เมทิลเอสเทอร์จากน้ำมันปาล์มโอเลอินโดยใช้ปฏิกิริยาทรานส์เอสเทอริฟิเคชันด้วยตัวเร่งปฏิกิริยา

แบบของแข็ง

นายทัตพงศ์ ทะนงค์

METHYL ESTERS FROM PALM OLEIN USING SOLID
CATALYZED-TRANSESTERIFICATION REACTION
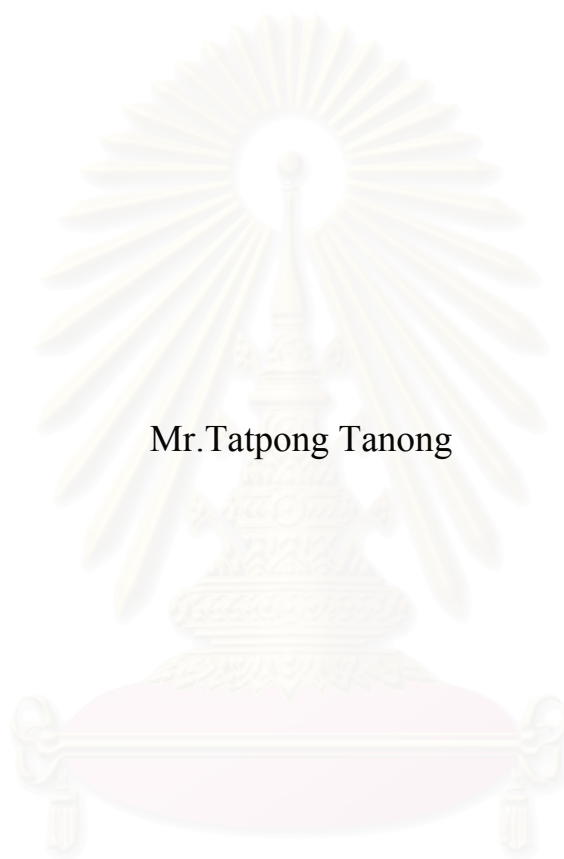
Mr.Tatpong Tanong

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Thesis Title   METHYL ESTERS FROM PALM OLEIN USING
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ทัตพงศ์ ทะนงค์ : เมทิลเอสเทอร์จากน้ำมันปาล์มโอเลอินโดยใช้ปฏิกิริยาทรานส์เอสเทอริฟิ
เคชันด้วยตัวเร่งปฏิกิริยาแบบของแข็ง (METHYL ESTERS FROM PALM OLEIN
USING SOLID CATALYZED-TRANSESTERIFICATION REACTION) อ. ที่ปรึกษา :
อ.ดร.เจิดศักดิ์ ไชยคุนา, 76 หน้า.

งานวิจัยนี้เป็นการศึกษาการเกิดปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมันปาล์มโอเลอิน
โดยใช้ตัวเร่งปฏิกิริยาแบบวิวิธพันธุ์ได้แก่ แคลเซียมออกไซด์ แคลเซียมคาร์บอเนต
แมกนีเซียมออกไซด์ แมกนีเซียมคาร์บอเนตโพแทสเซียมคาร์บอเนตและโซเดียมคาร์บอเนต
การทดลองเป็นแบบกะทำที่ความดันบรรยากาศและอุณหภูมิ 62 องศาเซลเซียสโดยใช้
ปริมาณของตัวเร่งปฏิกิริยาแบบวิวิธพันธุ์ร้อยละ 5 และร้อยละ 10 ตามน้ำหนักของน้ำมันและ
ปริมาณของเมทานอลมากเกินพอคิดเป็น 2 เท่าและ 5 เท่าของกฎทรงมวล เวลาที่ใช้ในการทำ
ปฏิกิริยาคือ 18 ชั่วโมง นอกจากนี้ยังได้ศึกษาเปรียบเทียบปริมาณการเกิดเมทิลเอสเทอร์กับ
ตัวเร่งปฏิกิริยาชนิดเอกพันธุ์ได้แก่โพแทสเซียมไฮดรอกไซด์และโซเดียมไฮดรอกไซด์

จากผลการทดลองพบว่าการใช้ตัวเร่งปฏิกิริยาแบบเอกพันธุ์ให้อัตราการเกิดปฏิกิริยาสูงกว่า
การใช้ตัวเร่งปฏิกิริยาแบบวิวิธพันธุ์ แคลเซียมออกไซด์เป็นตัวเร่งปฏิกิริยาแบบวิวิธพันธุ์ที่มีความ
สามารถสูงสุดในการใช้เป็นตัวเร่งปฏิกิริยาสำหรับปฏิกิริยาทรานส์เอสเทอริฟิเคชันของ
น้ำมันปาล์มโอเลอิน แมกนีเซียมออกไซด์และแมกนีเซียมคาร์บอเนตมีความสามารถใกล้เคียงกัน
ในการใช้เป็นตัวเร่งปฏิกิริยาส่วนแคลเซียมคาร์บอเนตมีความสามารถน้อยที่สุดในการใช้เป็นตัวเร่ง
ปฏิกิริยา ในกรณีของโพแทสเซียมคาร์บอเนตและโซเดียมคาร์บอเนตนั้นถึงแม้ว่าจะสามารถ
ใช้เป็นตัวเร่งปฏิกิริยาได้แต่โพแทสเซียมคาร์บอเนตและโซเดียมคาร์บอเนตละลายในสารตั้งต้นจึง
ไม่สามารถใช้เป็นตัวเร่งปฏิกิริยาแบบวิวิธพันธุ์และเมื่อเพิ่มปริมาณของตัวเร่งปฏิกิริยา
แบบวิวิธพันธุ์จากร้อยละ 5 เป็นร้อยละ 10 ตาม น้ำหนักน้ำมันและเพิ่มปริมาณของเมทานอล
มากเกินพอคิดเป็น 2 เท่าและ 5 เท่าของกฎทรงมวล สามารถเพิ่มปริมาณการเกิดเมทิลเอสเทอร์

ภาควิชา............วิศวกรรมเคมี............ลายมือชื่อนิสิต...
สาขาวิชา............วิศวกรรมเคมี............ลายมือชื่ออาจารย์ที่ปรึกษา.........................
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KEY WORD: TRANSESTERIFICATION / HETEROGENEOUS CATALYSTS / PALM OLEIN

TATPONG TANONG: METHYL ESTERS FROM PALM OLEIN USING SOLID CATALYZED-TRANSESTERIFICATION REACTION.

THESIS ADVISOR: JIRDSAK TSCHEIKUNA, Ph.D., 76 pp.

In this study, transesterification of palm olein using Calcium oxide, Calcium carbonate, Magnesium oxide, Magnesium carbonate, Potassium carbonate and Sodium carbonate as heterogeneous catalysts was investigated. The experiments were conducted in batch system at atmospheric pressure and temperature of 62°C. The amount of catalyst used 5% and 10% by weight of oil. Excess methanol of 2 and 5 times the stoichiometric ratio were used. The reaction time was 18 hours for every experiment. Comparisons of methyl esters production between heterogeneous catalysts and homogeneous catalysts (Potassium hydroxide and Sodium hydroxide) were also investigated.

The results show that homogeneous catalysts are more active than heterogeneous catalysts. The most active of these heterogeneous catalysts was Calcium oxide. Magnesium oxide and Magnesium carbonate show approximately equal activity. Calcium carbonate is the least active catalyst. Potassium carbonate and Sodium carbonate are soluble in the mixtures so they can not be classified as heterogeneous catalyst. Increasing the amount of heterogeneous catalyst from 5% to 10% by weight of oil and increasing excess methanol from 2 to 5 times the stoichiometric ratio result in the increased percentages of methyl esters production.

Department…...Chemical Engineering……Student's signature………………

Field of study…Chemical Engineering……Advisor's signature………………

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CHAPTER I

INTRODUCTION

Fatty acid methyl esters are aliphatic organic esters. They can be produced by transesterification of the natural triglycerides with methanol. Triglycerids are the major components of vegetable oil and the chemical compound formed of one molecule of glycerol and fatty acids. Transesterification reaction can be performed using acid catalyst such as sulfuric, sulfonic, phosphoric and hydrochloric acid, or using base catalysts, such as methal hydroxides, metal alkoxides, alkaline-earth oxides. However, base catalysts are preferred to acid catalysts because of the higher reaction rates and the lower process temperatures as compared to acid- catalyszed transesterification.

Fatty acid methyl esters are used extensively as intermediates in manufacture of detergents, emulsifiers, wetting agents, stabilizers, textile treatments, and waxes among other applications. Lesser volumes of fatty acid methyl esters are used in variety of direct and indirect food additive applications, including the dehydration of grapes to produce resins. Fatty acid methyl esters are also used as the alternative fuel (Biodiesel) and the lubricant.

Nowadays, most industrial applications are performed in batch system or continuous stirrer tank reactor using homogeneous base catalysts such as NaOH and KOH. However, the use of homogeneous base catalysts requires neutralization and separation from the mixture which leads to a series of environmental problems related to the use of high amount of solvent and energy.

Heterogeneous solid catalysts are able to catalyze the transesterification of vegetable oil to alkyl esters. They could solve these problems and can be

easily separated from the mixture. Being easy regeneration and having less corrosive character lead to safer, cheaper and more environmental friendly. It is interesting to investigate the possibility of replacing the homogeneous base catalysts by solid catalysts in transesterification reaction.

There are many studies about transesterification of vegetable oil using heterogeneous catalysts. Gryglewicz (1999) studied the transesterification of rapeseed oil using heterogeneous catalysts at boiling point of methanol. He reported that calcium methoxide can form on the surface of calcium oxide. Calcium methoxide is the real catalyst of the methanolysis of triglycerides because it is slightly soluble in methanol and it acts mainly as heterogeneous catalyst. Suppes et al. (2004) studied the transesterification of soybean oil with methanol using a series NaX faujasite zeolite, ETS-10 zeolite and metal catalysts (such as nickel, calcium carbonate, zinc carbonate, zinc oxide and palladium). He reported that methyl esters yield increased with an increasing in temperature and successfully used ETS-10 zeolite, zinc oxide and nickel in promoting the transesterification of soybean oil with methanol.

It is also a great challenge to explore on the heterogeneous catalysts for the transesterification of vegetable oil. It is believed that the heterogeneous catalysts will replace the homogeneous catalysts in the future because of environmental constraints and simplicity of the process as comparing to the existing one.

The objective of this research is the investigation of heterogeneous catalyst such as CaO, $CaCO_3$, MgO, $MgCO_3$, K_2CO_3 and Na_2CO_3 in transesterification of palm olein with methanol to produce methyl esters.

In this experiment, the transesterification of palm olein with methanol using heterogeneous solid catalysts (CaO, $CaCO_3$, MgO, $MgCO_3$, K_2CO_3 and Na_2CO_3) was investigated at temperature of 62ºC. In addition, the obtained

percentage of methyl esters as a function of time, a comparison between homogeneous (KOH and NaOH) and heterogeneous catalysts, the effect of amount of heterogeneous catalysts and the effect of excess of methanol were investigated.

CHAPTER II

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 oil are in the first section. The second section describes the tranesterification reaction of vegetable oils using homogeneous catalysts. Acid and alkaline-catalyzed in tranesterification are described in this section. The third section describes the tranesterification reaction of vegetable oils using heterogeneous catalysts and the last section refers to the analysis of methyl esters using gas chromatographic method.

2.1 Vegetable oil

Vegetable oil used in this studied was palm olein. Palm olein is the liquid fraction of palm 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 with small amounts of monoglycerides and diglycerides. The fatty acid chains present in the palm olein 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. The chain length of the fatty acids present in triglycerides of palm olein fall within a very narrow from 12 to 20 carbons as shown in Table 2.1.

It can be seen that about 50% of the fatty acids present in palm olein are saturated and about 50% are unsaturated. The three fatty acids in the triglycerides could be represented by the multitude of fatty acids liked in Table 2.1. The different placement of the fatty acids attached to the glycerol

molecule can lead to a large number of different triglycerides as showed in Equation (2.1).

Table 2.1 Fatty acid compositions of palm olein

Abbreviation	Systematic name	Common name	Formular
C12:0	Dodecanoic	Lauric	$C_{12}H_{24}O_2$
C14:0	Tetradecanoic	Myristic	$C_{14}H_{28}O_2$
C16:0	Hexadecanoic	Palmitic	$C_{16}H_{32}O_2$
C16:1	Cis-9-Hexadecenoic	Palmitoleic	$C_{16}H_{30}O_2$
C18:0	Octadecanoic	Stearic	$C_{18}H_{36}O_2$
C18:1	Cis-9-Octadecenoic	Oleic	$C_{18}H_{34}O_2$
C18:2	Cis-9,12-Octadecenoic	Linoleic	$C_{18}H_{32}O_2$
C18:3	Cis-9,12,15-Octadecatetraenoic	Linolenic	$C_{18}H_{30}O_2$
C20:0	Eicosanoic	Arachidic	$C_{20}H_{40}O_2$

3 Fatty acids   Glycerol   Triglyceride   Water
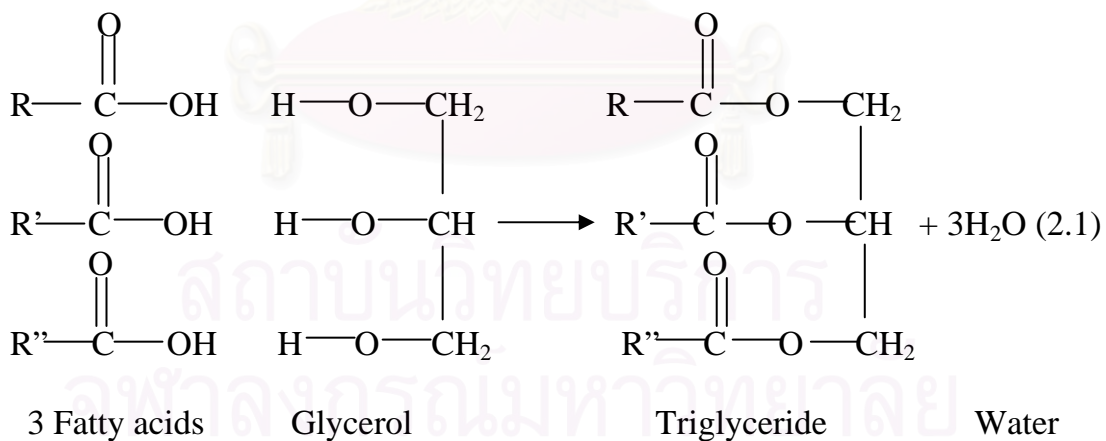
Equation (2.1) Formation of Triglyceride (Exconde, 2003)

2.2 Transesterification of vegetable oil 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 Equation (2.2) is reversible and thus an excess of alcohol is usually used to force the equilibrium to the product side (Mether, 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 Equation (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 (Fukuda, 2001).

$$
\begin{array}{lll}
CH_2\text{-}OOC\text{-}R_1 & & R_1\text{-}COO\text{-}R' \; + \; CH_2\text{-}OH \\
| & \text{catalyst} & | \\
CH\text{-}OOC\text{-}R_2 \; + \; 3R'OH \; \rightleftharpoons & & R_2\text{-}COO\text{-}R' \; + \; CH\text{-}OH \quad (2.2) \\
| & & | \\
CH_2OOC\text{-}R_3 & & R_3\text{-}COO\text{-}R' \; + \; CH_2\text{-}OH \\
\text{Triglyceride} \quad \text{Alcohol} & & \text{Alkyl esters} \qquad \text{Glycerol}
\end{array}
$$
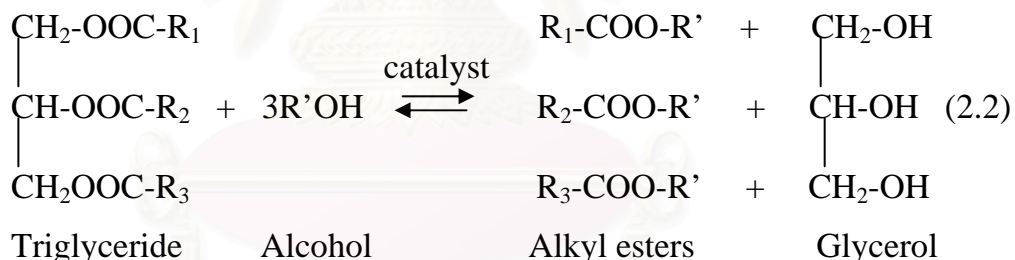
Equation (2.2) General equation of transesterification reaction (Fukuda, 2001)

$$
\begin{array}{lll}
& \text{catalyst} & \\
\text{Triglyceride} \;\; + \; R'OH \; \rightleftharpoons & \text{Diglyceride} & + \; R'COOR_1 \\
& \text{catalyst} & \\
\text{Diglyceride} \;\; + \; R'OH \; \rightleftharpoons & \text{Monoglyceride} \; + \; R'COOR_2 \quad (2.3) \\
& \text{catalyst} & \\
\text{Monoglyceride} \; + \; R'OH \; \rightleftharpoons & \text{Glycerol} & + \; R'COOR_3
\end{array}
$$
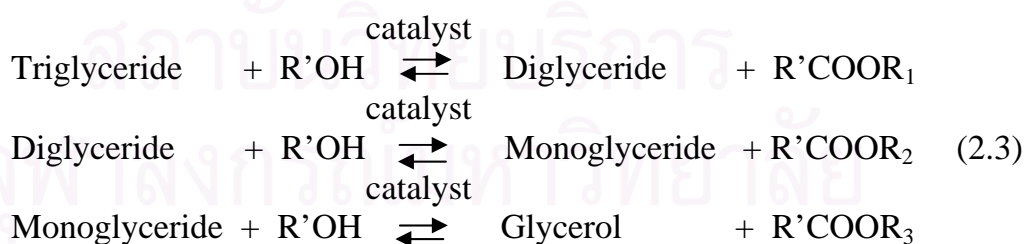
Equation (2.3) Transesterification of triglycerides: three consecutive and reversible reactions. R1, R2, R3 and R' represent alkyl groups (Fukuda, 2001)

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.

2.2.1 Alkaline-catalyzed transesterification

Common alkaline catalysts (such as NaOH and KOH) 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 as showed in Equation (2.4). 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. As can be seen that from Equation (2.5) and Equation (2.6).

$$NaOH \ + \ CH_3OH \ \rightleftharpoons \ CH_3O^- \ + \ H_2O \ + \ Na^+ \tag{2.4}$$

Equation (2.4) Formation of the active species in transesterification reactions using a base catalyst (Gryglewicz, 1999)

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \ + \ NaOH \ \xrightarrow{\text{Heat}} \ R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^+ \ + \ H_2O \tag{2.5}$$
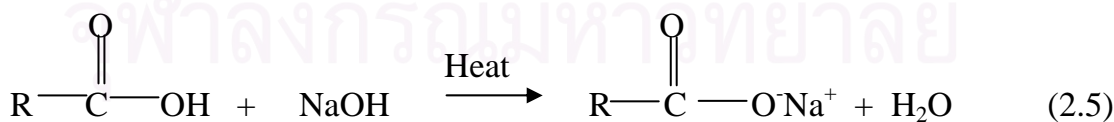
FFA   Metal alkoxide   Salt   Water

Equation (2.5) Saponification reaction from FFA

$$R - \overset{\overset{\displaystyle O}{\|}}{C} - OR' \ + \ NaOH \ \xrightarrow{\text{Water}} \ R - \overset{\overset{\displaystyle O}{\|}}{C} - O^-Na^+ \ + \ R'OH \qquad (2.6)$$

Ester   Metal alkoxide   Salt   Alcohol
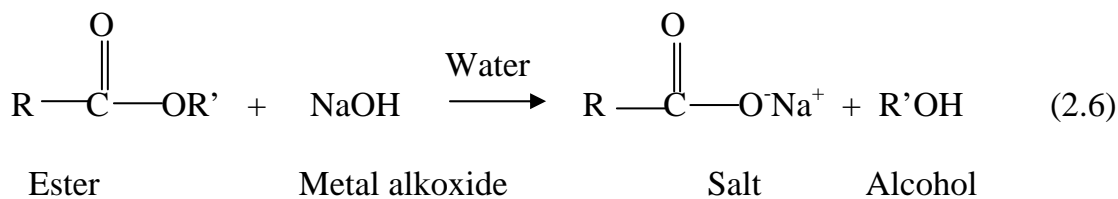
Equation (2.6) Saponification reaction from Ester

The mechanism of alkaline catalyzed transesterification is decribed in Figure 2.1. 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 an alcohol productes the alkoxide ion in the second step. In the last step the rearrangement of the tetrahedral intermediate gives rise to an ester and diglycerides.

The base catalysts NaOH and KOH were used by Muniyappa et al. (1996) for the glycerolysis of triglycerides at concentration ranging from 0.05 to 0.20% wt and at a maximum reaction temperature was 250ºC. It was determined that the key factor limiting the conversion of triglycerides is the degree of solubility between the phases. Saponification promoted the reaction through emulsification of the medium, and temperature increases resulted in an increased mutual solubility of the oil and glycerol phases, leading to faster reaction rates. It was concluded that the reductions in temperature and reaction time were feasible through effective contact between the immisible nonpolar phases.

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Pre-step

$$OH^- \;+\; ROH \;\rightleftharpoons\; RO^- \;+ H_2O$$

$$Or \quad NaOR \;\rightleftharpoons\; RO^- \;+\; Na^+$$

Step.1.

Step.2.

Step.3.

Where R" = CH₂

CH — OCOR'

CH₂ — OCOR'
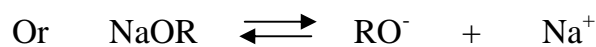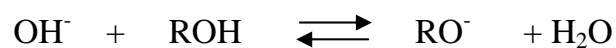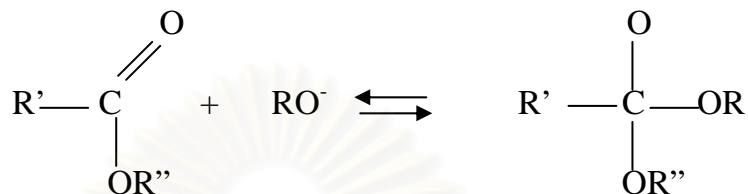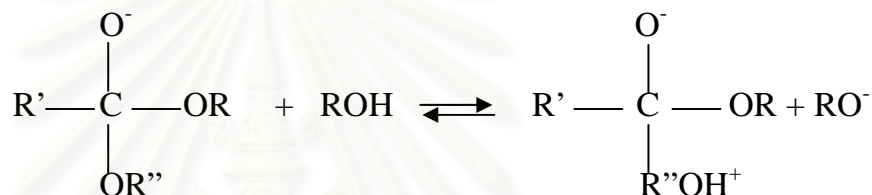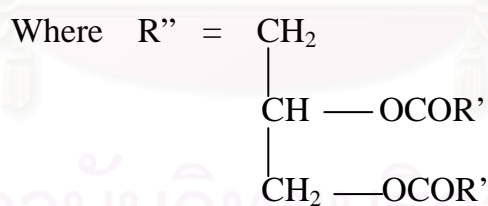
R' = Carbon chain of fatty acid

R = Alkyl group of alcohol

Figure 2.1 Mechanism of base catalyzed transesterification (Meher, 2006)

Tomasevic et al. (2003) studied the transesterification of used sunflower oil (which has an acid value of~4) 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 25ºC, 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.

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.

A pseudo-single-phase methanolysis of soybean oil with THF under basic conditions was studied by MaO et al. (2004) with a methanol to oil molar ratio of 6:1 at temperature of 23ºC. The results showed that the reaction starts as a single phase wherein fast reactions rates were observed, followed by a sudden shift in the reaction brought about by slower reaction rate as a two phase medium was formed. This was attributed to the formation and subsequent separation of a glycerol phase wherein the catalyst was located. The catalyst removal was seen as the major contributor to the deceleration in

the reaction rate; however, the decrease in methanol concentration was also seen as a source of the reaction rate deceleration. Furthermore, the concentration profiles for the homogeneous medium indicated that, toward the end of the reaction, the concentration of triglycerides is lower than concentrations of diglycerides and monoglycerides.

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 (3:1-9:1), the catalyst concentration (0.1%-1.5% wt of oil), the temperature of 25-65ºC, 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 65ºC. 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 of waste cooking oil that has an acid value in the range of 0.42-2.07, using NaOH as acatalyst. The effects of the molar ratio of alcohol to oil (3.6-5.4), the acid value (0.4-2.07), and the sodium hydroxide/frying oil mass ratio (0.2-1.0) 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/oil ratio of 0.6.

Alkaline catalysts (such as NaOH and KOH) can act as effective catalysts for the transesterification of the vegetable oil. The final product yield seems to be dependent on the free fatty acids content of the vegetable oil. Additional alkaline catalyst is required neutralize the free fatty acids of vegetable oil.

2.2.2 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 (for a monoglyceride) is shown in Figure 2.2. 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.

Canaki and Van Gerpen (1999) studied how 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.

Where   R"   =   ⎡—OH; glyceride
                  ⎣—OH

R'   =   Carbon chain of fatty acid

R   =   Alkyl group of alcohol
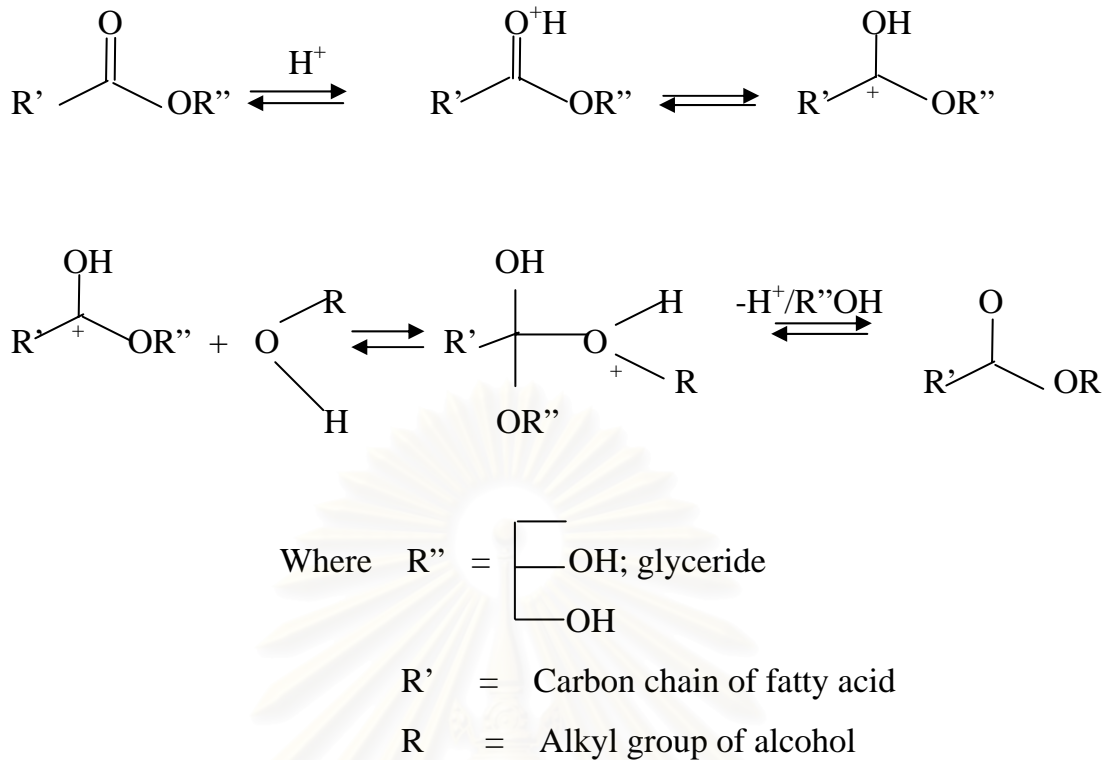
Figure 2.2 Mechanism of acid catalyzed transesterification (Meher, 2006)

Crabbe et al. (2001) investigated acid catalyzed (sulfuric acid) production of methyl ester (biodiesel) 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 3:1-40:1, the effect of amount of catalyst with in the range of 1-5% H_2SO_4 (vol/wt%) and temperature reaction. The optimized variables, 40:1methanol/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%.

AI-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.

Di serio 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 ofcalcium, 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.

2.3 Transesterification of vegetable oil 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, amberlyst-15, dowex, nafion NR 50 and zeolite). 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 proposed reaction mechanism consists of five steps as shown in Figure 2.3. 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 (anion-exchange resin), Amberlyst A27 (anion-exchange resin), Amberlyst 15 (cation-exchange resin), MELCat XZO682/01 (Sulfate doped zirconium hydroxide), MELCat XZO645/01 (Silica doped zirconium hydroxide), TIS (Titanium silicate), TISCOM STC (Titanium chelate), $SnCl_2$, 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.

Step 1-a

$$R—OH \;+\; —Mg—O— \quad\longrightarrow\quad \overset{R}{\underset{—Mg—}{\overset{|}{O^-}}} \;\; \overset{H^+}{\underset{O—}{=}}$$

Step 1-b

$$H_2C—CH_2—O—\overset{\overset{}{||}}{\underset{O}{C}}—CH_3 \;+\; —Mg—O— \quad\longrightarrow\quad H_3C—CH_2—O—\overset{}{\underset{—Mg—O—}{\overset{|}{C^+}}}—O—CH_3 \;\; \overset{}{\underset{}{O^-}}$$

Step 2

$$H_3C\text{-}CH_2\text{-}O\text{-}C^+\text{-}CH_3 \;\; R \qquad\qquad \overset{CH_3}{H_3C\text{-}CH_2\text{-}O\text{-}\underset{}{C}\text{-}O\text{-}R}$$

$$\underset{—Mg—O—Mg—O—}{O^- \quad O\text{-} \quad H^+} \quad\longrightarrow\quad \underset{—Mg—O—Mg—O—}{O^- \qquad\qquad H^+}$$

Step 3

$$\overset{CH3}{H_3C\text{-}CH_2\text{-}O\text{-}\underset{}{C}\text{-}O\text{-}R} \qquad\qquad \overset{H_3C—\underset{O}{\overset{||}{C}}\text{-}R}{}$$

$$\underset{—Mg—O—Mg—O—}{O^- \qquad\qquad H^+} \quad\longrightarrow\quad \underset{—Mg—O—Mg—O—}{H_3C\text{-}CH_2\text{-}O\text{-} \qquad\qquad H^+}$$

Step 4

$$H_3C—CH_2—O \qquad\qquad\qquad \overset{H_3C—CH_2—OH}{}$$

$$\underset{—Mg—O—Mg—O—}{= \qquad\qquad H^+} \quad\longrightarrow\quad —Mg—\;\;—O—$$
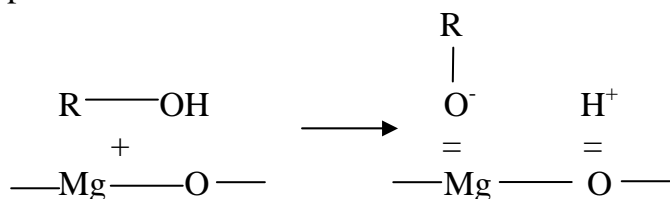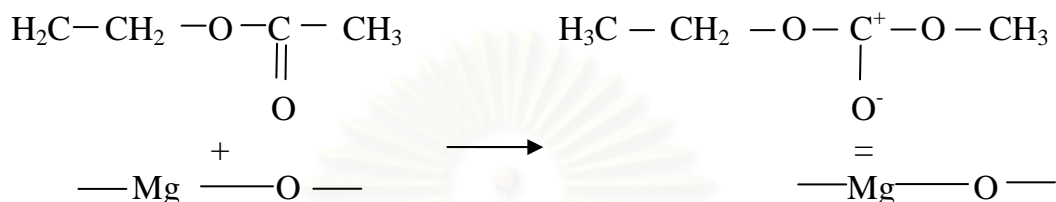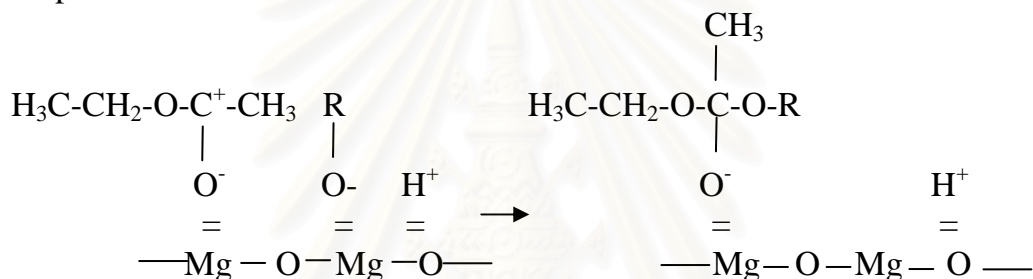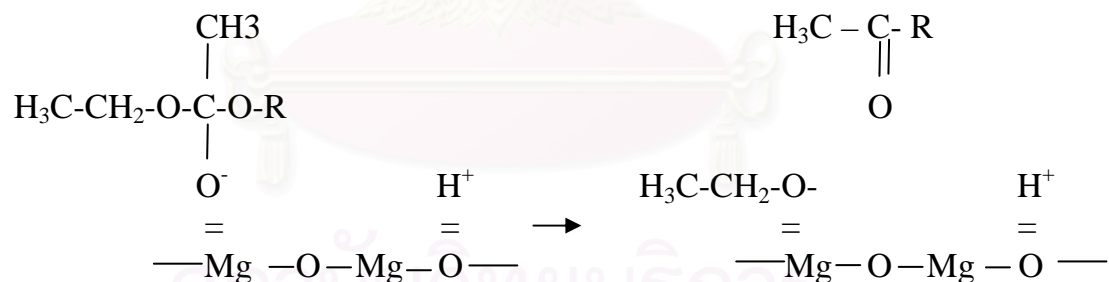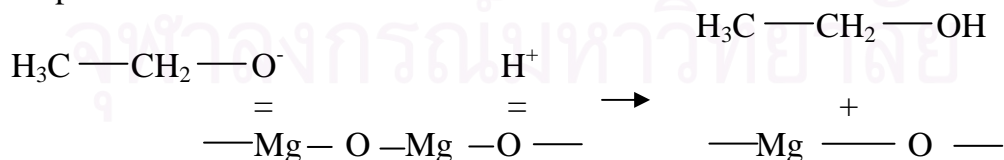
Figure 2.3 Reaction mechanisms for the transesterification of ethyl acetate

with alcohol catalyzed by solid catalyst proposed by Dossin et al.

(2005)

Gryglewicz (1999) showed that 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 (2003) studied the transesterification 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: (1) the temperature was 65-70°C, atmospheric pressure, 20:1 methanol to oil molar ratio, and a reaction time of 10 hours. (2) the temperature was 200°C at 50 bar, 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 60-70°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 ester content) at temperature of 200°C, pressure of 50 bar, 20:1 methanol to oil molar ratio, and a reaction time of 4 hours.

Ebiura et al. (2004) studied the transesterification of triolein (trioleoy glycerol) with methanol to methyl oleate and glycerol could be achieved at around 333 K 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. A K_2CO_3 loaded alumina catalyst prepared by evacuation at

823 K gives methyl oleate and glycerol in the highest yields of 94 and 89%, at 333 K in 1 hour.

Kim et al. (2004) studied the production of biodiesel from soybean oil using heterogeneous catalyst (Na/NaOH/γ-Al$_2$O$_3$). 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-Al$_2$O$_3$, 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.

Suppes et al. (2004) studied the transesterification of soybean oil with methanol using a series NaX faujasite zeolite, ETS-10 zeolite and metal catalysts. A 6:1 molar ratio of alcohol was used in this experiment. The reaction was carried out at temperature of 60, 120 and 150ºC. The stock zeolites were exchanged with potassium and cecium; NaX containing occluded sodium oxide (NaOx/NaX) and occluded sodium azide (naOx/Nax*). The catalysts were calcined at temperature of 500ºC prior to use in order to increase activity. The ETS-10 catalysts provided higher conversions than the zeolite-x type catalysts. The increased conversions were attributed to the higher basicity of ETS-10 zeolites and large pore structures that improved intra-particle diffusion. After calcinations ETS-10 zeolites exhibiting conversions greater than 90% in transesterification at temperature of 120 and 150ºC for 24 hours. Methyl ester yield increase with increase in temperature from 60 to 150ºC.

Zinc oxide and nickel showed 80% and 53% conversions in transesterification at temperature of 120ºC for 24 hours with out calcinations.

Dossin et al. (2005) investigated the transesterification of ethyl acetate with methanol over magnesium oxide as solid base catalyst. Intrinsic kinetic data have been obtained in a perfectly mixed slurry batch reactor. The influence of the temperature (283-323 K) and the initial methanol to ethyl acetate molar ratio (M/E: from 0.1-10) was investigated over a broad ethyl acetate conversion range (1-95%). A kinetic model was developed based on three-step 'Eley-Rideal' type of mechanism applied liquid phase, describing the experimental data over the investigated range of experimental conditions. Transesterification reaction occurs between methanol adsorbed on a magnesium oxide free basic site and ethyl acetate from the liquid phase. Methanol adsorption is assumed to be rate-determining. Other models derived from other mechanisms were rejected based on statistical analysis, mechanistic considerations and physicochemical interpretation of the parameters. The calculation of activity coefficients accounting for non-ideality had to be incorporate in the parameter estimation procedure.

Lopez et al. (2005) investigated the kinetics and selectivities of different solid catalysts for the transesterification of triacitin (a model compound for larger triglycerides as found in vegetable oils and fats) with methanol. Reaction was carried out at temperature of 60°C in a batch reactor with a variety of solid and liquid, acid and base catalyst. The homogeneous phase (i.e. liquid) catalysts (NaOH and H_2SO_4) were studied for comparison. Amberlyst-15, Nafion NR50, sulfated zirconia, and ETS-10 (Na, K) showed reasonable activities. The following conclusions can be draw from this study: (1) homogeneous catalyst were more active than heterogeneous ones on a weight basis, (2) ETS-10 exhibited probable homogeneous catalysis as the alkali methoxide species were leach out, (3) the solid acids studied underwent less deactivation than ETS-10 (Na,K) under this experimental conditions, (4)

internal mass transfer limitation may have severely limited the performance of microporous heterogeneous acid catalysts, such as ETS-10 (H) and zeolite Hß,(5) Amberlyst-15, Sulfate modified zirconia (SZ), Nafion NR50 and Tungsta modified zirconia (WZ) showed reasonably good activities at this moderate temperature (60°C), indicating that there are suitable alternatives to the homogeneous catalysts without the drawbacks of corrosion, difficulty in handling, and once through use provided more mass of catalyst is used, and finally (6) on a site basis SZ exhibited the same activity as sulfuric acid, suggesting that, since their acid strengths are similar, probably follow similar reaction mechanism.

Xie et al. (2006) studied the transesterification of soybean oil to methyl esters using alumina loaded with potassium as a solid base catalyst. The catalyst with 35% wt KNO_3 loaded on Al_2O_3 and after calcinated at 773 K for 5 hours was found to be optimum catalyst, which can give the highest basicity and the best catalytic activity for this reaction. When the reaction was carried out at reflux of methanol, with a molar ratio of methanol to soybean oil of 15:1 a reaction time 7 hour, and a catalyst amount 6.5% wt of oil, the highest conversion reached 87%. The catalytic activities of the heterogeneous base catalysts show a striking correlation with their corresponding basic properties. The decomposition products of the loaded KNO_3, forming either K_2O species or AL-O-K group in the composite, were probably the active site.

Heterogeneous catalysts able to catalyzed in transesterification of vegetable oil. Many heterogeneous catalysts were effective such as ETS-10, ZnO, CaO, Amberlyst-15 and KNO_3 loaded on Al_2O_3. They can be easily separated from the reaction mixture. Show easy regeneration and have corrosive character, leading to safer and more environmental friendly operation.

2.4 Analysis of methyl esters using gas chromatographic method

Chromatography has grown to be the premiere method for separating closely related chemical species. In addition, it can be employed for quanlitative identification and quantitative determination of separated species.

Freedman et al. (1984) studied the quatitation in the analysis of transesterified soybean oil by capillary gas chromatography. Standard solutions are containing of methyl linoliate. Mono-, di- and trilinolein were analyzed with a 1.8 m x 0.32 mm SE-30 fused silica column. The effect of carrier gas flow on reproducibility was determined. Prior to analysis, mono- (MG) and diglycerides (DG) were silylated with N, O-bis(trimethylsilyl) trifluoroacetamide. Tridecanoin was used as an internal standard. From plots of area and weight relationships, slopes and intercepts for all four compound classes were determined. Agreement between the measured and calculated compositions of the standard solutions was good; the the overall standard deviations was 0.4. Slopes and inter cepts also were determined for soybean oil and its methyl and buthyl esters. Complete separation of ester, MG, DG and triglyceride was obtained in 12 min by temperature programming from temperature of 160-350ºC. This method of analysis gave excellent results when used in a kinetic study of soybean oil transesterification.

Mittelbatch et al. (1993) have prepared the sample by mixing 100-500 µl rapeseed methyl ester (depending upon glycerol content) with 100 µl of 1, 4-butanediol standard solution in N, N-dimethylformamide (approximately 0.1 mg 1,4-butanediol/ml) and 600-200 µl of N,N-dimethylformamide. Finally 200 µl of bis-trimethylsilyl trifluoroacetamide is added to reach the final volume of 1 ml, the mixture was shaken vigorously and 2 µl aliquots were inject in gas chromatography after at lease 10 min. It is necessary to use fresh bis-trimethylsilyl trifluoroacetamide reagent to guarantee quantitative

derivatization. The gas chromatography capillary column used was fused silica, 60 x 0.25 mm, 0.25 µm DB-5 (Jand W Scientific Inc.).

Plank and Lorbeer (1995) developed a gas chromatographic procedure for the simultaneous determination of glycerol, mono-, di- and triglycerides in vegetable oil methyl esters. Quantitative information about this group of organic contaminants is very important for the quality of these oleochemical products when used as automotive diesel fuel substitutes. Trimethylsilylation of glycerol, mono- and diglycerides, followed by GC using a 10-m capillary column coated with a 0.1-/xm film of DB-5 allows the determination of all analytes in a single GC run. Calibration is performed by analysis of standard solutions containing glycerol, mono-, di- and triolein as well as two internal standards, 1, 2, 4-butanetriol and tricaprin. The recovery of the procedure at different concentration levels and the repeatability of the quantitative results are evaluated.

CHAPTER III

EXPERIMENTAL AND ANALYTICAL METHODS

The preparations of the experiment and analytical methods are described in this chapter. It is divided into four sections. The first section concerns with the materials. The second part describes the equipment of this experiment. The third section describes the method of the transesterification of vegetable oil and the last section refers to an analytical method and errors of the experiments.

3.1 Materials

3.1.1 Palm olein

Vegetable oil used in this studied was palm olein. The palm olein was a commercial grade available in supermarket: Oleen brand, Palm oleen CO, ltd.

3.1.2 Chemicals

All chemicals used in the experiment are shown in Table 3.1. They are used without further purification.

Table 3.1 Chemicals used in the research of palm olein with methanol

Name	Source	Purity
Methanol	Fisher Scientific	99.8% (analytical reagent grade)
Sodium hydroxide	Ajax Chemicals	98%(analytical reagent grade)
Potassium hydroxide	Ajax Chemicals	85%(analytical reagent grade)
Sodium carbonate	Riedel-deHaen	99.5-100% (anhydrous, puriss)
Potassium carbonate	Riedel-deHaen	98-100% (purifined)
Calcium carbonate	Riedel-deHaen	≥ 98.5 (precipitated, puriss)
Calcium oxide	Ajax Chemicals	96% (laboratory reagent)
Magnesium oxide	Sigma-Aldrich	$\geq$99% (-325 mesh)
Magnesium carbonate basic	Riedel-deHaen	$\leq$60% (light, powder, purum, $\geq$ 40% Mg (as MgO))
Methyl palmitate	Acros	95%
Oleic acid	Aldrich	90%
Stearic acid	Sigma-Aldrich	95%
Tetrahydrofuran	Fisher Scientific	99.99% (analytical reagent grade)

3.2 Equipment

3.2.1 Transesterification of palm olein

A one-necked flask equipped with a reflux condenser and thermometer are used in this experiment. The flask is immersed in a constant temperature-water-bath and a magnetic stirrer is used to provide agitation. The experiment set-up is shown in Figure 3.1.
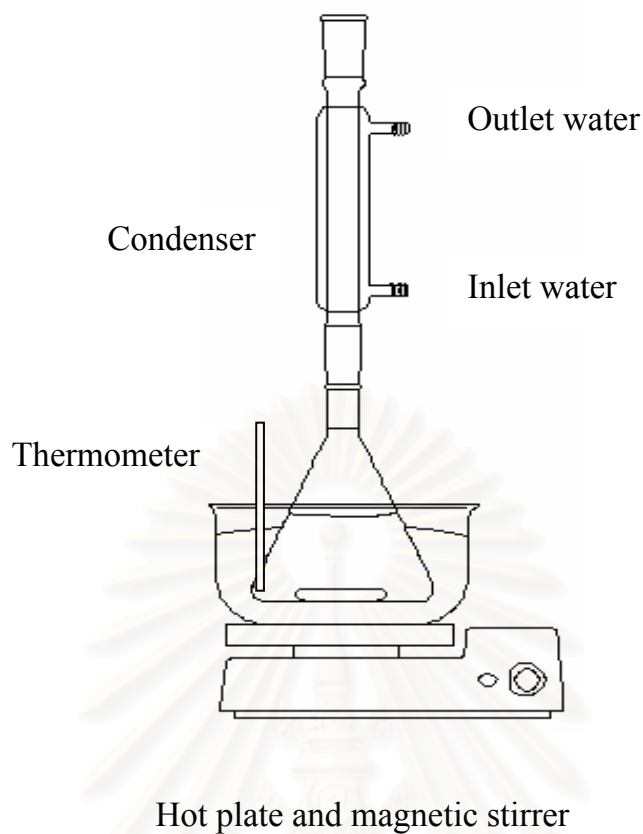
Figure 3.1 The experimental set-up

3.3 Methodology

3.3.1 Characterization of palm olein

Palm olein are analyzed based on density and kinematic viscosity at temperature of 40°C (ASTM D445), free fatty acid content, acid value and sponification value (AOCS Ca 5a-40).

3.3.2 Investigation tests of homogeneous and heterogeneous catalysis
transesterification

Heterogeneous catalysis

1. All heterogeneous catalysts are calcined at temperature of 400°C for
   5 hours.
2. Commercial grade palm olein is refined again to reduce water.
   This can be accomplished by heating to above 100°C to boil off the
   water.
3. A 1000 ml one necked glass flask with a reflux condenser which
   avoids methanol and THF losing is charged with a 300 g (0.374 mol,
   calculated from the average molecular weight of the palm olein) of
   palm olein, 100% wt excess methanol from its stoichiometric ratio,
   10% wt of heterogeneous catalysts and THF added to the flask. The
   mutual solubility of methanol, palm olein and THF are shown in
   Figure3.2.
4. The reactions are carried out at temperature of 62°C under stirring at
   750 rpm.
5. Every 3 hours, about 10 ml of the flask's contents are collected for
   chromatography analysis.
6. The samples are seperated by means centrifuge and purified by
   distilling the residual methanol and THF at temperature of 67°C.
7. The remaining catalyst is extracted by successive rinses with water.
8. The water present is eliminated by heating to above 100°C to boil off
   water.

Homogeneous catalysis

1. Commercial grade palm olein is refined again to reduce water content, this can be accomplished by heating to above 100ºC to boil off the water.

2. A 1000 ml one necked glass flask with a reflux condenser to avoid methanol loses is charged with a 300 g of palm olein, 100% mol excess methanol from its stoichiometric ratio and homogeneous catalysts (0.556% wt for KOH and 0.54% wt for NaOH) are added to the flask.

3. The reactions are carried out at temperature of 62°C under stirring at 750 rpm.

4. Every 3 hours about 10 ml of the flask's contents are collected for gas chromatography analysis.

5. The reaction mixture will separate into an upper layer of methyl esters and a lower layer of glycerol.

7. The catalyst is extracted by successive rinses with water.

8. The water presence is eliminated by heating to above 100°C to boil off water.

3.3.3 Transesterification of vegetable oils using heterogeneous catalysts

1. All heterogeneous catalysts are calcined at temperature of 400°C for 5 hours.

2. Commercial grade palm olein is refined again to reduce water. This can be accomplished by heating to above 100ºC to boil off the water.

3. A 250 ml one-necked glass flask with a reflux condenser is used in transesterification of palm olein to fatty acid methyl esters. A 50 g of palm olein, different excess of methanol (100% mol and 400% mol excess methanol from its stoichiometric ratio), different amount

of catalyst (5% wt and 10% wt of oil) and THF are added to the flask. The conditions are described again in Table 3.2.

4. The reactions are carried out at temperature of 62°C under stirring at 750 rpm for 18 hours.

5. Samples are taken out from the reaction.

6. The samples are seperated by mean centrifuge and purified by distilling the residual methanol and THF at 67°C.

7. The remaining catalyst is extracted by successive rinses with water.

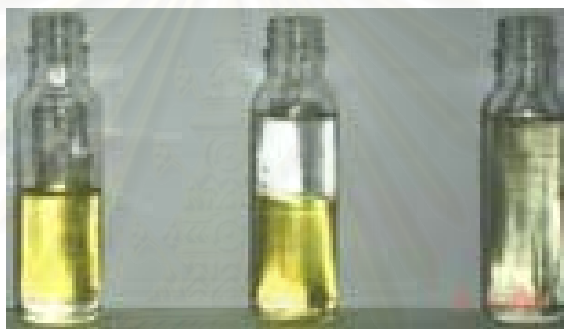8. The water presence is eliminated by heating to above 100°C to boil off water.

Oil   Methanol+Oil   Methanol+Oil+THF

Figure 3.2 The mutual solubility of methanol, palm olein and THF

Table 3.2 Conditions used in transesterification of palm olein using heterogeneous catalyst

Catalyst	Amount of catalyst (% base on weight of oil)	Excess of methanol (% mol) (base on its stoichiometric ratio)
Calcium oxide	5	100
Calcium oxide	10	100
Calcium oxide	10	400
Calcium carbonate	5	100
Calcium carbonate	10	100
Calcium carbonate	10	400
Magnesium oxide	5	100
Magnesium oxide	10	100
Magnesium oxide	10	400
Magnesium carbonate	5	100
Magnesium carbonate	10	100
Magnesium carbonate	10	400
Potassium carbonate	5	100
Potassium carbonate	10	100
Potassium carbonate	10	400
Sodium carbonate	5	100
Sodium carbonate	10	100
Sodium carbonate	10	400

3.3.4 Analysis of methyl esters

The methyl esters samples are analyzed by with a Perkin elmer 8700 gas chromatograph equipped with a flame ionization detection system. Seperations are carried out on an OV-5 fused silica column (30 m x 0.32 mm x 0.25 micron; Ohio Valley, Marietta, Ohio). The operating conditions are the following: The temperatures of injector and detector are set at temperature of 310ºC. The oven temperature program started at temperature of 120ºC, ramped at 1ºC/min to temperature of 130ºC, ramped at 15ºC/min to temperature of 200ºC, and then ramped at 10ºC/min to temperature of 310ºC (5 min). The split ratio was 1:2 and carrier gas used was helium. Samples of 0.5 g were dissolved in 1.5 g of THF and 0.5 µl of these was injected into the column. Standard calibration curves allowed the peak areas of the components divided by peak area for THF to be directly converted into concentration.

3.4 Experimental and Analytical error

Experimental error

In this section, the experiments are conducted to verify repeatability, an average, and a standard deviation value of the experiment. Equation (3.1) and Equation (3.2) define an average value and percent deviation respectively.

$$\text{Average value, } \overline{X} \;=\; \frac{\sum x}{n} \qquad\qquad (3.1)$$

$$\text{Standard deviation from average value} \;=\; \sqrt{\frac{\sum\left(X-\overline{X}\right)^2}{n}} \qquad\qquad (3.2)$$

Three experiments are performed at temperature of 62ºC for 24 hours. The reaction mixture had a 300 g of palm olein, 100% mol excess of methanol from its stoichiometric ratio, THF used as the co-solvent to form a single phase and calcium oxide as a catalyst (10% by weight of oil). The percentages of methyl esters are measured as a function of time. The experimental results, average results and maximum deviation results are shown in Table 3.3.

Table 3.3 Average percents of methyl esters and percent deviation on experiment of transesterification of palm olein with methanol

Time (hours)	Methyl esters (% wt)					Average deviation (% wt)
	Exp. No.1	Exp. No.2	Exp. No.3	Average (% wt)	Deviation from mean (% wt)	
3	4.84	4.70	4.67	4.74	0.08	
6	10.43	8.35	10.04	9.60	0.90	
9	20.75	18.47	17.01	18.74	1.54	
12	39.61	24.16	28.83	30.87	6.47	
15	82.10	60.35	65.20	69.22	9.32	3.70
18	74.98	67.89	68.85	70.57	3.14	
21	73.40	69.88	62.75	68.68	4.43	
24	75.46	77.55	68.91	73.97	3.68	

The results show that the maximum and average experimental error is approximately 9.32% wt and 3.70% wt
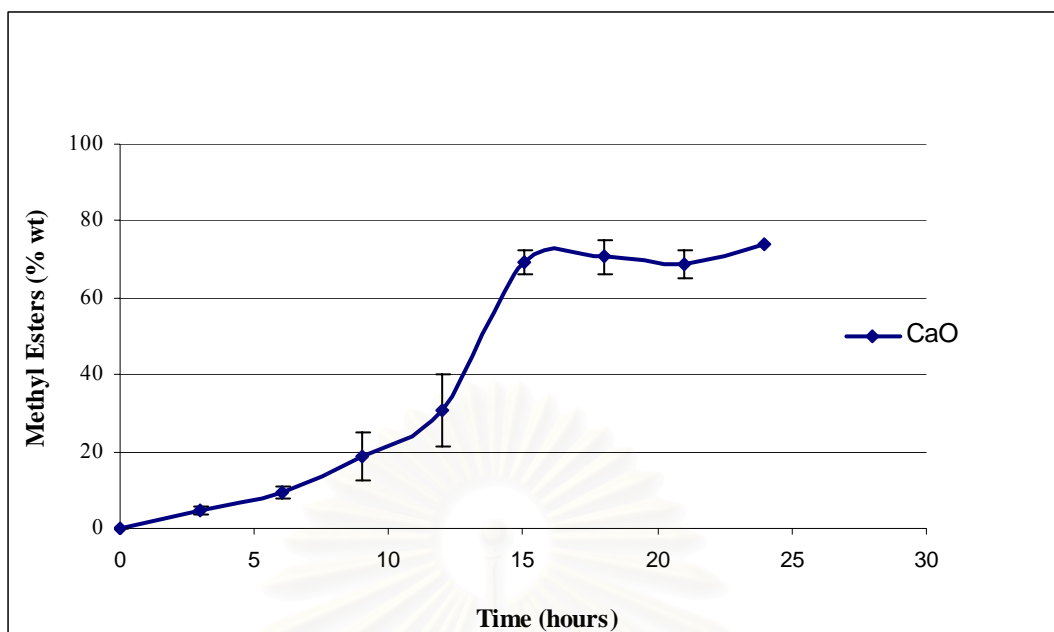
Figure 3.3 Percent deviation from mean on experiment of transesterification of
palm olein with methanol

Analytical error

In this section, the experiment is conducted to verify analytical error,
average and deviation of experiment. Samples of the transesterification of
palm olein with methanol at temperature of 62ºC for 18 hours, 100% excess
methanol from its stoichiometric ratio, THF used as the co-solvent to form a
single phase, magnesium oxide as a catalyst (10% by weight of oil) and
reaction time of 24 hours are analyzed by gas chromatography. The same
sample has been analyzed for 3 times by gas chromatography at the same
condition. Average percentage of methyl esters and deviation of this analysis
are shown in Table 3.4.

Table 3.4 Average percentage of methyl esters and percents deviation from the
analysis of transesterification of palm olein with methanol

Methyl esters (% wt)			Average (% wt)	Deviation from mean (% wt)
Analysis No.1	Analysis No.2	Analysis No.3		
16.04	13.22	16.44	15.23	1.43

The result shows that the percents deviation of methyl esters analysis is
1.43% wt.

CHAPTER IV

RESULTS AND DISCUSSIONS

Transesterification of palm olein with methanol using homogeneous and heterogeneous catalysts are described in this chapter. KOH and NaOH are used as homogeneous catalysts. CaO, $CaCO_3$, MgO, $MgCO_3$, K_2CO_3 and Na_2CO_3 are used as heterogeneous catalysts. Conditions for each experiment are summarized in Table 4.3. Discussion of the results is divided into six parts:

4.1 Characterization of palm olein.

4.2 Homogeneous and heterogeneous catalysts for transesterification.

4.3 Effect of reaction time on transesterification catalyzed by calcium oxide.

4.4 Effect of the amount of heterogeneous catalysts.

4.5 Effect of the excess of methanol on transesterification catalyzed by heterogeneous catalysts.

4.6 Comparison between homogeneous and heterogeneous catalysis.

4.1 Characterization of palm olein

Palm olein used in this study was a commercial grade available in supermarket. It is analyzed in our laboratory and the analysis results are summarized in Table 4.1. The result shows a small value of acid value and it can be confirmed that palm olein is a vegetable oil which contains a small amount of free fatty acid.

Table 4.1 Properties of palm olein

Identity characterization	Palm olein
Density at 40ºC, g/ml	0.9055
Viscosity at 40ºC, cP	36.8
Free fatty acid (as palmitic acid), %	0.26
Acid value, mg KOH/g	0.56
Saponification value, mg KOH/g oil	210
Molecular weight	802
Color	Clear yellow liquid

In this study, the fatty acid compositions can be analyzed in term of fatty acid methyl esters. Fatty acid compositions of palm olein are shown in Table 4.2. The major components of palm olein are oleic acid, palmitic acid, linoleic acid and stearic acid.

Table 4.2 Fatty acid compositions of palm olein

Fatty acid	Palm olein, % wt
Palmitic acid, C16:0	36.69
Stearic acid, C18:0	4.30
Oleic acid, C18:1	49.23*
Linoleic acid, C18:2	

* Oleic acid and linoleic acid can not be individually identified.

4.2 Homogeneous and heterogeneous catalysts for transesterification

According to this test, transesterification reaction of palm olein and methanol is conducted on both heterogeneous and homogeneous catalysts. The experiments are conducted at different operating conditions as indicated in Table 4.3. The reaction is carried out at temperature of 62ºC and at atmospheric pressure.

The samples are analyzed by gas chromatography. The peak area is used for calculation of methyl esters concentration. The percentages of methyl esters is defined as a ratio of weight of methyl esters, which is determined by using GC, to weight of sample as shown in Equation (4.1).

$$\text{Methyl esters (\% wt)} = \frac{\text{weight of methyl esters (determined by GC) x100}}{\text{weight of sample}} \quad (4.1)$$

Table 4.3 Transesterification of palm olein with different catalysts

Catalyst	Type of catalyst	Amount of catalyst (% wt)	Excess of methanol (% mol) (base on its stoichiometric ratio)
KOH	Homogeneous	0.556	100
NaOH	Homogeneous	0.54	100
CaO	Heterogeneous	5	100
		10	100
			400
$CaCO_3$	Heterogeneous	5	100
		10	100
			400
MgO	Heterogeneous	5	100
		10	100
			400
$MgCO_3$	Heterogeneous	5	100
		10	100
			400
K_2CO_3	Heterogeneous	5	100
		10	100
			400
Na_2CO_3	Heterogeneous	5	100
		10	100
			400

4.2.1 Homogeneous catalysis

Several researches are indicated that KOH and NaOH were effective homogeneous catalysts for transesterification. In the characterization of palm olein, is showed that it contains 0.26% wt of fatty acid so that KOH and NaOH can be used in the neutralization. The amount of KOH and NaOH needed to neutralize are determined. The values of KOH and NaOH needed to neutralize 100 g of palm olein are 0.056 g and 0.04 g respectively. In order to account this effect, the amount of KOH and NaOH are corrected by adding the amount needed for neutralization and the amount of KOH and NaOH as catalyst. The 0.5% wt KOH and NaOH as catalyst are chosen to be appropriate in the reaction. The amount of KOH and NaOH are 0.556 g and 0.54 g respectively used as catalyst for 100 g of palm olein. The reactions are carried out at temperature of 62ºC, 100% wt excess methanol from its stoichiometric ratio and the results are shown in Table 4.4 and Figure 4.1.

As it can be observed, the reaction is very fast. After 3 hours, the percentages of methyl esters are in the range between 66-78% wt and 61-77% wt for KOH and NaOH respectively. The reaction seems to be in equilibrium. These results are similar to those found in the literature. In this way, Gryglewicz (1999) obtained high yield of methyl esters from methanolysis of rapeseed oil using NaOH as catalyst. Also, in methanolysis of sunflower oil, Antolin et al. (2002) and Vicente et al. (1998) obtained high yield of methyl esters using KOH and NaOH as catalyst. Leung and Guo (2006) obtained high yield of methyl esters from methanolysis of used frying oil using KOH and NaOH as catalyst.

Table 4.4 Percentages of methyl esters as a function of time in transesterification of palm olein with methanol using homogeneous catalyst

Reaction time (hours)	Methyl esters (% wt)	
	KOH	NaOH
3	74	61
6	77	73
9	68	63
12	78	76
15	70	71
18	66	76
21	74	73
24	67	77

In the case of alkaline catalysis, the literature presents several studies relating to these processes. In each case, the more suitable catalyst depends on the type of oil utilization, the more effective action can be shown. The result showed that KOH and NaOH perform well.

In transesterification, the effective specie of catalysis is the methoxide radicals (CH_3O^-). The activity of a catalyst depends on the amount of methoxide radicals which is available for the reaction. For sodium and potassium hydroxide, methoxide ion is prepared by reacting of hydroxide with methanol as shown in Equation (2.3).

$$NaOH \quad + \quad CH_3OH \quad \rightleftharpoons \quad CH_3O^- \quad + \quad H_2O \quad + \quad Na^+ \qquad (2.3)$$
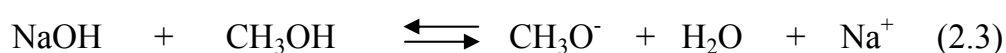
Because of the difference in the chemical molecular weights, the amount of methoxides which are available for each mole of triglyceride will differ at the same weight concentration. Therefore, the proper comparison of the

effectiveness of catalysts should be conducted on the molar concentration of the catalyst formulation, not weight concentration.

Although, chemical transesterification using an alkaline catalysis process gives high percentages of methyl esters, the reaction has several drawbacks: the alkaline has to be removed from the product and alkaline waste water required treatment.
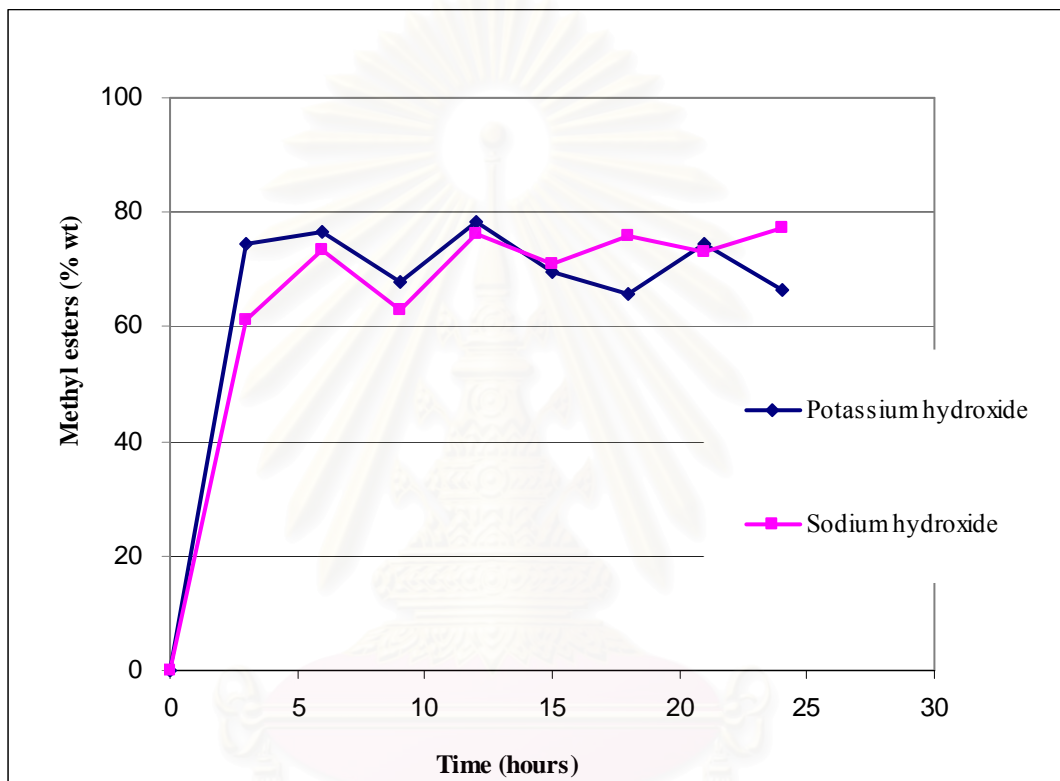

Figure 4.1 Percentages of methyl esters as a function of time in transesterification of palm olein with methanol using homogeneous catalysts

4.2.2 Heterogeneous catalysis

In this study, the processes are carried out at temperature of 62ºC, 100% mol excess methanol from its stoichiometric ratio and using a 10% of the catalyst (based on the weight of palm olein). The addition of THF in purpose of eliminating the interface and the mass transfer barrier to form a single phase in which methanol, oil, and THF are mutually soluble. The results are shown in Table 4.6 and Figure 4.2. The solubility of heterogeneous catalysts is summarized in Table 4.5.

Table 4.5 The solubility of heterogeneous catalysts in methanol

Catalyst	CaO	$CaCO_3$	MgO	$MgCO_3$	K_2CO_3	Na_2CO_3
Solubility in methanol (%)	0.636	0.59	1.71	1.48	39.34	18.09

The result shows that MgO, $MgCO_3$, CaO and $CaCO_3$ were slightly soluble in methanol more than Na_2CO_3 and K_2CO_3.

As it can be seen, K_2CO_3, CaO and Na_2CO_3 are the most active catalysts whereas MgO, $MgCO_3$ and $CaCO_3$ have low performance.

K_2CO_3 can catalyze the transesterification of palm olein and has a good percentage of methyl esters. K_2CO_3 showed 93% wt methyl esters after 15 hours. However, K_2CO_3 could not be use as heterogeneous catalyst since K_2CO_3 is highly soluble in methanol.

Na_2CO_3 is considered that it is effective in the catalyzed reaction. Na_2CO_3 showed 56% wt of methyl esters after 24 hours as a reaction time. However, Na_2CO_3 is highly soluble in methanol.

Table 4.6 Percentages of methyl esters as a function of time in transesterification of palm olein with methanol using heterogeneous catalyst

Reaction time (hours)	Methyl esters (% wt)					
	CaO	$CaCO_3$	MgO	$MgCO_3$	K_2CO_3	Na_2CO_3
3	5	2	4	7	70	22
6	10	3	7	10	80	29
9	19	3	8	8	84	29
12	31	3	9	8	91	33
15	69	2	11	9	92	35
18	71	3	11	9	83	48
21	69	3	9	10	82	51
24	74	3	10	10	73	57

MgO showed 10% wt of methyl esters after 24 hours. According to the data of Vicente (1998) and Gryglewicz (1999), Vicente showed 11% conversion of MgO from transesterification of refined sunflower oil with methanol at temperature of 60ºC for 18 hours and methanol to oil molar ratio of 6:1 and Gryglewicz (1999) reported that it was low or no activity using MgO in transesterification reaction performed at boiling point of methanol due to its weak basic property. It was confirmed in this study that MgO has low performance.

$MgCO_3$ was tested in this study and showed an activity near to MgO (10% wt of methyl esters after 24 hours). The results are shown in Figure 4.2.

In this study, the lowest of an effective heterogeneous catalyst in transesterification reaction of palm olein and methanol was $CaCO_3$. It showed percentage of methyl esters lower than 10% wt for 24 hours,whereas, Suppes who reported that 1.7% wt of methyl esters using $CaCO_3$ in transesterification reaction of soybean oil with methanol at temperatures of 120ºC for 24 hours with out calcinations.
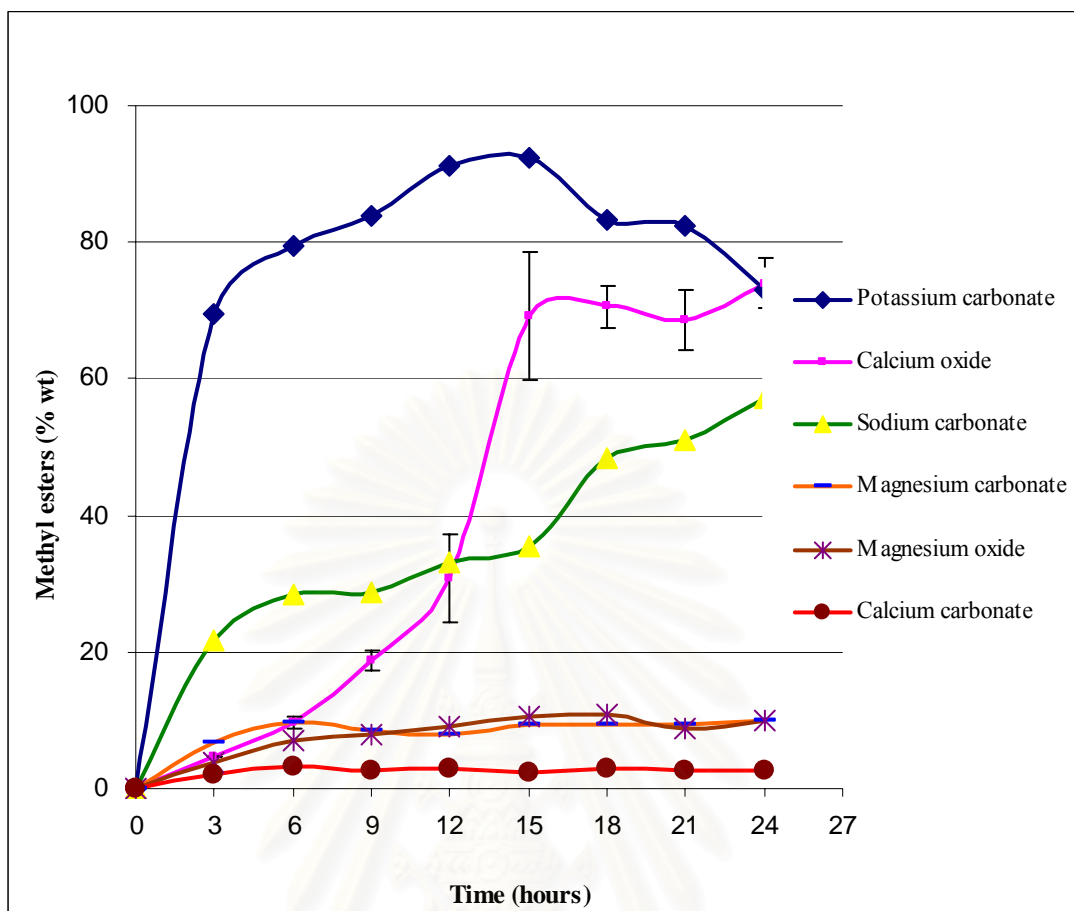
Figure 4.2 Percentages of methyl esters as a function of time in transesterification of palm olein with methanol using heterogeneous catalysts

CaO is reported as a good catalyst for transesterification between methanol and soybean oil (Gryglewicz, 1999). Gryglewicz reported that Calcium methoxide, which can form on the surface of CaO, is the real catalyst of methanolysis of triglycerides. Because of its slightly soluble in methanol, calcium methoxide acts mainly as a heterogeneous catalyst. Calcium methoxide, which is strongly basic, shows high catalytic activity. It is not soluble in methanol but it forms a suspension, whereby, its active surface is very well developed. In this study, CaO showed 74% wt methyl esters after 24 hours. It can be used as heterogeneous catalyst for methyl esters production.

Gryglewicz (2000) reported that the alkaline earth metal oxide can be ordered according to their basicity as the following: CaO > MgO.

Undoubtedly, alkaline-earth metal alkoxides are strong bases and nucleophilic reagents. Magnesium and calcium are not bases but they can form bases, i.e. alkoxides with alcohols because they are reducers as shown in Figure 4.3.

In according to these facts, the observation in catalytic reactivity of alkaline-earth metal compounds in alcoholysis can be related to their basicity. The classic mechanism of alcoholysis assumes an attack of an alkoxide anion on the trigonal hybridised carbon atom in the ester group converting it to a tetrahedral intermediate. However, the considered alkaline-earth metal alkoxides are slightly soluble in methanol. Therefore, it seems that an alcoholysis can be catalyzed not only by free alkoxilate ions but also by solid alkoxilate which can be regarded as adducts of a strong alkoxilate ion base and a metal cation acid.

Magnesium oxide, in which the covalent bonds involve, have a high contribution. It does not react with methanol to form magnesium methoxide.

$$H_3CO^- - {}^{2+}Ca - {}^-OCH_3 + \underset{OR_1}{\overset{O}{\underset{|}{\overset{\|}{C}} - R}} \rightleftarrows H_3CO^- - {}^{2+}Ca[H_3CO - \underset{OR_1}{\overset{O^-}{\underset{|}{\overset{|}{C}} - R}}] \rightleftarrows$$

strong basic site

$$\rightleftarrows H_3CO^- - {}^{2+}Ca - {}^-OR_1 + \underset{OCH_3}{\overset{O}{\underset{|}{\overset{\|}{C}} - R}}$$

$$H_3CO^- - {}^{2+}Ca - {}^-OR_1 + CH_3OH \rightleftharpoons H_3CO^- - {}^{2+}Ca - {}^-OCH_3 + R_1OH$$
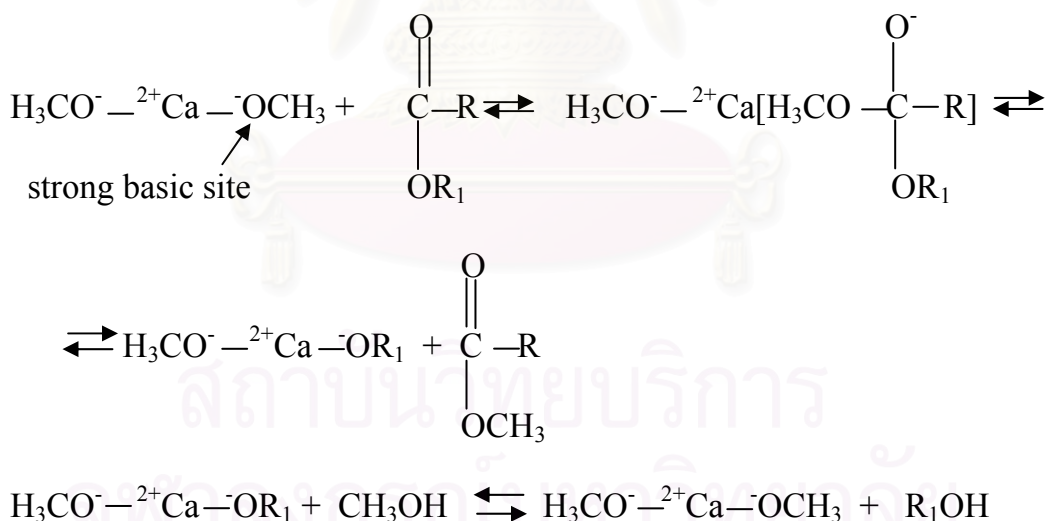
Figure 4.3 Mechanism of calcium oxide catalytic activity (Gryglewicz, 2000)

4.3 Effect of reaction time on transesterification catalyzed by heterogeneous catalysts

Heterogeneous catalysts in this experiment are CaO, $CaCO_3$, MgO and $MgCO_3$. K_2CO_3 and Na_2CO_3 are not heterogeneous catalysts because they are soluble in the mixture. The activity of CaO was found to be larger than that measured for all the other heterogeneous catalysts.

The results are shown in Table 4.6 and Figure 4.2. The percentages of methyl esters increase slowly related to increasing reaction time in the range between 3 and 24 hours for methanolysis of palm olein using MgO, $MgCO_3$ and $CaCO_3$.

In this experiment, CaO is studied for the effect of reaction time on transesterification of palm olein. It can be seen that the percentages of methyl esters was increased in the range of reaction time between 3 and 15 hours, thereafter, it remained constantly as a representative of a nearly equilibrium. The nearly equilibrium was found to be about 69% wt methyl esters at 15 hours of reaction time. 18 hours of reaction time was chosen for the methanolysis of palm olein because it seems to be equilibrium.

4.4 Effect of the amount of heterogeneous catalysts

The effect of the amount of heterogeneous catalysts in transesterification of palm olein are shown in Table 4.7 and compared in Figure 4.4. The 5% and 10% of heterogeneous catalysts by weight of palm olein were chosen to be appropriate in the reaction. The reaction was carried out with 100% mol of methanol from its stoichiometric ratio, at temperature of 62°C and the reaction time was 18 hours. The results are shown in Figure 4.4, the percentages of methyl esters were increased with the increasing of catalyst from 5% and 10% by weight of oil.

Table 4.7 Effect of the amount of heterogeneous catalysts

Catalyst	Methyl esters (% wt)	
	5% wt of oil	10% wt of oil
Calcium oxide	51.8	66.1
Calcium carbonate	2.7	2.9
Magnesium oxide	4.7	13.2
Magnesium carbonate	5.1	16.4
Potassium carbonate	91.0	94.0
Sodium carbonate	50.7	56.0
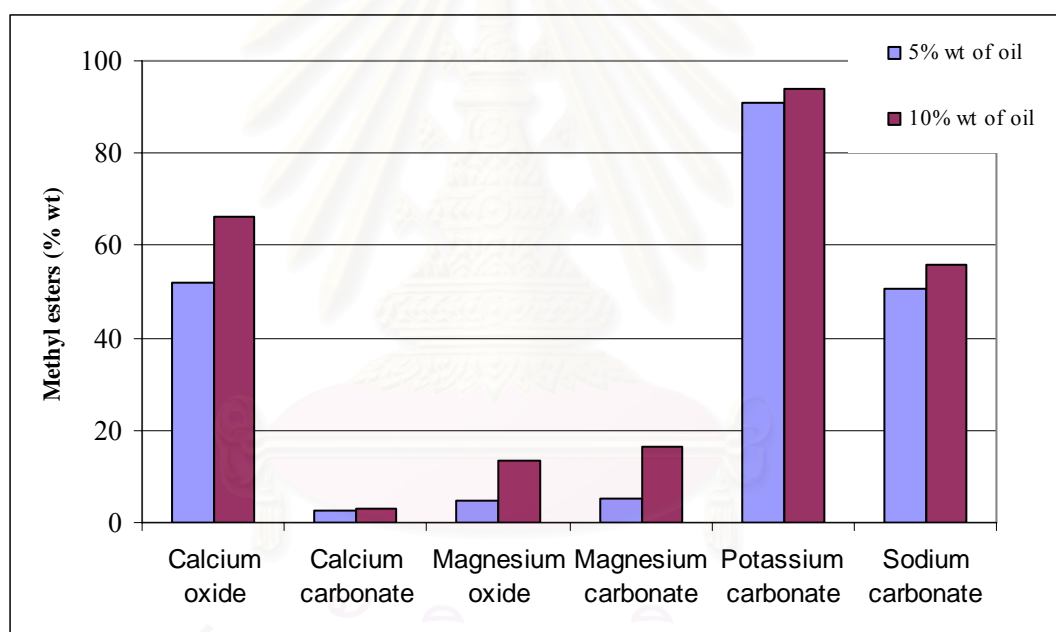
Figure 4.4 Effect of the amount of heterogeneous catalyst

There are many studies about the amount of homogeneous catalyst which have influenced on the methyl ester conversion. Freedman et al. (1984) studied the transesterification of soybean oil with butanol. The catalysts were 0.5% and 1% sodium buthoxide by weight of oil and molar ratio of butanol to oil of 30:1. The reaction was carried out at temperature of 20-60ºC. They reported that the reaction rates for the 1% wt-catalyzed reaction should have been higher than those for the 5% wt-catalyzed reactions. A number of kinetic

studies have shown that reaction rates increase with catalyst concentration. Crabbe et al. (2001) investigated acid catalyzed (sulfuric acid) production of methyl ester (biodiesel) from crude palm oil. The reactions were carried out at temperature of 95°C. The concentrations of H_2SO_4 were in the range of 1-5% (vol/% wt) and methanol to oil molar ratio was 23:1. They reported that ester yield had been increased as the acid concentration increased. The highest yield of 82% wt was obtained by an acid concentration of 5% wt.

In a study of the amount of heterogeneous catalyst, Xie et al. (2004) studied transesterification of soybean oil to methyl esters as 5 hours of reaction time and methanol to oil molar ratio of 15:1. The catalyst (35% wt KNO_3 loaded on Al_2O_3) amount was varied in the range of 1.0-9.0% by weight of oil. The conversion was increased firstly with the increasing of catalyst amount from 1 to 6.5% wt but the conversion was decreased with the increasing of catalyst amount from 6.5 to 9.0% wt.

Generally, the higher amount of catalyst will increase surface area of the catalyst. Several studies have shown that percentages of methyl esters increased with the increasing of catalyst amount.

As the concentration of the catalyst was increased, a number of adsorbed reactant molecules would increase owing to the increased number of catalyst particles. Above certain level, the available reactant molecules are not sufficient for adsorption when a number of catalyst particles are increased. Hence, the additional catalyst powder is not involved in the catalysis activity and the rate does not increase with an increasing in the amount of catalyst beyond a certain limit. Thus, 2 times of catalyst concentration were increased but not 2 times of methyl esters would be increased.

4.5 Effect of the excess of methanol on transesterification catalyzed by heterogeneous catalysts

One of the most important variables affecting the yield of ester is the excess of methanol. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right for the maximum conversions.

The effect of excess of methanol in transesterification of palm olein are shown in Table 4.8 and compared in Figure 4.5. The reaction was carried out with 100% wt and 400% mol excess methanol from its stoichiometric ratio, at temperature of 62°C, catalyst amount 10% by weight of oil and the reaction time was 18 hours.

Table 4.8 Effect of the excess of methanol

Catalyst	Methyl esters (% wt)	
	100% mol excess of methanol from its stoichiometric ratio	400% mol excess of methanol from its stoichiometric ratio
Calcium oxide	66.1	69.7
Calcium carbonate	2.9	4.4
Magnesium oxide	13.2	20.3
Magnesium carbonate	16.4	21.0
Potassium carbonate	94.0	97.7
Sodium carbonate	56.0	72.5

In the studies of homogeneous catalysts, Encinar et al. (2005) studied the transesterification of used frying oil with methanol. They used molar ratios of methanol to oil in the range of 3:1 and 9:1, 1% wt of potassium hydroxide,

the temperature was 65ºC and 2 hours for reaction time. The ester yields increased as the percentages of methanol increased, with the best results being for a molar ratio of 6:1. When the reaction was incompleted at 9:1 methanol to oil molar ratio, the yield of esters were decreased because a part of the glycerol still remained in methyl esters. Tomasevic et al. (2003) studied the transesterification 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 optimum conditions which developed for the good-quality biodiesel production were 6:1 molar ratio of methanol to oil.
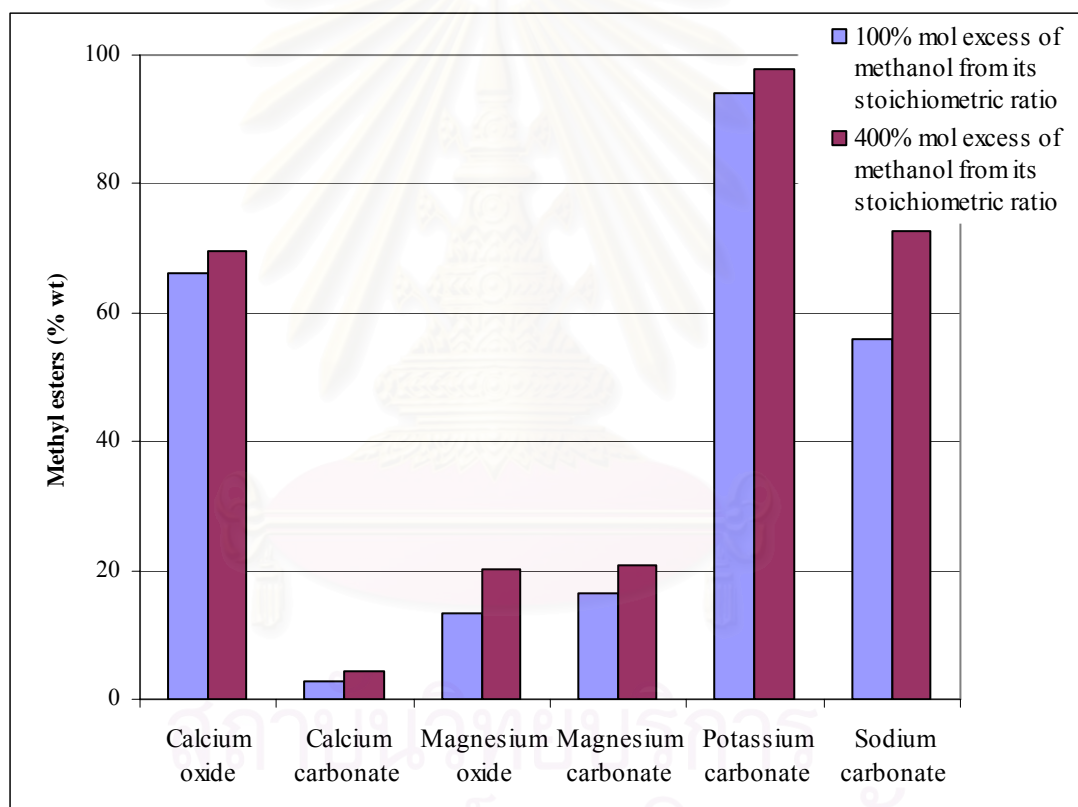

Figure 4.5 Effect of the excess of methanol

In the studies of heterogeneous catalysts, Reis et al. (2005) studied the effects of the methanol/oil molar ratio from the transesterification of Babassu coconut oil with methanol, in which the molar ratio was varied from 120:1 to 800:1 (methanol/oil), using the same amount of Amberlyst 15 resin (1 g) (reaction followed for 6 hour). For mole ratios of 300:1, 400:1,

600:1 and 800:1, the conversion to esters after 6 hours of reaction time are similar. For mole ratios lower than 300:1, a smaller conversion is observed. Consequently, the esters yield did not significantly increase when mole ratios were higher than 300:1. Arzamendi et al. (2006) reported that the excess of alcohol helps to shift the forward reactions leading to improve the conversion of triglycerides. However, several studies indicated that methanolysis rate decreases whereas the excess of alcohol increases. In this regard, this would be compatible with a dilution effect. It should be noted that the reactions were conducted with the same amount of catalysts, which was kept constantly. Therefore, in this series of reactions, the catalyst concentration decreases whereas the excess of methanol increases. Xie et al. (2004) studied transesterification of soybean oil to methyl esters, the different methanol to oil molar ratios which are from 2:1 to 20:1, the amount of catalyst with 6.25% by weight of oil and 5 hours of reaction time. They reported that the conversion was increased with increasing the molar ratios. However, the maximum conversion was obtained when the molar ratio was very close to 15:1 (400% excess of methanol from its stoichiometric ratio).

Based on Arzamendi et al. (2006) and Xie et al. (2006), the optimum 400% mol excess of methanol from its stoichiometric ratio was used in this study.

The results in Figure 4.3 show the percentages of methyl esters increased with increasing the excess of methanol 100% mol to 400% mol excess of methanol from its stoichiometric ratio. A large excess of alcohol is required to drive the reaction to the right so that the reaction will be more complete and gives higher percentages of methyl esters.

4.6 Comparison between heterogeneous and homogeneous catalysis

The results are shown in Figure 4.1 and Figure 4.2, homogeneous catalysts are more effective than heterogeneous catalysts in methanolysis of palm olein. Homogeneous catalysts show fast rate of reaction, whereas heterogeneous catalysts show slow rate of reaction.

In this study, the most effective heterogeneous catalyst is CaO. Undoubtedly, a drawback of CaO as a catalyst is its low catalytic activity in methanolysis of palm olein in comparison to KOH and NaOH. If CaO is used instead of NaOH and KOH, the reaction time is increased.

Homogeneous catalysts are robust and ideal for liquid-phase reaction since they form uniform mixtures with the reactants, resulting in minimum mass transfer limitations and high reaction rates. Although homogeneous catalysts have preferred characteristically in many liquid-phase reactions, they are also associated with difficulties in recovering the catalysts, disposal of potential toxic wastes, and separation of desired production. These unfavorable attributions have led to the substitution of homogeneous catalysts with heterogeneous catalysts in many reactions used for large-scale chemical production. Although heterogeneous catalysts have the positive features, the application of heterogeneous catalyst in liquid-phase reactions has been limited because of poor reactant/catalyst contacting from either pore diffusion limitations or low activity for catalytic reaction.

CHAPTER V

CONCLUSIONS AND RECOMENDATIONS

5.1 Conclusions

The following conclusions can be drawn from the study:

1. Homogeneous catalysts are more active than heterogeneous catalysts.

2. The most active of these heterogeneous catalysts is Calcium oxide. Magnesium oxide and Magnesium carbonate show approximately equal activity. Calcium carbonate is the least active catalyst. Calcium oxide is active because it can form calcium methoxide at the surface.

3. Potassium carbonate and Sodium carbonate are soluble in the mixtures so they can not be classified as heterogeneous catalyst

4. Increasing the amount of heterogeneous catalyst from 5% to 10% by weight of oil and increasing excess methanol from 2 to 5 times the stoichiometric ratio results the increasing percentages of methyl esters production. The results shows that a large excess of alcohol is required to drive the reaction to the right so that the reaction will be more complete and the higher amount of catalyst will increase surface area of the catalyst.

Recommendations

Recommendation for future studies and research are as follows:

1. The experiment should be conducted the factor of calcination of catalysts to verify the effect of calcination of catalysts on the transesterification reaction.

2. The experiment should be studied a wide range of temperature and pressure to determine the best condition.

Transesterification of vegetable oil to product methyl esters using heterogeneous catalyst is very important in chemical engineering. They can be easily separated from the mixture, easy to regenerate, more environmental friendly and used in packed-bed reactor.

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APPENDICES

APPENDIX A

Raw data in the characterization of palm olein

Table A1 Density measurement

	Palm olein		
	Exp. No.1	Exp. No.2	Exp. No.3
W pycnometer, g	17.4736	17.4665	17.4823
W pycno + oil, g	26.6608	26.5237	26.7032
W oil, g	9.0872	9.0572	9.0209
V pycno, ml	10	10	10
Density, g/ml	0.9087	0.9057	0.9021
Averange density, g/ml	0.9055		

Table A2 Kinematic viscosity measurement

Exp. No.1	Exp. No.2	Exp. No.3	Average , cP
36.4	36.9	37.1	36.8

Table A3 Free fatty acid value

	Palm olein
weight of oil, g	5.0052
Conc of KOH, N	0.1
Volume of KOH used, mL	0.5
acid value, milligram KOH/ g oil	0.56
%free fatty acid (palmitic acid)	0.26
Amount needed to neutralize oil	
KOH neutralization, milligram KOH/ g oil	0.56
g KOH/100 g oil	0.056
NaOH molecular weight, g	40
KOH molecular weight, g	56.1
NaOH neutralization, milligram KOH/g oil	0.400
g NaOH/100 g oil	0.04

Formula:

Acid value = (Ml. KOH x N x 56.1)/(weight of sample)

%FFA (palmitic acid) = Acid value/2.19

NaOH needed to neutralize oil = Acid value x 40/56.1

Table A4 Saponification value

	Palm olein
weight of oil, g	2.0001
Conc of HCl, N	0.5
Volume of HCl used for blank, mL	21.7
Volume of HCl used , mL	6.7
saponification value	210

Table A5 Molecular weight determination

	Palm olein
Mean MW fatty acids value	254.54
Molecular weight	802

Formula:

$$\text{Mean MW fatty acids value} = \frac{56108 - 12.67(SV - AV)}{SV}$$

Table A6 The solubility of heterogeneous catalysts in methanol determination

Catalyst	CaO	CaCO$_3$	MgO	MgCO$_3$	K$_2$CO$_3$	Na$_2$CO$_3$
Weight of catalyst, g	1.029	1.045	1.0492	1.0361	1.0292	1.0575
Weight of filter, g	0.9063	0.9057	0.9251	0.0916	0.8837	0.9216
Weight of catalyst+ filter, g	1.9353	1.9507	1.9743	1.1277	1.9129	1.9791
Weight (catalyst+ filter), g	1.92894	1.9448	1.9572	1.1129	1.5195	1.7982
Solubility, g	0.00636	0.0059	0.0171	0.0148	0.3934	0.1809
% solubllity, %	0.636	0.59	1.71	1.48	39.34	18.09

APPENDIX B

Calibration curve of fatty acids methyl esters
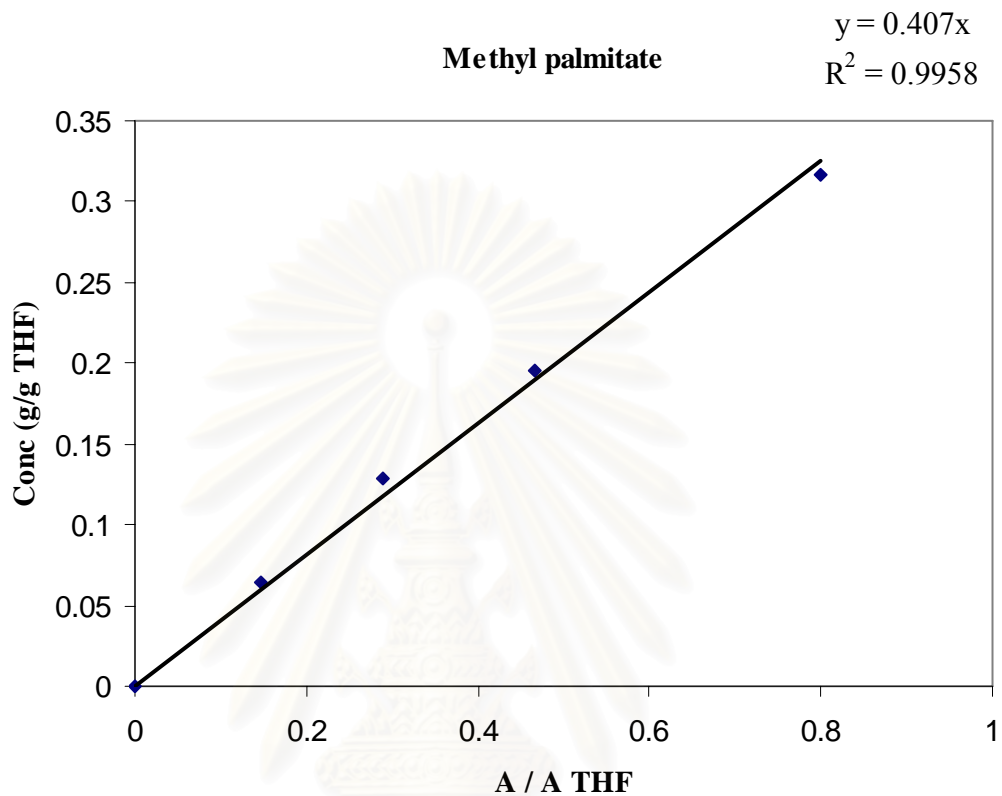
Figure B1 Calibration curve of methyl palmitate

Methyl oleate

$$y = 0.4201x$$
$$R^2 = 0.9998$$
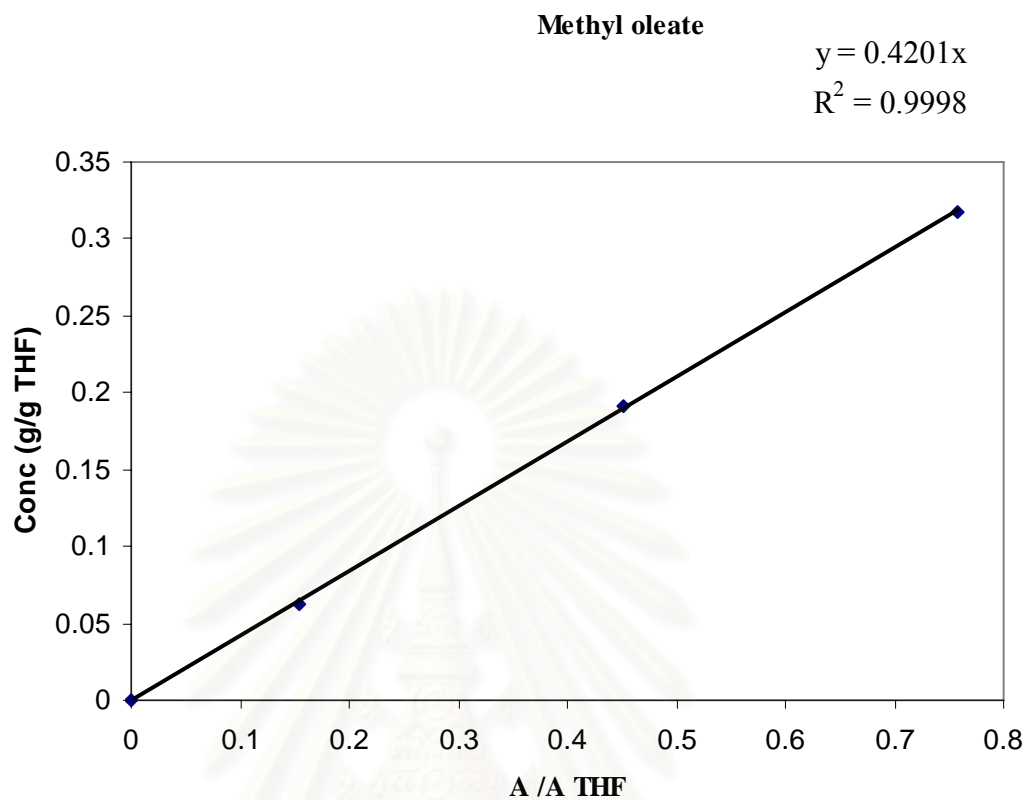
Figure B2 Calibration curve of methyl oleate
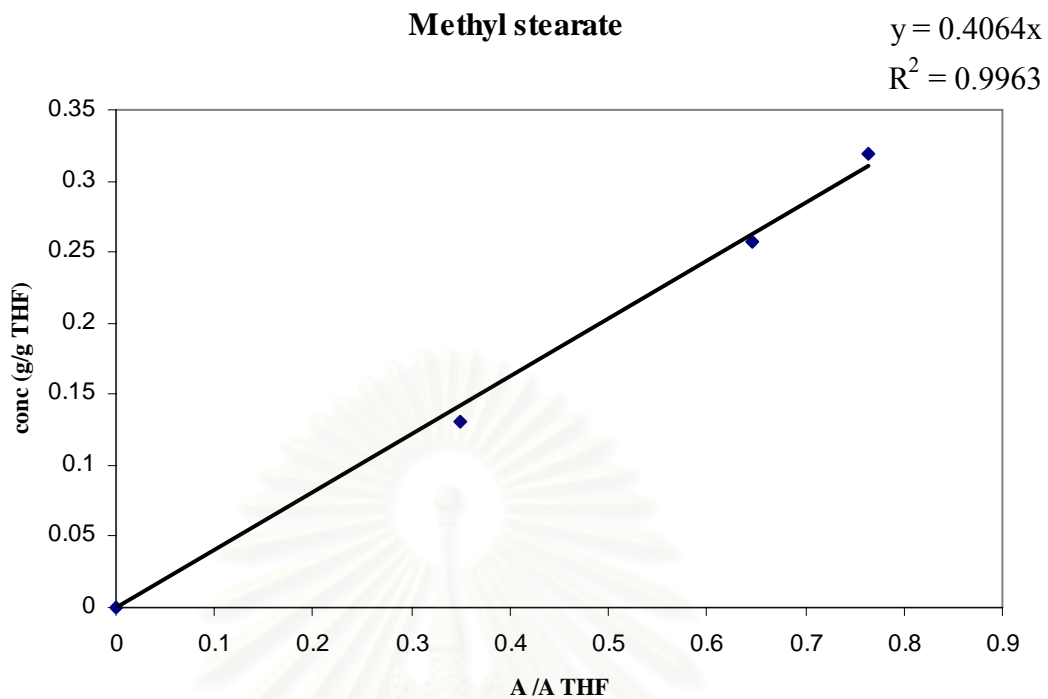
Figure B3 Calibration curve of methyl stearate

APPENDIX C

Raw data and GC chromatograms for Homogeneous and heterogeneous transesterification

Table C1 Palm olein heterogeneous transesterification. Reaction conditions: T = 62ºC, THF, 10% catalyst
wt/wt of oil, 100% mol excess of methanol from its stoichiometric ratio and reaction time
24 hours

Exp. No.	Catalyst	Wt. Oil, g	Wt. MeOH, g	Wt. Catalyst., g	Wt. THF, g
1	CaO	300	71.8621	15.0785	120
2	CaO	300	71.8725	15.0875	120
3	CaO	300	71.8653	15.0235	120
4	CaCO$_3$	300	71.8598	15.0781	120
5	MgO	300	71.8561	15.0155	120
6	MgCO$_3$	300	71.8742	15.0982	120
7	K$_2$CO$_3$	300	71.8736	15.0414	120
8	Na$_2$CO$_3$	300	71.8623	15.0653	120

Table C2 Percentages of methyl esters. Reaction conditions: T = 62ºC, 10% catalyst wt/wt of oil, 100%

mol excess of methanol from its stoichiometric ratio and reaction time 24 hours

Exp. No.	Catalyst	Methyl esters (% wt)							
		3 hours	6 hours	9 hours	12 hours	15 hours	18 hours	21 hours	24 hours
1	CaO	4.8431	10.4255	20.7541	39.6122	82.1028	74.9806	73.4034	75.4600
2	CaO	4.6695	8.3523	18.4709	24.1647	62.3520	67.8942	69.8808	77.2855
3	CaO	4.6665	10.0372	17.0052	28.8332	65.1957	68.8490	62.7489	68.9132
4	CaCO$_3$	2.1456	3.1051	2.7611	2.9786	2.4509	2.7890	2.6742	2.6162
5	MgO	3.8103	7.0216	7.9325	9.1972	10.6270	10.8230	8.7305	9.8493
6	MgCO$_3$	6.6428	9.6115	8.4216	7.8558	9.3366	9.3915	9.5011	10.0228
7	K$_2$CO$_3$	69.6447	79.5020	83.7323	91.0668	92.3899	83.3427	82.4138	72.9738
8	Na$_2$CO$_3$	21.5550	28.5724	28.6905	33.0664	35.4023	48.3852	51.0916	57.2186

Table C3 Palm olein homogeneous transesterification. Reaction conditions: T = 62ºC, 0.556% wt for KOH, 0.54% wt for NaOH, 100% mol excess of methanol from its stoichiometric ratio and reaction time 24 hour

Exp. No.	Catalyst	Wt. Oil, g	Wt. MeOH, g	Wt. Catalyst., g
1	KOH	300	71.8671	1.668
2	NaOH	300	71.8742	1.62

Table C4 Percentages of methyl esters. Reaction conditions: T = 62ºC, 0.556 % wt for KOH, 0.54% wt for NaOH, 100% mol excess of methanol from its stoichiometric ration and reaction time 24 hours

Exp. No.	Catalyst	Methyl esters (% wt)							
		3 hours	6 hours	9 hours	12 hours	15 hours	18 hours	21 hours	24 hours
1	KOH	74.4132	76.6980	67.7424	78.4584	69.5665	65.5686	74.4404	66.5535
2	NaOH	61.1037	73.3267	62.9908	76.3342	70.9433	75.8798	73.1122	77.2095

Table C5 Palm olein heterogeneous transesterification. Reaction conditions: T = 62ºC, 100% mol and 400% mol excess of methanol from its stoichiometric ratio, catalyst amount 5% wt and 10% wt by weight of oil and reaction time 18 hours

Exp. No.	Catalyst	Wt. Oil, g	Wt. MeOH, g	Wt. Catalyst, g	Wt. THF, g	Methyl esters (% wt)
1	CaO	50.2	12.1	2.5	20.1	51.82172
2	CaO	50.1	12	5.1	20.2	66.13027
3	CaO	50.2	29.9	5	33.1	69.69439
4	CaCO$_3$	50.3	12	2.5	20.1	2.653081
5	CaCO$_3$	50.1	12	5	20	2.852719
6	CaCO$_3$	50.2	29.9	5.1	33.2	4.356474
7	MgO	50.1	12.1	2.5	20.1	4.704154
8	MgO	50.2	12	5	20	13.22042
9	MgO	50.3	29.9	5.1	33.1	20.25678
10	MgCO$_3$	50.2	12	2.5	20	5.116645
11	MgCO$_3$	50.2	12	5.1	20.1	16.37642
12	MgCO$_3$	50.3	29.9	5	33.1	20.96143
13	K$_2$CO$_3$	50.1	12.1	2.5	20.1	91.01362
14	K$_2$CO$_3$	50.3	12	5	20	93.99301
15	K$_2$CO$_3$	50.2	29.9	5	33.2	97.67609
16	Na$_2$CO$_3$	50.1	12.1	2.5	20	50.71425
17	Na$_2$CO$_3$	50.2	12	5	20.1	56.02046
18	Na$_2$CO$_3$	50.1	29.9	5.1	33.2	72.53557
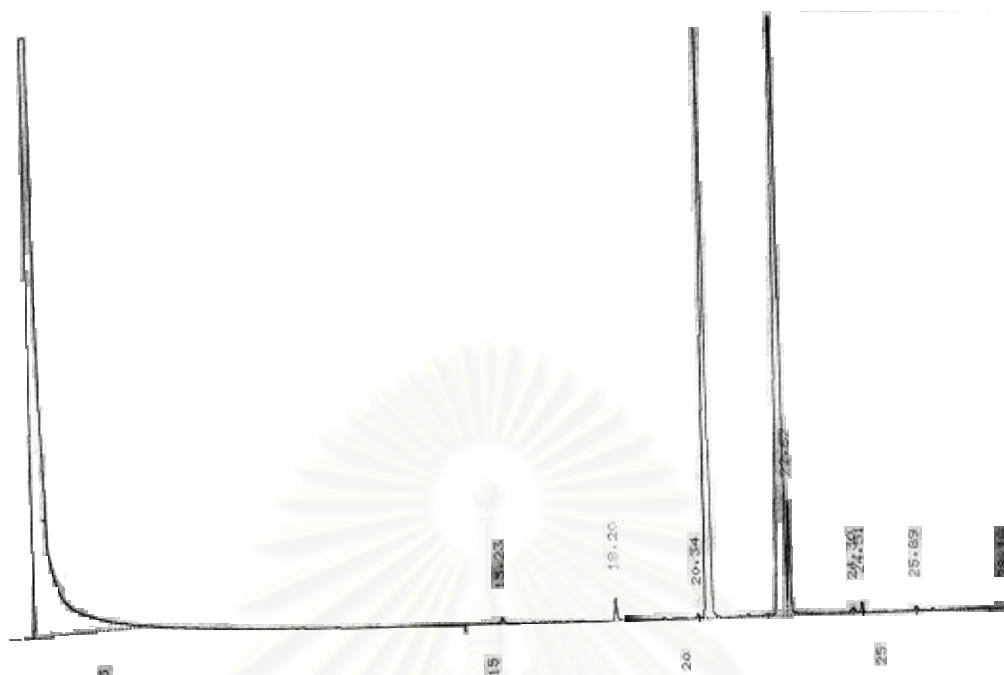
```
RUN  13   10:36  97/01/01

METHOD CURRENT          CALCULATION:      %

DETECTOR 2

   RT          AREA         BC         AREA%

  0.611        0.0202       V         0.0171
  1.364        0.0257                 0.0218
  3.28        75.0624                63.5710
 15.23         0.3265       T         0.2765
 18.20         0.4738       V         0.4012
 20.34         0.0987       T         0.0836
 20.66        15.1827       T        12.8583
 22.54        23.6220       T        20.0057
 22.67         2.1372       T         1.8100
 24.30         0.2008       T         0.1701
 24.51         0.2378       T         0.2014
 25.89         0.3000       T         0.2540
 28.18         0.3880       V         0.3286
```

Figure C1 Chromatogram. Reaction conditions: 100% mol excess of methanol

from its stoichiometric ratio, CaO 10% by weight of oil, temperature
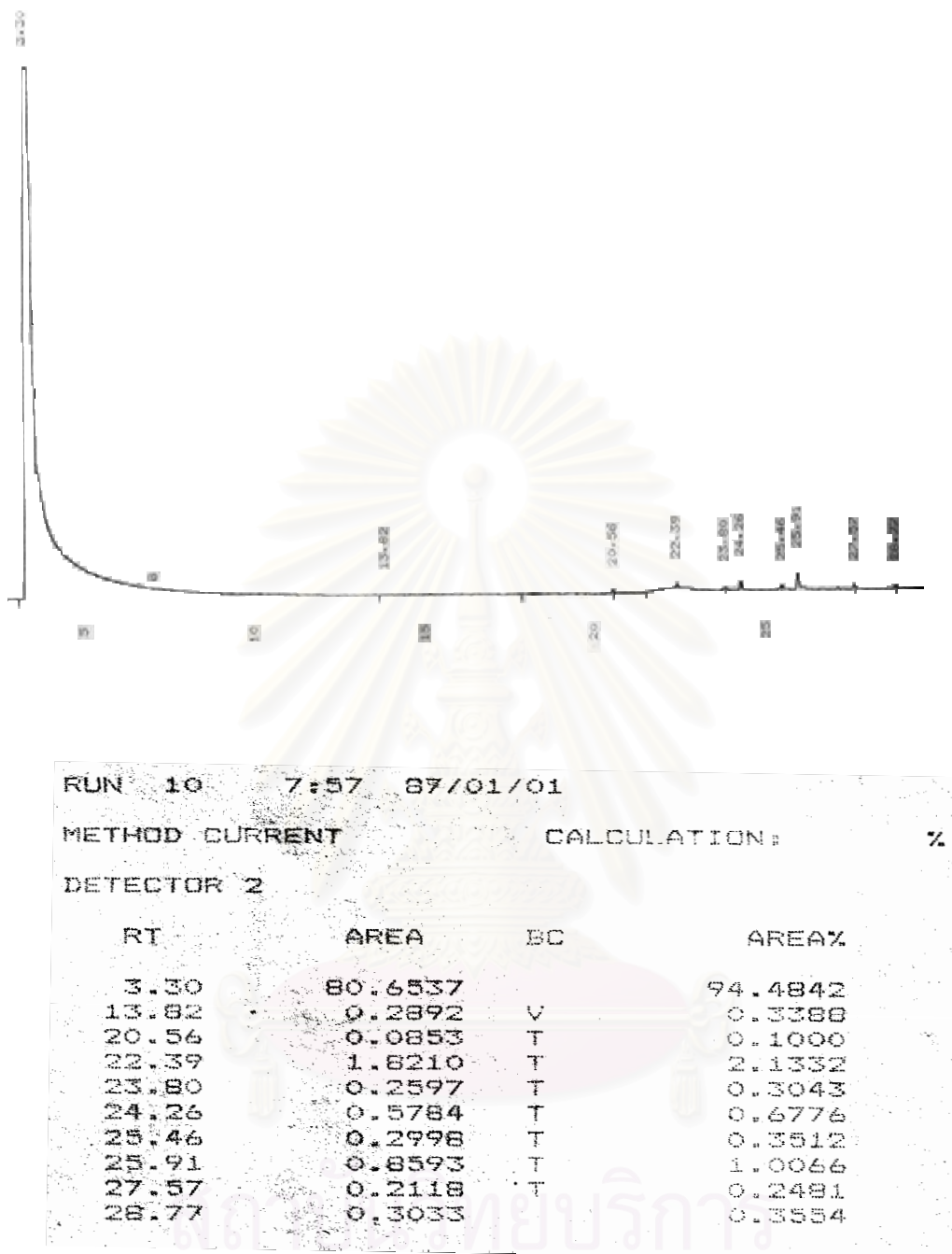
62ºC and reaction time 18 hours

Figure C2 Chromatogram. Reaction conditions: 100% mol excess of methanol
from its stoichiometric ratio, CaCO$_3$ 10% by weight of oil, temperature
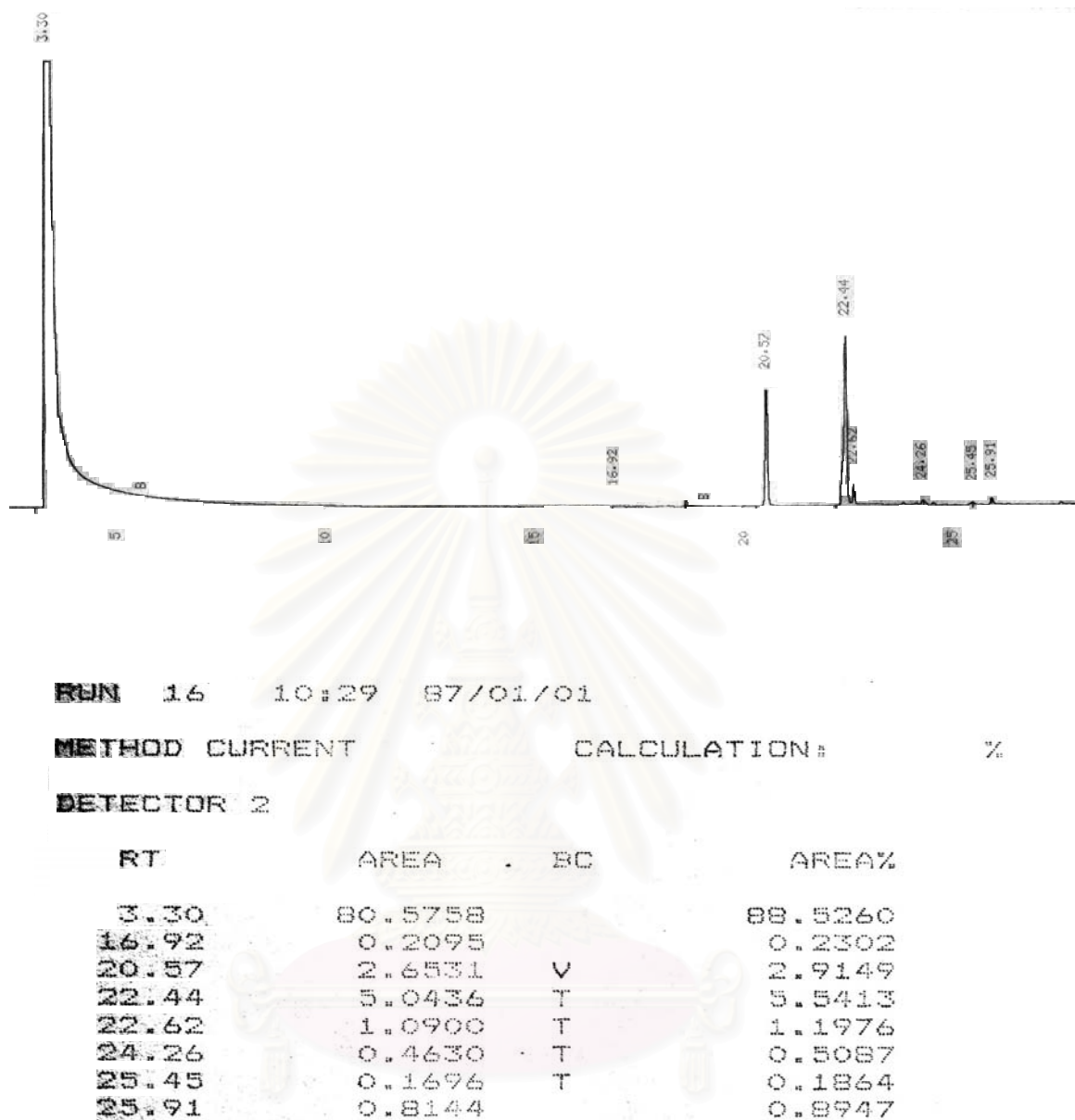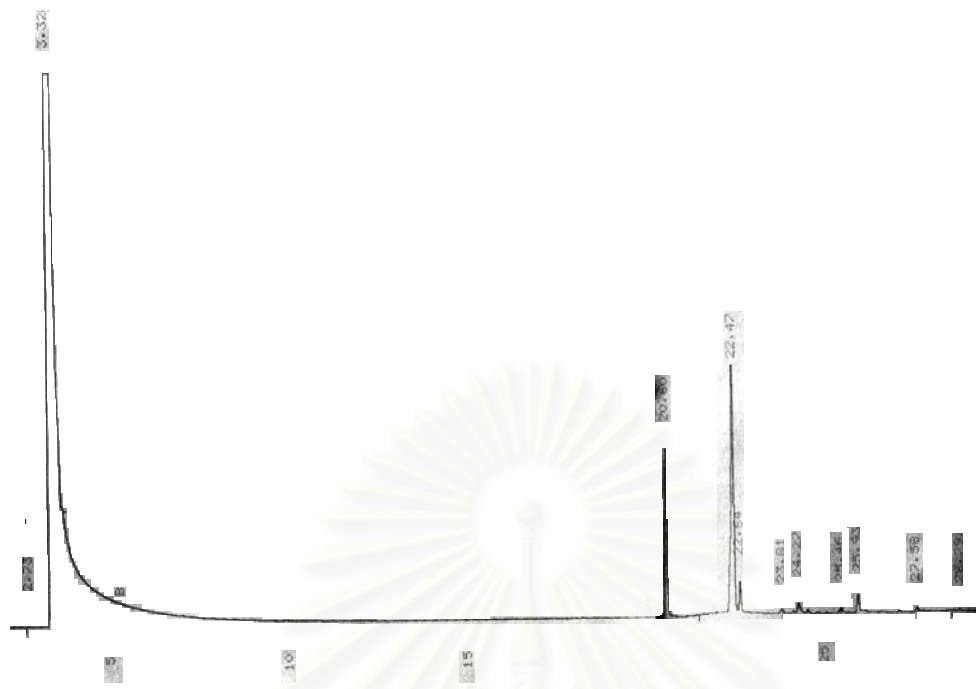62°C and reaction time 18 hours

```
RUN   16    10:29   97/01/01

METHOD CURRENT                CALCULATION:        %

DETECTOR 2

    RT          AREA    .  BC          AREA%

   3.30        80.5758              88.5260
  16.92         0.2095               0.2302
  20.57         2.6531    V          2.9149
  22.44         5.0436    T          5.5413
  22.62         1.0900    T          1.1976
  24.26         0.4630  . T          0.5087
  25.45         0.1696    T          0.1864
  25.91         0.8144               0.8947
```

Figure C3 Chromatogram. Reaction conditions: 100% mol excess of methanol
from its stoichiometric ratio, MgO 10% by weight of oil, temperature
62ºC and reaction time 18 hours
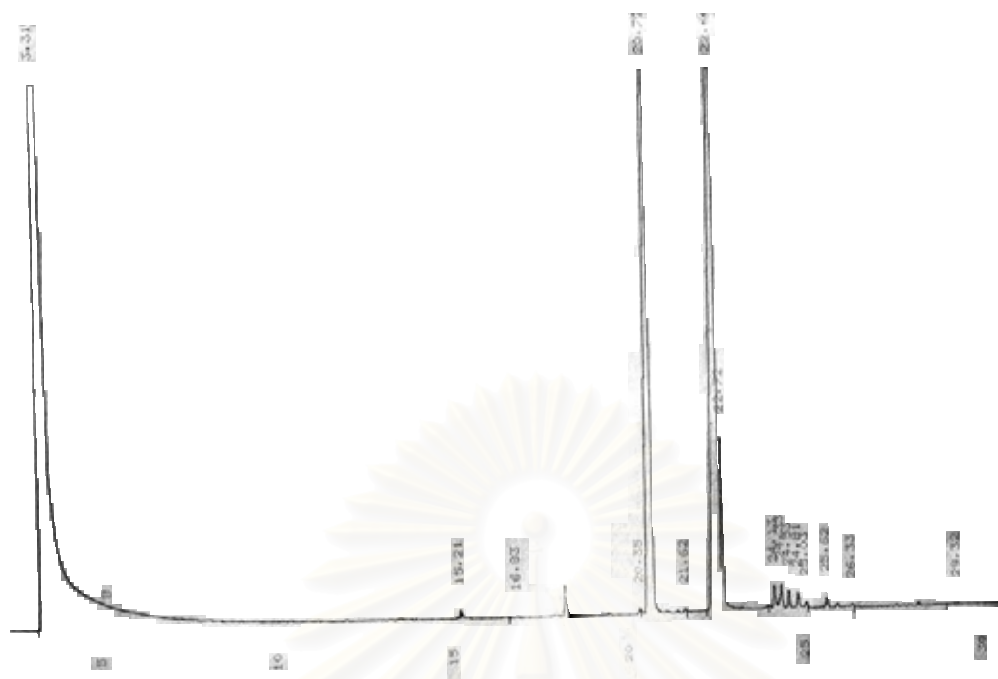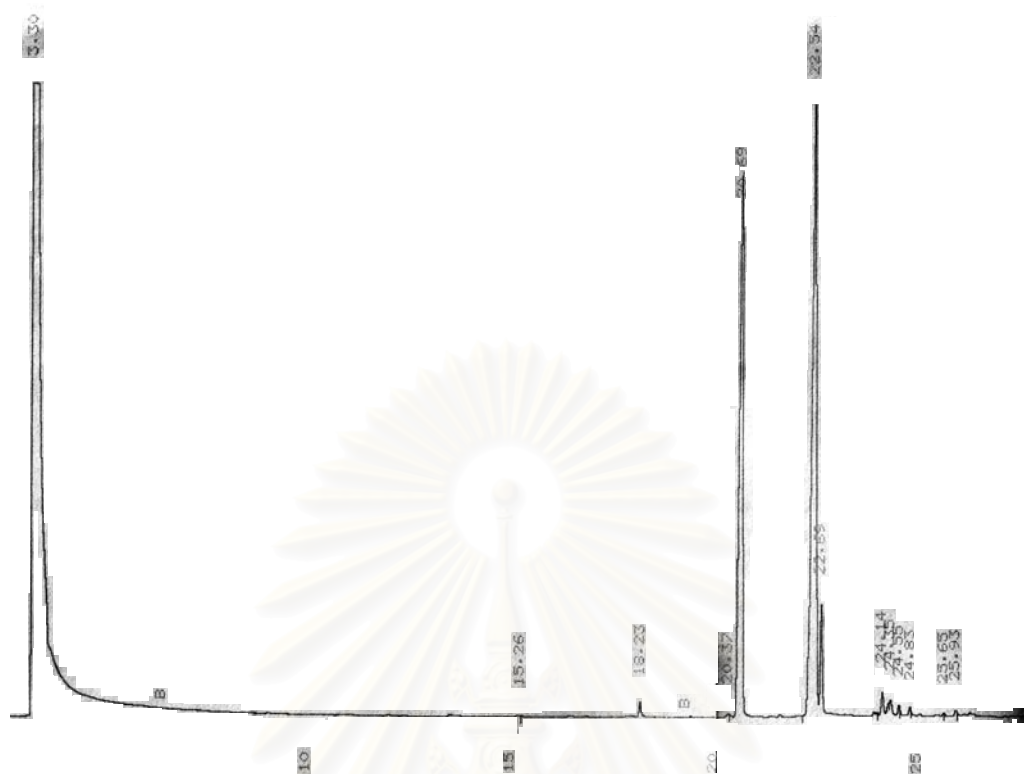
RUN   7   5:59   87/01/01

METHOD CURRENT   CALCULATION: %

DETECTOR 2

RT	AREA	BC	AREA%
0.488	0.0467		0.0490
2.73	0.0378	V	0.0397
3.32	80.9528		84.9678
20.60	3.0486	T	3.1999
22.47	7.1208	T	7.4740
22.64	1.2654	T	1.3282
23.81	0.2492	T	0.2615
24.27	0.7328	T	0.7691
25.46	0.2584	T	0.2712
25.93	0.8116	T	0.8518
27.58	0.2621	T	0.2751
28.79	0.4880		0.5122

Figure C4 Chromatogram. Reaction conditions: 100% mol excess of methanol
from its stoichiometric ratio, $MgCO_3$ 10% by weight of oil,
temperature 62ºC and reaction time 18 hours

RUN   12   7:55   87/01/01

METHOD CURRENT   CALCULATION: %

DETECTOR 2

RT	AREA	BC	AREA%
1.841	0.0164	V	0.0105
3.31	84.4328		54.4777
15.21	0.2393	T	0.1544
16.83	0.0948	T	0.0612
18.21	0.7541	V	0.4865
20.35	0.1538	T	0.0992
20.72	25.7750	T	16.6306
21.62	0.1099	T	0.0709
22.60	36.0020	T	23.2292
22.72	3.6585	T	2.3605
24.13	0.8328	T	0.5373
24.33	0.6469	T	0.4174
24.53	0.3609	T	0.2328
24.81	0.4894	T	0.3157
25.03	0.1764	T	0.1138
25.62	0.5010	T	0.3233
26.33	0.4880	T	0.3148
29.32	0.2530		0.1632

Figure C5 Chromatogram. Reaction conditions: 100% mol excess of methanol
from its stoichiometric ratio, K_2CO_3 10% by weight of oil, temperature
62ºC and reaction time 18 hours

Figure C6 Chromatogram. Reaction conditions: 100% mol excess of methanol

from its stoichiometric ratio, Na_2CO_3 10% by weight of oil,

temperature 62ºC and reaction time 18 hours

VITA

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