K bicarbonates, sodium phosphates as well as Ca and Mg oxides. Catalysts behaviour mainly depended

on their homogeneous or heterogeneous character; that is, on their solubility in methanol. The alkaline metals hydroxides acted as homogeneous catalyst and were the most active ones; little differences were found among them. The K and Na carbonates, Na phosphate and CaO gave good results also. The evolution with reaction time of the selectivity for the different products also depended on the homogeneous or heterogeneous character of the catalyst, as well as on the alkaline or alkaline-earth nature of the metal. The chemical stability under reaction conditions of the most active heterogeneous catalysts has been investigated by checking the presence of the metals in the reaction mixture. This issue has received very little attention in the majority of the previous studies on heterogeneously-catalyzed biodiesel production. It must be stressed that a significant solubility in methanol of the solids has been found in some instances (e.g. K_2CO_3), therefore a contribution of homogeneous reaction routes cannot be discarded.

Chawalit et al. (2008) studied the transesterification reaction of palm kernel oil with methanol over mixed oxides of Ca and Zn has been investigated batchwise at 60°C and 1 atm. CaO.ZnO catalysts were prepared via a conventional coprecipitation of the correspondingmixed metal nitrate solution in the presence of a soluble carbonate salt at near neutral conditions. The catalysts were characterized by using techniques of X-ray diffraction (XRD), scanning electron microscope (SEM), and thermogravimetric analysis (TGA). The results indicated that the mixed oxides possess relatively small particle sizes and high surface areas, compared to pure CaO and ZnO. Moreover, the combination of Ca and Zn reduced the calcination temperature required for decomposition of metal carbonate precipitates to active oxides. Influences of Ca/Zn atomic ratio in the mixed oxide catalyst, catalyst amount, methanol/oilmolar ratio, reaction time, and water amount on the methyl esters (ME) content were studied. Under the suitable transesterification conditions at 60°C (catalyst amount of 10 %wt, methanol to oil molar ratio of 30, reaction

time of 1 h), the ME content of more than 94% can be achieved over CaO.ZnO catalyst with the Ca/Zn ratio of 0.25. The mixed oxide can be also applied to transesterification of palm olein, soybean, and sunflower oils. Furthermore, the effects of different regeneration methods on the reusability of CaO.ZnO catalyst were investigated.

Granados et al. (2008) studied the activity of activated CaO as a catalyst in the production of biodiesel by transesterification of triglycerides with methanol. Three basic aspects were investigated: the role of H_2O and CO_2 in the deterioration of the catalytic performance by contact with room air, the stability of the catalyst by reutilization in successive runs and the heterogeneous character of the catalytic reaction. The characterization by X-ray diffraction (XRD), evolved gas analysis by mass spectrometry (EGA-MS) during heating the sample under programmed temperature, X-ray photoelectron (XPS) and Fourier transform-infrared (FT-IR) spectroscopies allowed to concluding that CaO is rapidly hydrated and carbonated by contact with room air. Few minutes are enough to chemisorb significant amount of H_2O and CO_2. It is demonstrated that the CO_2 is the main deactivating agent whereas the negative effect water is less important. As a matter of fact the surface of the activated catalyst is better described as an inner core of CaO particles covered by very few layers of $Ca(OH)_2$. The activation by outgassing at temperatures $700°C$ is required to revert the CO_2 poisoning. The catalyst can be reused for several runs without significant deactivation. The catalytic reaction is the result of the heterogeneous and homogeneous contributions. Part of the reaction takes place on basic sites at the surface of the catalyst the rest is due to the dissolution of the activated CaO in methanol that creates homogeneous leached active species.

Masato et al. (2008) studied and developed a process of biodiesel production with environmental benignity much interest has been focused on solid base catalysts such as calcium oxide for transesterification of vegetable

oils with methanol. In this paper, the active phase of calcium oxide was investigated by characterizing the catalyst collected after achieving the conversion of edible soybean oil into its methyl esters at reflux of methanol in a glass batch reactor. Calcium oxide combined with the by-produced glycerol, so that calcium diglyceroxide was a major constituent of the collected catalyst. The absence of calcium methoxide was clear from the spectrum of solid-state 13C-NMR. The chemical change of calcium oxide was not observed, when the yield of FAME reached 30%. The collected catalyst was not as active as the fresh one (calcium oxide), but was reused without any deactivation. In order to identify the active phase of the collected catalyst, we prepared calcium diglyceroxide by immersion of calcium oxide with refluxing methanol in the presence of glycerol. Calcium diglyceroxide prepared as the reference sample was as active as the collected catalyst in the transesterification, and was tolerant to air-exposure.

Masato et al. (2008) studied solid base catalyst for biodiesel production with environmental benignity transesterification of edible soybean oil with refluxing methanol was carried out in the presence of calcium oxide (CaO), hydroxide ($Ca(OH)_2$), or -carbonate ($CaCO_3$). At 1 h of reaction time, yield of FAME was 93% for CaO, 12% for $Ca(OH)_2$, and 0% for $CaCO_3$. Under the same reacting condition, sodium hydroxide with the homogeneous catalysis brought about the complete conversion into FAME. Also, CaO was used for the further tests transesterifying waste cooking oil (WCO) with acid value of 5.1 mg-KOH/g. The yield of FAME was above 99% at 2 h of reaction time, but a portion of catalyst changed into calcium soap by reacting with free fatty acids included in WCO at initial stage of the transesterification. Owing to the neutralizing reaction of the catalyst, concentration of calcium in FAME increased from 187 ppm to 3065 ppm. By processing WCO at reflux of methanol in the presence of cation-exchange resin, only the free fatty acids could be converted into FAME. The transesterification of the processed WCO

with acid value of 0.3 mg-KOH/g resulted in the production of FAME including calcium of 565 ppm.

2.5 Transesterification of vegetable oils using heterogeneous modified with metal catalysts catalysts

The heterogeneous catalysts have many advantages, lower methyl esters content and yield is still a problem. For this reason, improving the methyl esters content and yield in this catalytic system is of interest.

Ebiura et al. (2005) studied the transesterification reaction of triolein (trioleoy glycerol) with methanol to methyl oleate and glycerol could be achieved at around 60°C using alumina loaded with alkaline metal salt as a solid-base catalyst. The catalytic activities are shown to be relatively insensitive to the presence of water. K_2CO_3 loaded alumina catalyst prepared by evacuation at 550°C gives methyl oleate and glycerol in the highest yields of 94 and 89%, at 60°C in 1 hour.

Xie et al. (2006) studied biodiesel production from soybean oil with methanol using potassium nitrate (KNO_3) loaded on alumina (Al_2O_3). The catalytic activity of the solid catalyst was also investigated to determine the optimal condition. The effects of KNO_3 loading, calcination temperature, methanol to oil molar ratio, catalyst amount and reaction time were investigated. The alumina had a surface area of 126 m^2/g. Potassium nitrate was loaded on to alumina by impregnation method from aqueous solution, followed by drying at 120°C for 16 h. The catalyst was calcined at 500°C for 5 h. The results showed that the conversion of soybean oil increase with increasing the KNO_3 loading, molar ratio methanol to oil, catalyst amount and reaction time. However, excess KNO_3 loading decreased the conversion of soybean oil because the dispersion limitation. The conversion of soybean oil was decreased when the calcination temperature was higher than 500°C and that possibly because of the loss of K. When the reaction was carried out at

reflux of methanol, with molar ratio of methanol to oil of 15:1, a reaction time 7 h and a catalyst amount of 6.5 %wt the highest conversion was reached 87 %.

Jitputti et al. (2006) studied biodiesel production from crude palm kernel oil (PKO) and crude palm coconut oil (CCO) by using solid and zeolite catalysts. The catalyst studied were zinc oxide (ZnO), sulphated zirconia (SO_4^{2-}/ZrO_2), sulphated stannous oxide (SO_4^{2-}/SnO_2), KNO_3/KL zeolite and zirconia-supported potassium nitrate (KNO_3/ZrO_2). All catalysts were calcined at desired temperatures. Transesterification reaction was used for reducing the viscosity of vegetable oil by using Parr series reactor. The conditions for experiment were at 200°C, 4 h and 6:1 methanol to oil molar ratio. For PKO, all catalysts showed the high activity for transesterification of PKO with methanol. Moreover, soap information was not observed when these catalysts were used. The yield of methyl esters from solid and zeolite catalysts were followed by this order: (SO_4^{2-}/ZrO_2) and (SO_4^{2-}/SnO_2) >ZnO >KNO_3/ZrO_2 > KNO_3/KL zeolite with methyl esters yields of 90.3 %, 90.3 %, 86.1 %, 71.4 % and 64.5 %, respectively. For CCO, SO42-/ZrO2 gave the highest methyl esters yield (86.3 %), followed by SO_4^{2-}/SnO_2, ZnO, KNO_3/KL zeolite and KNO_3/ZrO_2 with methyl esters yields of 86.3 %, 80.6 %, 77.5 %, 77.2 % and 65.5 % respectively. The methyl esters yield that produced from PKO is higher than that from CCO. This may be due to the higher amount of free fatty acid and water content of CCO which have an effect on the reaction.

Kim et al. (2004) studied the production of biodiesel from soybean oil using heterogeneous catalyst (Na/NaOH/γ-Al2O3). The reaction was carried out at temperature of 60°C in a stainless steel batch reactor, 9:1 methanol to oil molar ratio, n-hexane was used at co-solvent and a reaction of 2 hours. Both the sodium aluminate formed by loading on γ-Al2O3, and the ionization of sodium, originate the strong basic strengths. The reaction conditions for the system were optimized to maximize the biodiesel production yield. A

utilization of a co-solvent was found to be inevitable for transesterification of vegetable oil to biodiesel. Among the co-solvent tested, n-hexane was the most effective with a loading amount of 5:1 vegetable oil to hexane molar ratio. The optimum methanol to oil loading ratio was found to be 9:1. The Na/NaOH/γ-Al$_2$O$_3$ heterogeneous base catalyst showed almost the same activity under optimized reaction conditions compared to the conventional homogeneous NaOH catalyst.

Xie et al. (2006) studied transesterification reaction of soy bean oil using potassium iodide (KI) loaded onto alumina (Al$_2$O$_3$) as a solid catalyst. The effects of KI loadings, molar ratio of methanol to oil, catalyst amount and reaction time were investigated. The catalyst was prepared by impregnation method followed by calcination at 500°C for 3 h. The results showed, the conversion of soybean oil was increase with increasing the KI loadings (up to 35 %wt), molar ratio of methanol to oil, catalyst amount and reaction time. However, when the KI loading was more than 35 wt% the conversion decreased due to the excess KI could cover the basic sites on the surface of catalyst. Moreover, the conversion of soybean oil was decreased when the calcination temperature was higher than 500°C and the catalyst amount was higher than 2.5 %wt similarly due to poor catalyst dispersion best KI loading was of 35 %wt for this catalyst. And when it was used at 510°C for 8 h, 15:1 methanol to oil molar ratio and 2.5 %wt catalyst amount, the highest conversion of soybean oil of 96 % was obtain.

Huaping et al. (2006) studied biodiesel produced by the transesterification of vegetable oils is promising alternative fuel to diesel because of the limited resources of fossil fuel and environmental concerns. An environmentally benign process was developed for the production of biodiesel from jatropha curcas oil using a heterogeneous solid super base catalyst, calcium oxide. The results showed that the base strength of calcium oxide was more than 26.5 after dipping in an ammonium carbonate solution followed by

calcination. A study for optimizing the reaction conditions for the transesterification of jatropha curcas oil was performed. Under the optimum conditions of catalyst calcination temperature of 900°C, reaction temperature of 70°C, reaction time of 2.5 h, catalyst dosage of 1.5%, and methanol/oil molar ratio of 9:1, the oil conversion was 93%. The purification of the as-synthesized biodiesel with decalcifying agents to eliminate the remaining calcium was investigated. Citric acid showed good performance for the decalcification. The properties of the refined biodiesel accorded with the domestic and foreign standards.

Boonsirm and Apinya (2007) studied transesterification reaction of palm olein oil to biodiesel using $Ca(NO_3)_2/CaO$ as a heterogeneous catalyst was studied. Influences of supports, catalyst amount and calcination temperature have been investigated. The transesterification reactions were carried out at 60°C with a 1:30 molar ratio of palm olein oil to methanol and reaction time 1 h. The highest catalytic activity (89%) was obtained from the catalyst prepared by loading $Ca(NO_3)_2$ of 38 wt% on CaO followed by calcination at 420°C.

Chawalit et al. (2007) studied heterogeneously catalyzed transesterification of palm kernel oil with methanol over various modified dolomites has been studied at 60°C. The modification of dolomite was performed via a conventional precipitation method using various nitrate salt solutions of alkali earth metals and trivalent metals. Influences of a variety of metals, calcination temperature of the parent dolomite, methanol/oil molar ratios, reaction time, catalyst amount, and catalyst reuse have been investigated. The results indicated that the calcination temperature of the parent dolomite is a crucial factor affecting the activity and the basicity of the resulting catalyst. The catalyst modified from dolomite calcined at 600 and 700°C, followed by the precipitation from $Ca(NO_3)_2$ and the subsequent calcination at 800°C, exhibited the most active catalyst, giving the methyl

esters content as high as 99.9% under the suitable reaction conditions, the methanol/oil molar ratio of 15:1, amount of catalyst of 10 %wt., and reaction time of 3 h. As suggested by the TGA results, the high activity of the catalyst should be due to the presence of two active CaO sites generated from the precipitated $Ca(OH)_2$ located in the crystalline phase of dolomite and from $CaCO_3$ remaining after the calcination of the parent dolomite at 600 to 700°C.

Albuquerque et al. (2008) studied a new group of basic catalysts supported on mesoporous solids has been prepared with the being used as heterogeneous catalysis in biodiesel production. These catalysts based on calcium oxide supported on porous silica (SBA-15, MCM-41 and fumed silica) have been characterized and evaluated in transesterification processes. They were characterized by DRX, XPS, SEM, FT-IR, CO_2-TPD and N_2 adsorption. The catalytic activity was evaluated in the transesterification of ethyl butyrate with methanol, and different reaction parameterswere optimized by a factorial design response surface methodology. Thus, a sample containing 14 %wt of CaO supported on SBA-15 was the most active, and, unlike commercial CaO, no lixiviation of the active phasewas detected in the reaction medium. The transesterification activity of vegetable oils confirms the results obtained in the reaction of ethyl butyrate with methanol, reaching conversion as high as 95% with sunflower oil (after 5 h of reaction) and 65% (after 1 h) for castor oil.

Macleod et al. (2008) studied series of alkali-doped metal oxide catalysts were prepared and evaluated for activity in the transesterification of rapeseed oil to biodiesel. of those evaluated, $LiNO_3$/CaO, $NaNO_3$/CaO, KNO_3/CaO and $LiNO_3$/MgO exhibited more than 90% conversion in a standard 3 h test. There was a clear correlation between base strength and activity. These catalysts appeared to be promising candidates to replace conventional homogeneous catalysts for biodiesel production as the reaction times are low enough to be practical in continuous processes and the preparations are neither prohibitively difficult nor costly. However, metal leaching from the catalyst

was detected and this resulted in some homogeneous activity. This would have to be resolved before these catalysts would be viable for large-scale biodiesel production facilities.

Sita et al. (2008) studied transesterification reactiom of palm kernel oil (PKO) and coconut oil (CCO) with methanolwas investigated under a heterogeneous catalysis system. Various Al_2O_3-supported alkali and alkali earthmetal oxides prepared via animpregnationmethodwere applied as solid catalysts. The supported alkalimetal catalysts, $LiNO_3/Al_2O_3$, $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3, with activemetal oxides formed at calcination temperatures of 450 to 550°C, showed very high methyl esters (ME) content more than 93%. XRF analysis suggests this is likely to be due to a homogeneous catalysis of dissoluted alkali oxides. On the other hand, $Ca(NO_3)_2/$ Al_2O_3 calcined at 450°C yielded the methyl esters content as high as 94% with only a small loss of active oxides from the catalyst, which calcined $Mg(NO_3)_2/Al_2O_3$ catalyst possessed an inactive magnesium-aluminate phase, resulting in very low ME formation. At calcination temperatures of more than 650°C, alkali metal and alkali earth metal-aluminate compounds were formed. Whilst the water-soluble alkali metal aluminates formed over $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3 were catalytically active, the aluminate compounds on $LiNO_3/Al_2O_3$ and $Ca(NO_3)_2/Al_2O_3$ are less soluble, giving very low methyl esters content. The suitable conditions for heterogeneously catalyzed transesterification of PKO and CCO over $Ca(NO_3)_2/Al_2O_3$ are the methanol/oil molar ratio of 65, temperature of 60∘C and reaction time of 3 h, with 10 and 15 to 20% (w/w) catalyst to oil ratio for PKO and CCO, respectively. Some important physical and fuel properties of the resultant biodiesel products meet the standards of diesel fuel and biodiesel issued by Department of Energy Business, Ministry of Energy, Thailand.

Xuejun Liu et al. (2008) studied transesterification reaction of soybean oil to biodiesel using CaO as a solid base catalyst was studied. The reaction

mechanism was proposed and the separate effects of the molar ratio of methanol to oil, reaction temperature, mass ratio of catalyst to oil and water content were investigated. The experimental results showed that a 12:1 molar ratio of methanol to oil, addition of 8% CaO catalyst, 65°C reaction temperature and 2.03% water content in methanol gave the best results, and the biodiesel yield exceeded 95% at 3 h. The catalyst lifetime was longer than that of calcined K_2CO_3/c-Al_2O_3 and KF/c-Al_2O_3 catalysts. CaO maintained sustained activity even after being repeatedly used for 20 cycles and the biodiesel yield at 1.5 h.