ไบโอดีเซลจากน้ำมันปาล์มโดยใช้ปฏิกิริยาทรานส์เอสเทอร์ริฟิเคชัน ด้วยตัวเร่งปฏิกิริยาแบบของแข็ง

นายวัฒนชัย เยาวรัตน์

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BIODIESEL FROM PALM OILS USING SOLID CATALYZED-TRANSESTERIFICATION REACTION

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
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Field of Study	Chemical Engineering
Thesis Advisor	Jirdsak Tscheikuna, Ph.D.

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วัฒนชัย เยาวรัตน์ : ไบโอดีเซลจากน้ำมันปาล์มโดยใช้ปฏิกิริยาทรานส์เอสเทอร์ริฟิเคชันด้วยตัวเร่งปฏิกิริยาแบบของแข็ง (BIODIESEL FROM PALM OILS USING SOLID CATALYZED-TRANSESTERIFICATION REACTION) อ. ที่ ปรึกษา: อ. ดร. เจิดศักดิ์ ไชยคุนา, 66 หน้า.

งานวิจัยนี้เป็นการศึกษาการสังเคราะห์ไบโอดีเซลโดยใช้ปฏิกิริยาทรานส์เอสเทอร์ริฟิเคชันด้วยตัวเร่งปฏิกิริยาแบบวิวิธพันธุ์ คือ โดเวก (Dowex) และ แอมเบอร์ลิสต์-15 (Amberlyst-15) ซึ่งเป็นสารจำพวกเรซินแลกเปลี่ยนประจุ (ion exchange resin) และ ตัวเร่งปฏิกิริยาแบบเอกพันธ์ คือ โซเดียมไฮดรอกไซด์ การทดลองนี้เป็นแบบกะที่ความดันบรรยากาศ โดยใช้น้ำมัน 3 ชนิด ได้แก่ น้ำมันปาล์มบริสุทธิ์ น้ำมันปาล์มใช้แล้ว และ น้ำมันปาล์มดิบ ปริมาณของตัวเร่งปฏิกิริยาโซเดียมไฮดรอกไซด์ ร้อยละ 0.25 0.50 และ 1.0 โดยน้ำหนักของน้ำมันปาล์ม ปริมาณของตัวเร่งปฏิกิริยาโดเวก (Dowex) และ แอมเบอร์ลิสต์-15 (Amberlyst-15) ร้อยละ 25.0 และ 50.0 โดยน้ำหนักของน้ำมันปาล์ม อุณหภูมิในการทำปฏิกิริยา คือ 40 50 และ 60 องศาเซลเซียส และ เวลาในการทำปฏิกิริยาสำหรับปฏิกิริยาแบบเอกพันธ์ คือ 2 ชั่วโมง ส่วนปฏิกิริยาแบบวิวิธพันธุ์ คือ 8 ชั่วโมง

จากผลการทดลองพบว่า สภาวะที่เหมาะสมในการทำปฏิกิริยาทรานส์เอสเทอร์ริฟิเคชันด้วยตัวเร่งปฏิกิริยาแบบวิวิธพันธุ์ คือ น้ำมันปาล์มดิบใช้ตัวเร่งปฏิกิริยา คือ แอมเบอร์ลิสต์-15 ปริมาณร้อยละ 50 ของน้ำมันปาล์ม ซึ่งได้ปริมาณของเมทิลเอสเทอร์เท่ากับ ร้อยละ 57.89 และ สภาวะที่เหมาะสมในการทำปฏิกิริยาทรานส์เอสเทอร์ริฟิเคชันด้วยตัวเร่งปฏิกิริยาแบบเอกพันธ์ คือ น้ำมันปาล์มบริสุทธิ์ใช้ตัวเร่งปฏิกิริยาร้อยละ 1 ของน้ำมันปาล์มที่อุณหภูมิ 60 องศาเซลเซียส ซึ่งได้ปริมาณ ของเมทิลเอสเทอร์ เท่ากับ ร้อยละ 96.29

ภาควิชา..........วิศวกรรมเคมี.................ลายมือชื่อนิสิต..
สาขาวิชา........วิศวกรรมเคมี.................. ลายมือชื่ออาจารย์ที่ปรึกษา....................................
ปีการศึกษา.....2549..............................ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..............................

4670485921: MAJOR CHEMICAL ENGINEERING DEPARTMENT
KEY WORD: TRANSESTERIFICATION/BIODIESEL/HOMOGENEOUS/
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WATTANACHAI YAOWARAT: BIODIESEL FROM PALM OILS USING SOLID CATALYZED-TRANSESTERIFICATION REACTION. THESIS ADVISOR: JIRDSAK TSCHEIKUNA, Ph.D., 66 pp.

In this study, transesterification using Dowex, Amberlyst-15 and Sodium hydroxide was investigated. The experiments were conducted in batch system at atmospheric pressure. Types of palm oil used refined oil, used oil and crude oil. Amounts of Sodium hydroxide used 0.25%, 0.50% and 1% by weight of palm oil. Amount of Dowex and Amberlyst-15 used 25% and 50% by weight of palm oil. Temperatures of 40, 50, and 60°C were used in the reaction. Reaction time for homogeneous catalyzed-transesterification was two hours. Reaction time for heterogeneous catalyzed-transesterification was eight hours.

The results show that an optimum condition for transesterification using heterogeneous catalyst was crude palm oil using Amberlyst-15 50% by weight of oil which gives methyl ester of 57.89% and an optimum condition for transesterification using homogeneous catalyst was refined palm oil using catalyst 1% by weight of oil at 60°C which gives methyl ester of 96.29%.

Department.......Chemical Engineering.........Student's Signature.............................

Field of Study......Chemical Engineering.........Advisor's Signature.............................

Academic Year...2006...............................Co-advisor's Signature.........................

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CHAPTER I

INTRODUCTION

Vegetable oils are a renewable energy source. However, the direct use of vegetable oils in diesel engines is problematic owing to their high viscosity and low volatility. Many different produces have been considered to reduce the high viscosity of vegetable oils. Transesterification with alcohol is a possible choice, since many physical characteristics of fatty acid methyl esters (FAME) are similar to those of diesel fuel (M.A. Hanna et at., 1999).

Transesterification consists of a sequence of consecutive reversible reactions wherein the triglyceride (TG) is successively transformed into diglyceride (DG), monoglyceride (MG), and finally into glycerol and fatty alky esters. The stoichiometry of this reaction thus requires 3 mol of alcohol per 1 mol of TG to give 3 mol of fatty alkyl ester and 1 mol of glycerol (Schuchardt et al., 1998). However, in practice, a higher alcohol/TG mole ratio is used to increase ester production.

The alcohols used most frequently are methanol and ethanol. Several parameters including the typing of catalyst (alkaline or acid), alcohol/vegetable oil mole ratio, temperature, and purity of the reactants (main contaminants are water and free fatty acid (FFA)), have an influence on the transesterification reaction (Freedman et al., 1984).

There are different processes that can be applied to synthesize FAME (biodiesel): (1) based-catalyzed transesterification (J.A. Almeida et al., 2002), (2) acid-catalyzed transesterification (M. Mittelbach et al., 1996), (3) integrated acid- catalyzed pre-esterification of FFA and based- catalyzed transesterification (M. Canakci et al., 2001), (4)enzyme-catalyzed transesterification (D. Wei et al., 2004), (5) hydrolysis and acid-catalyzed esterification, (6) pyrolysis (A. Demirbas, 2003), and (7) supercritical alcohol transesterification (S. Saka et al., 2001).

Most of the commercial biodiesel that is currently produced from transesterification using homogeneous base (NaOH or KOH) catalyzed processes (M.A. Hanna et at., 1999). The base catalyzed process is less corrosive than the homogeneous acid (H_2SO_4) catalyzed one and proceeds at a much higher rate (Freedman et al., 1986). The disadvantage in using homogeneous catalysts is their miscibility in the reaction medium, which causes separation problems. Moreover, at higher acid catalyst concentrations, equipment corrosion and secondary reactions can occur. Hence, the use heterogeneous catalysts such as zeolites and ion-exchange resins have clear advantages since they are non-corrosive and are easy to separate from the reaction mixture; furthermore, no washing of the ester is required, presenting fewer disposal problems (Sasidharan et al., 2004, Suppes et al., 2004, Costa-Lopez et al., 2002). Ion – exchange resins are convenient catalysts for etherification, esterification, and transesterification reactions and a large number of applications have been reported in the literature (Sharma et al., 1995, Hamer et al., 2001).

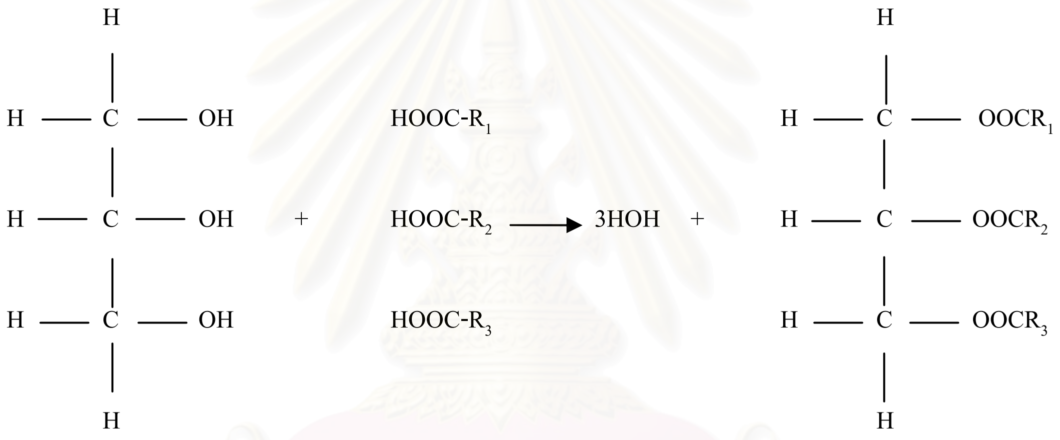
The objective of the thesis is study the transesterification of triglycerides on solid catalysts compare homogeneous catalyst. The solid catalysts studied were Amberlyst-15 and Dowex. Several types of palm oils which are crude palm oil, used palm oil, and refined palm oil were studied in transesterification with methanol. The reaction results using these solid catalysts were compared to those using NaOH as homogeneous catalyst.

CHAPTER II

LITERATURE REVIEW

2.1 Vegetable oils

Vegetable oils are part of a larger family of chemical compounds known as fats or lipids. They are made up predominantly of triesters of glycerol with fatty acids and commonly are called triglycerides, and are generally formed as follows (Goering et al., 1982).



Glycerol Fatty acids Water Triglyceride

Differences in vegetable oils result from differences in fatty acids with which glycerol may be combined. The most common fatty acids in nature are listed in Table 2.1.

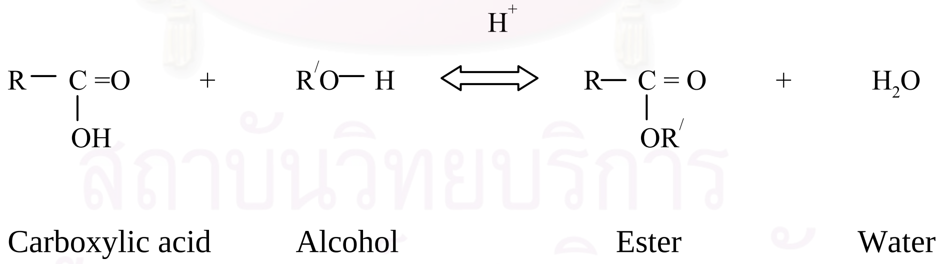
Table 2.1 Common fatty acids in nature (Weiss, 1970)

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

2.2 Synthesis of Esters

The formation of esters occurs through a condensation reaction known as esterification. This requires two reactants, carboxylic acids (fatty acids) and alcohols. Esters are usually prepared by the most common methods outlined by Morrison and Boyd (1992) as below:

- From acids



$$R{-}\underset{\displaystyle OH}{\underset{|}{C}}{=}O \quad + \quad R'O{-}H \quad \overset{H^+}{\Longleftrightarrow} \quad R{-}\underset{\displaystyle OR'}{\underset{|}{C}}{=}O \quad + \quad H_2O$$

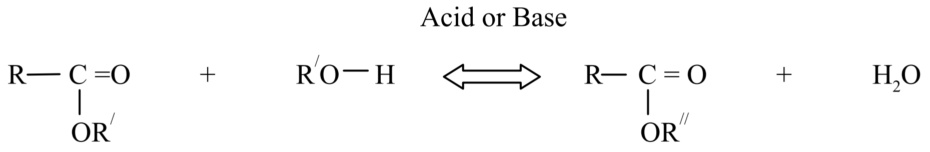
R may be alkyl or aryl $\qquad$ R' is usually alkyl

- From acid chlorides or anhydrides

$$RCO{-}Cl \quad + \quad R'O{-}H \text{ (or ArOH)} \longrightarrow RCO{-}OR' \text{ (or } RCO{-}OAr) \quad + \quad HCl$$

$$(RCO)_2O \quad + \quad R'OH \text{ (or ArOH)} \longrightarrow RCOOR' \text{ (or RCOOAr)} \quad + \quad RCOOH$$

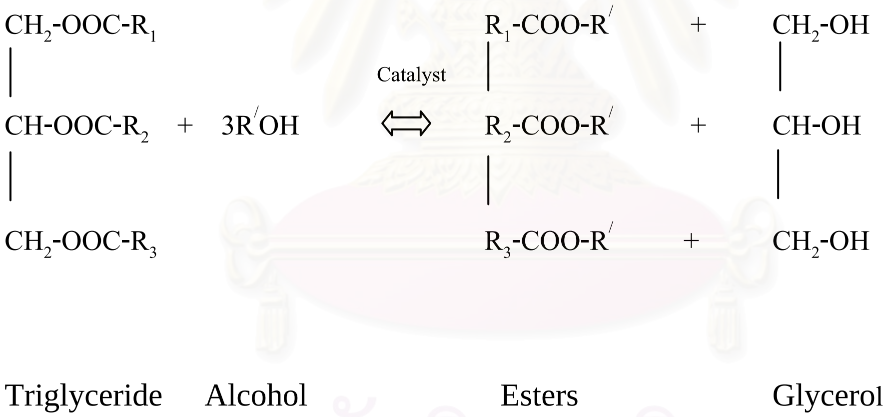
- From esters



$$R-\underset{\displaystyle OR'}{\overset{}{C}}=O \; + \; R'O-H \; \xLeftrightarrow{\text{Acid or Base}} \; R-\underset{\displaystyle OR''}{C}=O \; + \; H_2O$$

2.3 Transesterification of vegetable oils using homogeneous catalyst

Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. The reaction is shown in Equation 2.1 (Fangrui, 1999). A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side.



$$\begin{array}{lcccl} CH_2\text{-}OOC\text{-}R_1 & & & R_1\text{-}COO\text{-}R' \; + & CH_2\text{-}OH \\ | & & \text{Catalyst} & | & | \\ CH\text{-}OOC\text{-}R_2 \; + & 3R'OH & \Leftrightarrow & R_2\text{-}COO\text{-}R' \; + & CH\text{-}OH \\ | & & & | & | \\ CH_2\text{-}OOC\text{-}R_3 & & & R_3\text{-}COO\text{-}R' \; + & CH_2\text{-}OH \end{array}$$

(2.1)

The alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). Transesterification consists of a number of consecutive, reversible reactions (Schwab et al., 1987; Freedman et al., 1986). The triglyceride is converted stepwise to diglyceride, monoglyceride, and finally glycerol. The step reactions are shown in Figure 2.1.

$$\text{1. Triglyceride (TG)} + R^{/}OH \overset{k_1}{\underset{k_4}{\longleftrightarrow}} \text{Diglyceride (DG)} + R^{/}COOR_1$$

$$\text{2. Diglyceride (DG)} + R^{/}OH \overset{k_2}{\underset{k_5}{\longleftrightarrow}} \text{Monoglyceride (MG)} + R^{/}COOR_2$$

$$\text{3. Monoglyceride (MG)} + R^{/}OH \overset{k_3}{\underset{k_6}{\longleftrightarrow}} \text{Glycerol (GL)} + R^{/}COOR_3$$

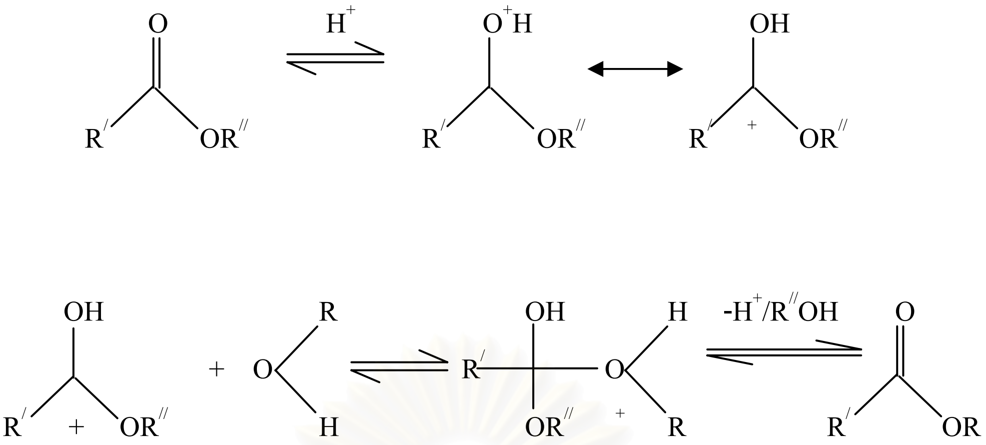
Figure 2.1 Transesterification reaction of vegetable oil with alcohol to esters and glycerol (Freedman et al., 1986)

The reaction can be catalyzed by alkalis or acids. The alkalis include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Sulfuric acid, sulfonic acids, and hydrochloric acid are usually used as acid catalysts.

Freedman et al. (1984) showed that the methanolysis of soybean oil, in presence of 1 mole% H_2SO_4, with an alcohol/oil molar ratio of 30:1 at 65°C, takes 50 hours to reach complete conversion while the bytanolysis (at 117°C) and ethanolysis (at 78°C), using the same quantities of catalyst and alcohol, take 3 and 18 hours, respectively (Schuchardt, 1998).

The mechanism of the acid-catalyzed transesterification of vegetable oil is shown in Figure 2.2.

Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially. The mechanism of the base-catalyzed transesterification of vegetable oil was mentioned by Schuchardt et al. (1998) and is shown in Figure 2.3.



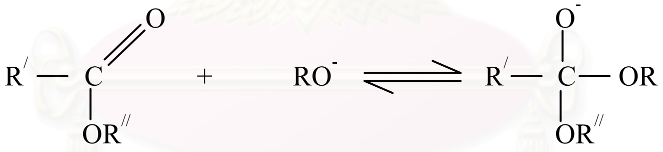
R'' = glyceride
R' = carbon chain of fatty acid
R = alkyl group of the alcohol

Figure 2.2 Mechanism of acid catalyzed transesterification

Pre-step $OH^- + ROH \rightleftharpoons RO^- + H_2O$

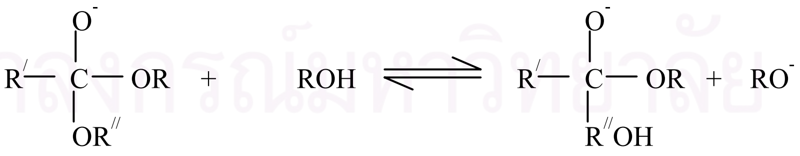
Or $NaOR \rightleftharpoons RO^- + Na^+$

Step.1



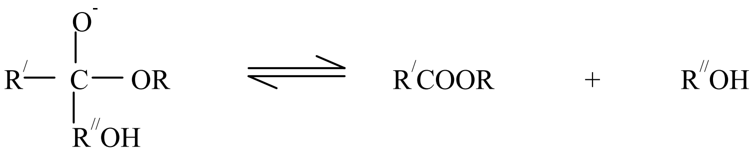
$$R'-C(=O)-OR'' + RO^- \rightleftharpoons R'-C(O^-)(OR)-OR''$$

Step.2



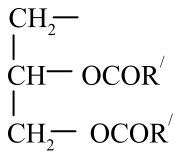
$$R'-C(O^-)(OR)-OR'' + ROH \rightleftharpoons R'-C(O^-)(OR)-R''OH + RO^-$$

Step.3



$$R'-C(O^-)(OR)-R''OH \rightleftharpoons R'COOR + R''OH$$

Where $R^{//}$ =



$$\begin{array}{l} CH_2- \\ | \\ CH- OCOR^{/} \\ | \\ CH_2- OCOR^{/} \end{array}$$

$R^{/}$ = carbon chain of fatty acid
R = alkyl group of alcohol

Figure 2.3 Mechanism of base catalyzed transesterification

Genna Vicente et al. (2003) studied a comparison is made of different basic catalysts (sodium methoxide, potassium methoxide, sodium hydroxide, and potassium hydroxide) for methanolysis of sunflower oil. All the reactions were carried out under the same experimental conditions in a batch stirred reactor and the subsequent separation and purification stages in a decanter. The analytical methods included gas chromatography and the determination of fat and oil conventional parameters. The biodiesel purity was near 100 wt.% for all catalysts. However, near 100 wt.% biodiesel yields were only obtained with the methoxide catalysts.

The result of the investigation on methyl esters by A.V. Tomasevic et al. (2002) obtained on the basis of heated refined sunflower oil and used frying oils are given in the paper. Transesterification reaction conditions that affect yield and purity of the product esters including oil quality, molar ratio of methanol to vegetable oil, type and concentration of alkaline catalyst, temperature and reaction time were examined. The methanolysis of different oils at 25°C with 0.5–1.5% potassium hydroxide or sodium hydroxide were studied. The effect of molar ratio 4.5:1, 6:1, and 9:1 on ester yield and its quality were investigated. With 1% potassium hydroxide, temperature at 25°C, molar ratio 6:1, and 30 min, all investigated oils were sufficiently transesterified and could be used as fuel in diesel engines.

Three principal variables, molar ratio of methanol to oil, amount of catalyst, and reaction temperature, affecting the yield of acid-catalyzed production of methyl ester (biodiesel) from crude palm oil were investigated by Edward Crabbe et al. (2001). The optimized variables, 40:1 methanol/oil (mol/mol) with 5% H_2S0_4 (vol/wt) reacted at 95°C for 9 hours, gave a maximum ester yield of 97%.

Transesterified vegetable oils (VOs) are cheap and renewable but currently disposed of inadequately. Mohamad I. Al-Widyan et al. (2002) studied the transesterification of waste palm oil under various conditions. H_2SO_4 and different concentrations of HCl and ethanol at different excess levels were used. Higher catalyst concentrations (1.5–2.25 M) produced biodiesel with lower specific gravity, in a much shorter reaction time than lower concentrations. The H_2SO_4 performed better than HCl at 2.25 M, as it resulted in lower specific gravity. Moreover, a 100% excess alcohol effected significant reductions in reaction time and lower relative to lower excess levels. The best process combination was 2.25M H_2SO_4 with 100% excess ethanol which reduced from an initial value of 0.916 to a final value of 0.8737 in about 3 hours of reaction time.

All of the studies done in the transesterification of vegetable oil involve the use of homogeneous catalysts. Although the reaction proceeds nicely, major problems such as removal of solute catalyst and formation of side products were encountered. These hurdle lead to the idea of investigating heterogeneous catalyst.

2.4 Transesterification of vegetable oils using heterogeneous catalyst

Several attempts have been done using heterogeneous catalysts on the transesterification of vegetable oils.

Transesterification of soybean oil with methanol was carried out at 60, 120, and 150°C in the presence of a series NaX faujasite zeolite, ETS-10 zeolite and metal catalysts by Galen J. Suppes et al. (2003). The catalysts were calcined at 500°C prior to use in order to increase activity. The results showed that 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 larger pore structures that improved intra-particle diffusion. Methyl ester yield increased with an increase in temperature from 60 to 150°C. The metal catalysts increased conversion by one to over two orders of magnitude over the homogeneous reaction with several of the zeolite catalysts performing better than the metal catalysts.

Frederique R. Abreu et al. (2003) reported the use of Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O)$_2$ (**1**), Pb(3-hydroxy-2-methyl-4-pyrone)$_2$(H_2O)$_2$ (**2**), and Zn(3-hydroxy-2-methyl-4-pyrone)$_2$(H2O)$_2$ (**3**) as catalysts in the transesterification reaction of different alkyl-chain triglycerides and alcohols. The methanolysis of native oils from Brazilian's Savannah and Amazonian regions, such as Andiroba (*Carapa guianensis*), Babassu (*Orbignia sp.*), Cumaru (*Dipteryx odorata*), Palm tree (*Elaeis sp.*), Piqui (*Caryocar sp.*), and Soybean oil as well as the alcoholysis of Soybean oil with several alcohols (ethanol, propanol, *iso*-propanol, *n*-butanol, *terc*-butanol and *cyclo*-hexanol) was studied. Activities of the tin and lead pyrone complexes were observed in all the alcohol studies. For linear alcohols, the reaction activities decreased with increasing carbonic chain length. It was also shown that the catalytic activities are higher when vegetable oil with short chain fatty acids or with a high unsaturated degree and short and linear chain alcohols are used.

Hak-Joo Kim et al. (2004) studied Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. Na/NaOH/γ-Al_2O_3 heterogeneous base catalyst was firstly used for the production of biodiesel from the soybean oil. Both the sodium aluminate formed by loading sodium hydroxide on γ-Al_2O_3, and the ionization of sodium, originated the strong basic sites of the catalysts. The activities of the heterogeneous base catalysts correlated with their 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 the 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 *n*-hexane molar ratio. The optimum methanol to oil loading ratio was found to be 9:1. The Na/NaOH/γ -Al_2O_3 heterogeneous base catalyst showed almost the same activity under optimized reaction conditions compared to the conventional homogeneous NaOH catalyst.

Dora E. Lo´pez et al. (2005) investigated the kinetics and selectivities of different solid catalysts for the transesterification of triacetin (a model compound for larger triglycerides as found in vegetable oils and fats) with methanol. Reaction was carried out at 60°C in a batch reactor with a variety of solid and liquid, acid and base catalysts. The homogeneous phase (i.e., liquid) catalysts (NaOH and H_2SO_4) were studied for a comparison. The following conclusions can be drawn from this study: (1) homogeneous catalysts were more active than heterogeneous ones on a weight basis, (2) ETS-10 exhibited probable homogeneous catalysis as the alkali methoxide species were leached out, (3) the solid acids studied underwent less deactivation than ETS-10 (Na, K) under these 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 Hβ, (5) Amberlyst-15, SZ, Nafion NR50, and 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 mechanisms.

The Transesterification of several Brazilian vegetable oils with methanol was carried out at 60°C in the presence of several ion-exchange resins having different structures by Simone C.M. dos Reis et al. (2005). The vegetable oils used were from Babassu coconut, corn, palm, palm kernel, and soybean. The effect of the methanol/oil mole ratio and the influences of the structure of the ion-exchange resin and the type of vegetable oil used on the catalytic activity of the ion-exchange resins were investigated. The resins used were Amberlyst 15, Amberlyst 31, Amberlyst 35, and Amberlyst 36. Amberlyst 15 produced the best results for the Transesterification of vegetable oils. The methyl ester yield is higher for palm kernel oil and Babassu coconut than for soybean oil, probably owing to their higher content of shorter-chain fatty acid. Therefore, it was shown that the catalytic activity of the resin depends on the fatty acid composition of the vegetable oil employed.

2.5 Analysis of Biodiesel

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

Michal Holcapek et al. (1999) used Gradient elution reversed-phase high-performance liquid chromatography (RP-HPLC) in the determination of compounds occurring during the production of biodiesel from rapeseed oil. Individual triacylglycerols (TGs), diacylglycerols, monoacylglycerols, and methyl esters of oleic, linoleic and linolenic acids and free fatty acids were separated in 25 mins using a combined linear gradient with aqueous–organic and non-aqueous mobile phase steps: 70% acetonitrile, 130% water in 0 min, 100% acetonitrile in 10 mins, 50% acetonitrile150% 2-propanol–hexane (5:4, v/v) in 20 mins and 5 mins final hold-up. Another method with a non-aqueous linear mobile phase gradient [from 100% methanol to 50% methanol, 150% 2-propanol–hexane (5:4, v/v) in 15 mins] was used for fast monitoring of conversion of rapeseed oil triacylglycerols to fatty acid methyl esters and for quantitation of residual TGs in the final biodiesel product. Sensitivity and linearity of various detection modes (UV detection at 205 nm, evaporative light scattering detection and mass spectrometric detection) were compared. The individual sample compounds were identified using coupled HPLC–atmospheric pressure chemical ionization mass spectrometry in the positive-ion mode.

Meanwhile Marquardt (1998) improved the separation of saturated methyl esters ranging from C_{12} to C_{22} by utilizing the reversed-phase thin layer chromatography (TLC) which employs silver nitrate in mobile phase containing acetonitrile/1,4-dioxane/ acetic acid.

Plank (1995) applied capillary gas chromatography (GC) equipped with flame ionization detector (FID) is determining the glycerol, mono-, di-, and triglycerides in methyl esters. However, this method is less convenient because derivatization such as transmethylsilylation before analysis is needed for the free hydroxyl groups in the mono-, di-, and triglycerides. Furthermore, Michal Holcapek et al. (1999) mentioned that the derivatization step is unessential when high temperature (approximately 350°C) and a short capillary column with good temperature stability is employed.

CHAPTER III

EXPERIMENTS

Experiment and analytical method are described in this chapter. It is divided into four sections. The first section about materials in experimental. The second part describes the experimental apparatus. The third section refers to methodology of transesterification. And the last section describes analytical methods and errors of the experiments.

3.1 Materials

3.1.1 Vegetable Oils

Vegetable Oils used in this research were refined palm oil, used palm oil, and crude palm oil. Refined palm oil was obtained from Oleen brand, Palm Oleen Co., Ltd., while crude palm oil was from Taksinpalm (21) company.

3.1.2 Chemicals

All chemicals used in the experiment are shown in Table 3.1.

3.2 Equipments

3.2.1 Transesterification of vegetable oils using homogeneous catalysts

A batch reactor equipped four baffles and thermocouple was used in the experiments. The reactor was encircled with heating tape. The six-blade was used to provide agitation. The experimental set-up was shown in Figure 3.1.

3.2.2 Transesterification of vegetable oils using heterogeneous catalysts

A flask equipped with a reflux condenser. Thermocouple was put in water bath. The flask was immersed in a constant temperature-water bath and a magnetic stirrer was used to provide agitation. The experimental set-up was shown in Figure 3.2.

Table3.1 Chemicals used in the research

Name	**Source**	**Purity**
Sodium Hydroxide	Ajax finechem	AR grade
Dowex	Sigma-aldrich	Gel type
Amberlyst-15	Sigma-aldrich	Moisture<1.5%
Phenolphthalein	APS	Laboratory grade
Methanol	Fisher chemicals	AR grade(99.8%)
Ethanol	SR lab	Commercial grade
Potassium Hydroxide	Fisher chemicals	AR grade
Tetrahydrofuran	Fisher chemicals	AR grade

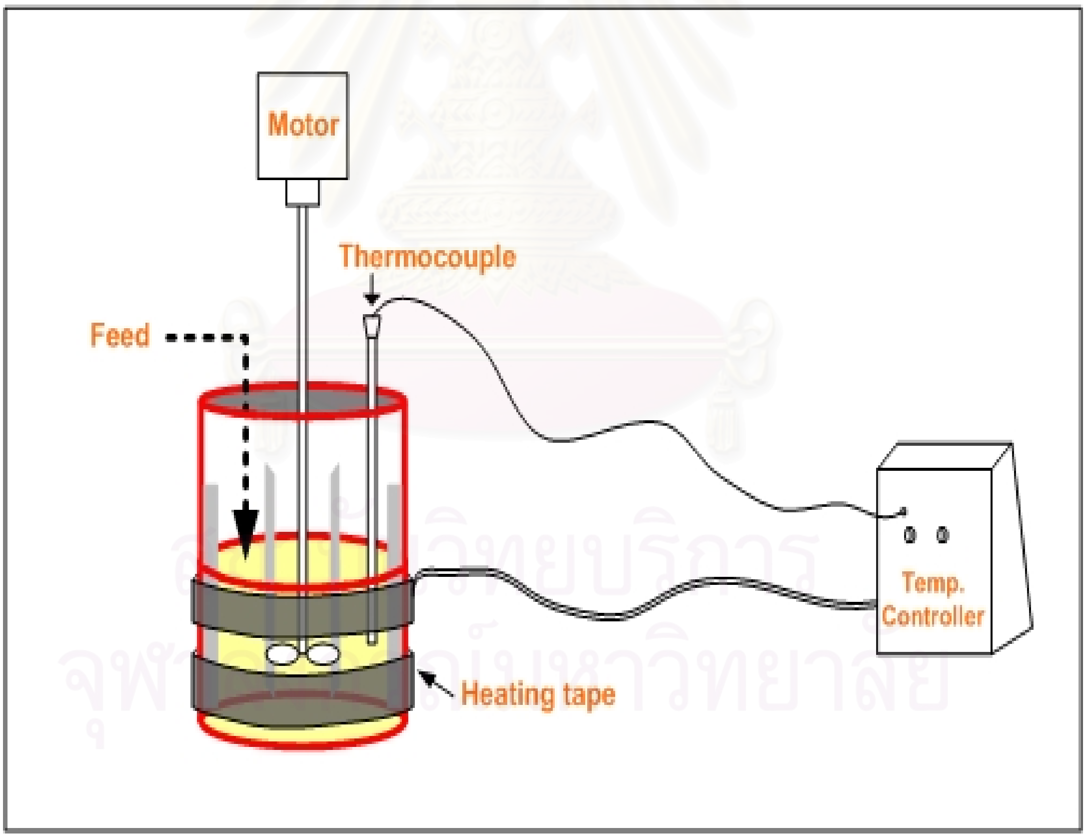


Figure 3.1 Experimental set-up used for the study of homogeneous catalyst

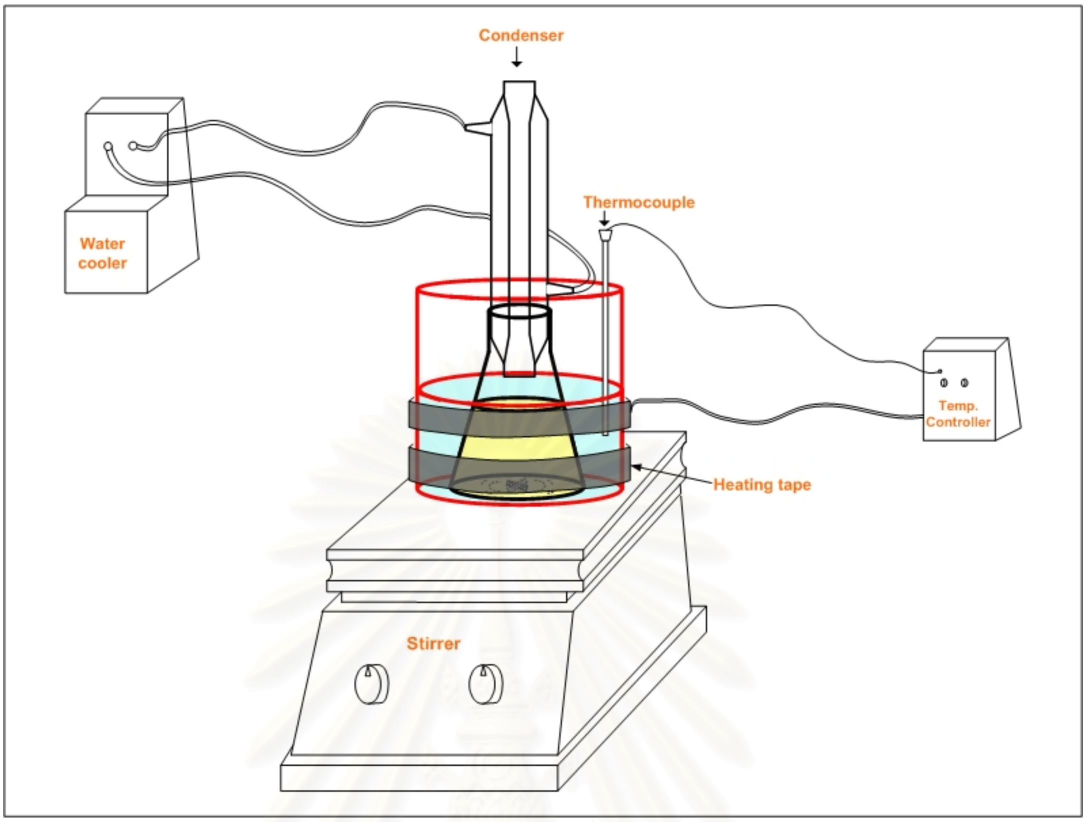


Figure 3.2 Experimental set-up used for the study of heterogeneous catalyst

3.3 Methodology

3.3.1 Characterization of vegetable oils

Refined, used, and crude palm oil were analyzed based on density at 40°C, kinematic viscosity (ASTM D-445), free fatty acid content (AOCS Cd 3d-63), saponification value (AOCS Cd 3b-76), flash point (ASTM D-93), and molecular weight.

3.3.2 Transesterification of vegetable oils using homogeneous catalysts

1. First, heated oil at 100°C in order to eradicate moisture.
2. Weighed 2416 g of heated oil and put in a batch reactor, then heated it at required temperature as per each experiment.
3. Mixed the catalyst, sodium hydroxide, and 100%excess methanol, together until they were all dissolved.
4. Added the methoxide solution and stirred it for two hours.
5. Immersed the reactor in water bath to stop the reaction.
6. Put the mixture in a separatory funnel overnight to ensure the separation of methyl esters (biodiesel) and glycerol phase.
7. Removed the glycerol phase.

8. Washed Biodiesel (the top layer) by using a small air pump, an aquarium aerator pump with a bubble stone.

9. Added water in the biodiesel in the wash tank, usually a quarter of biodiesel.

10. Threw in the bubble stone and switched on the pump.

11. Waited until biodiesel and water mixed well, and then switched off.

12. Leave it separate, and then drained the water out.

13. Checked pH value of both biodiesel and the water.

14. If the pH value was not seven, begin the washing process again until their pH value equal seven.

15. Finally, heated the biodiesel at 120°C to remove moisture. The conditions used were shown in Table 3.2.

3.3.3 Transesterification of vegetable oils using heterogeneous catalysts

Prior to use the catalysts, Amberlyst-15 was dried at 105°C for 12 hours. After that, poured methanol through both Amberlyst-15 and Dowex to finish preparing.

1. Heated oil at 100°C to eradicate moisture.
2. Put 10 grams of heated oil in a flask and heated it up to 60°C.
3. Put methanol and co-solvent (THF) together as well as weighed catalyst as per each experiment in the flask and stir for 8 hours.
4. Used filter paper to separate the catalysts out.
5. Condensed the mixture afterward to recover methanol and co-solvent.

There would be two layers in the flask which the top one was biodiesel and the bottom one was glycerol. The reactions were carried out using methanol: oil molar ratio (300:1). The conditions used were shown in Table 3.3.

Table 3.2 Conditions used for homogeneous catalyst

Sample No.	Oil	Amount of NaOH as catalyst(%wt of oil)	Temperature (°C)
1	Refined palm oil	0.25	40
2	Refined palm oil	0.25	50
3	Refined palm oil	0.25	60
4	Refined palm oil	0.50	40
5	Refined palm oil	0.50	50
6	Refined palm oil	0.50	60
7	Refined palm oil	1.0	40
8	Refined palm oil	1.0	50
9	Refined palm oil	1.0	60
10	Used palm oil	0.25	40
11	Used palm oil	0.25	50
12	Used palm oil	0.25	60

Sample No.	Oil	Amount of NaOH as catalyst(%wt of oil)	Temperature (°C)
13	Used palm oil	0.50	40
14	Used palm oil	0.50	50
15	Used palm oil	0.50	60
16	Used palm oil	1.0	40
17	Used palm oil	1.0	50
18	Used palm oil	1.0	60
19	Crude palm oil	0.25	40
20	Crude palm oil	0.25	50
21	Crude palm oil	0.25	60
22	Crude palm oil	0.50	40
23	Crude palm oil	0.50	50
24	Crude palm oil	0.50	60
25	Crude palm oil	1.0	40
26	Crude palm oil	1.0	50
27	Crude palm oil	1.0	60

Table 3.3 Conditions used for heterogeneous catalyst

Sample No.	Oil	Catalyst	Amount of catalyst (%wt of oil)
111	Refined palm oil	Dowex	25
112	Refined palm oil	Dowex	50
121	Refined palm oil	Amberlyst-15	25
122	Refined palm oil	Amberlyst-15	50
211	Used palm oil	Dowex	25
212	Used palm oil	Dowex	50
221	Used palm oil	Amberlyst-15	25
222	Used palm oil	Amberlyst-15	50
311	Crude palm oil	Dowex	25
312	Crude palm oil	Dowex	50
321	Crude palm oil	Amberlyst-15	25
322	Crude palm oil	Amberlyst-15	50

3.3.4 Analysis of Biodiesel

Biodiesel samples are analyzed density at 40°C, kinematic viscosity (ASTM D-445), flash point (ASTM D-93), beside they are analyzed by gas chromatography (GC) at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, using Perkin elmer 8700 gas chromatograph with a flame ionization detection system. There were separations carried out on a OV-5 fused silica column (30 m × 0.32 mm × 0.25 micron; Ohio Valley. Marietta, Ohio). The operating conditions were in Table 3.4. The temperatures of injector and detector were set at 310°C, and the carrier gas was 9.5 Psig. The split ratio was 1:4 and carrier gas used was helium. The samples of 0.5 g were dissolved in 1.5 g of THF after that 0.5 μl of sample was injected into the column.

Table 3.4 Conditions analyzed by Perkin elmer 8700 gas chromatograph

Oven temperature	Iso time.	Ramp rate
1=120°C	1=0.0	1=1.0
2=130°C	2=0.0	2=15.0
3=200°C	3=0.0	3=10.0
4=310°C	4=5.0	4=0.0

The percentages of methyl esters is defined as a ratio of weight of methyl ester, which was determined by using gas chromatography (GC) to weight of sample, which was shown in equation 3.1**.**

$$\%\ \text{Methyl esters} = \frac{\text{weight of methyl esters} \times 100}{\text{weight of sample}} \qquad (3.1)$$

Biodiesel from homogeneous-catalyzed transesterification were analyzed for percentages of yield, which equation 3.2 had defined as follows.

$$\%\text{yield} = \frac{\text{weigh of top layer X 100}}{\text{weight of palm oil}} \qquad (3.2)$$

3.4 Experimental and Analytical Error

In this section, experiments were conducted to verify repeatability, an average, and a standard deviation value of the experiment. Equation 3.3 and Equation 3.4 had defined an average value and percent deviation.

$$\text{Average value, } \overline{X} = \frac{\sum x}{n} \tag{3.3}$$

$$\text{Percent deviation from average value} = \frac{\sqrt{(X-\overline{X})^2}}{\overline{X}} \times 100 \tag{3.4}$$

The experiments were repeated for 3 times at the same condition. Here below were the results of the experiments.

property	**Experiment 1**	**Experiment 2**	**Experiment 3**	**Average value**	**standard deviation value**
Density	0.9123	0.9110	0.9232	0.9155	0.0067%
Flash point	173	175	177	175	2.0%
Viscosity	4.66	4.45	4.48	4.53	0.11%
Percentage of methyl esters	70.75	72.52	71.23	71.50	0.92%
Percentage of yield	81.9	92.6	92.8	89.1	6.24%

CHAPTER IV

RESULTS AND DISCUSSION

Transesterification is the reaction of a fat or oil with an alcohol to form esters and glycerol. In this study, palm oil and methanol were used as reactants. NaOH (sodium hydroxide), Dowex, and Amberlyst-15 were used as catalysts. Conditions for each experiment are summarized in Table 3.2 and 3.3. The discussion of the results was divided into five parts:

4.1 Characterization of vegetable oils
4.2 Homogeneous catalyst
4.3 Heterogeneous catalyst
4.4 Investigating of heterogeneous catalysts for transesterification
4.5 Effect of free fatty acid content between homogeneous and heterogeneous catalyst

4.1 Characterization of vegetable oils

The vegetable oils used in this study were refined palm oil, used palm oil, and crude palm oil. Refined palm oil is a commercial grade palm olein available in markets. Used palm oil is waste frying oil from restaurants. Crude palm oil is obtained from a palm oil mill in southern part of Thailand. Density at 40°C, free fatty acid (%oleic acid), acid value, saponification value, and molecular weight were calculated into Appendix A. Properties of oils were shown in Table 4.1.

Table 4.1 Properties of oils

Property	Refined palm oil	Used palm oil	Crude palm oil
Density at 40°C(g/ml)	0.9155	0.9124	0.9102
Kinetic viscosity at 40°C(cSt)	36.8	36.8	36.7
Acid value	1.12	4.45	28.51
Saponification value	210	210	202
Color	Yellow	Yellow-brown	Reddish-brown
Molecular weight	801.74	802.34	838.64
Free fatty acid	0.56	2.24	14.34

Densities, saponification values, and kinetic viscosities of palm oils used in this study were approximately the same values. Acid value had clearly differentiated value because of an amount of free fatty acid in palm oil. Increasing the amount of free fatty acid resulted in acid value increases.

The major fatty acid components for palm oil are palmitic, oleic, linoleic, and stearic acid. In this study, the fatty acid compositions would be analyzed in term of fatty acid methyl esters. The fatty acid compositions of palm oils were shown in Table 4.2.

Table 4.2 The fatty acid compositions of palm oil

Fatty acid	Palm oil
palmitic	34.4
Oleic	58.4*
Linoleic	
stearic	3.6

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

4.2 Homogenous catalyst

Based on stoichiometry, number of mole for chemical reaction of palm oil and methanol to produce esters is 1 mole to 3 moles. Since transesterification is a reversible reaction, excess methanol is required to push the reaction to the right in order to produce more methyl esters. Undesirable and unavoidable side reactions also occur. These reactions were shown as following Equation 4.1 and Equation 4.2. Amount of catalyst required in each experiment must be determined. The suitable amount is equal to the amount of catalyst required for neutralization of free fatty acid in palm oil plus 0.5 wt%.

In this study, the vegetable oils are refined palm oil, used palm oil, and crude palm oil. NaOH is used as catalyst. The experiments are conducted for 2 hours, at a stirrer speed of 400 rpm, 100%excess methanol by weight or mole. Amount of catalyst used in each experiment were 0.25, 0.50, and 1.0%wt of oil. Temperature of 40, 50, and 60°C were used.

Neutralization: Unavoidable side reaction (FFA)

$$\text{Fatty acid + alkali} \xrightarrow{(H_2O)} \text{soap + water} \qquad (4.1)$$

Saponification: Undesired side reaction (H_2O)

$$\text{Triglyceride + alkali} \xrightarrow{(H_2O)} \text{soap + glycerol} \qquad (4.2)$$

After each experiment, the reaction product was left overnight for complete separation between an oil phase and a glycerol phase. Figure 4.8 to 4.12 showed palm oils and their reaction products. The oil phase or the top layer was washed with water to remove catalyst and unreacted methanol. It was kept for analysis of methyl ester. Before washing, methyl ester layer was determined percentage of yield which was shown in Table 4.3. Percentage of yield of biodiesel was shown as following Equation 4.3.

$$\%\text{yield} = \frac{\text{weight of top layer X 100}}{\text{weight of palm oil}} \qquad (4.3)$$

Table 4.3 Percentage of yield of methyl ester from transesterification

Oil	**Amount of NaOH as catalyst(%wt of oil)**	**Temperature (°C)**	**%Yield**
Refined palm oil	0.25	40	90.5
Refined palm oil	0.25	50	94.1
Refined palm oil	0.25	60	97.4
Refined palm oil	0.50	40	91.2
Refined palm oil	0.50	50	96.8
Refined palm oil	0.50	60	99.3
Refined palm oil	1.0	40	90.7
Refined palm oil	1.0	50	94.6
Refined palm oil	1.0	60	97.7
Used palm oil	0.25	40	89.1
Used palm oil	0.25	50	92.7
Used palm oil	0.25	60	95.4
Used palm oil	0.50	40	90.4
Used palm oil	0.50	50	94.8
Used palm oil	0.50	60	96.6
Used palm oil	1.0	40	89.7
Used palm oil	1.0	50	92.5
Used palm oil	1.0	60	95.8
Crude palm oil	0.25	40	-*
Crude palm oil	0.25	50	-
Crude palm oil	0.25	60	-
Crude palm oil	0.50	40	-
Crude palm oil	0.50	50	-
Crude palm oil	0.50	60	-
Crude palm oil	1.0	40	-
Crude palm oil	1.0	50	-
Crude palm oil	1.0	60	-

* Crude palm oil can not be determined (see Figure 4.13).

Since triglycerides were transformed to Methyl esters, so properties of methyl were tested such as density, viscosity, and flash point. Their properties were shown in Table 4.4.

Table 4.4 Properties of methyl ester in comparison with the oil and diesel fuel

Analysis	The oil	Methyl ester	Diesel*
Density at (40°C)	0.9102-0.9155	0.8602-0.8733	0.8302
Viscosity at (40°C)	36.7-36.8	4.53-4.86	3.34
Flash point(°C)	280-320	171-177	69

* Data from PTT Public Company Limited

The results, as summarized in Table 4.4, showed that transesterification improved fuel properties of the oil. The comparison of these properties with diesel fuel showed that the methyl ester has relatively closer fuel properties to diesel fuel than that of oil. The viscosity was substantially reduced from 36.7-36.8 to 4.53-4.86 cSt. Physical properties of methyl esters (density, viscosity, and flash point) can be discussed in three parts.

- Effect of reaction temperature
- Effect of amount of catalyst
- Effect of types of palm oil

- <u>Effect of reaction temperature</u>

As shown in Table 4.4, the results of density, viscosity, and flash point were shown in Figure 4.1, 4.2, and 4.3, respectively.

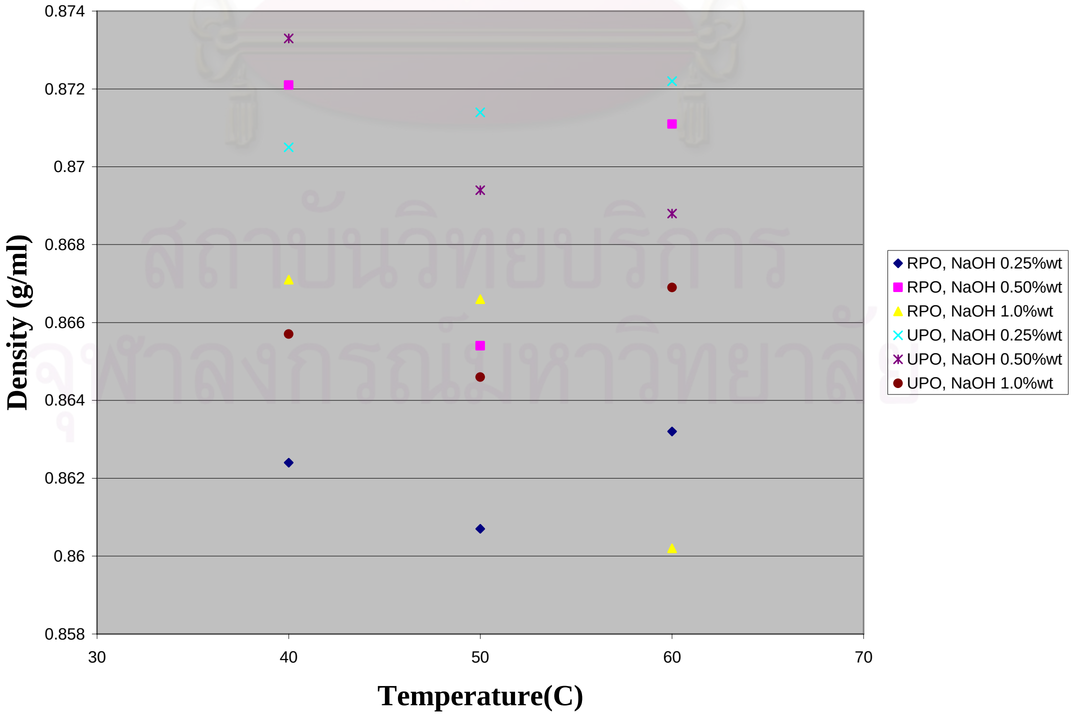


Figure 4.1 Effect of reaction temperature of density

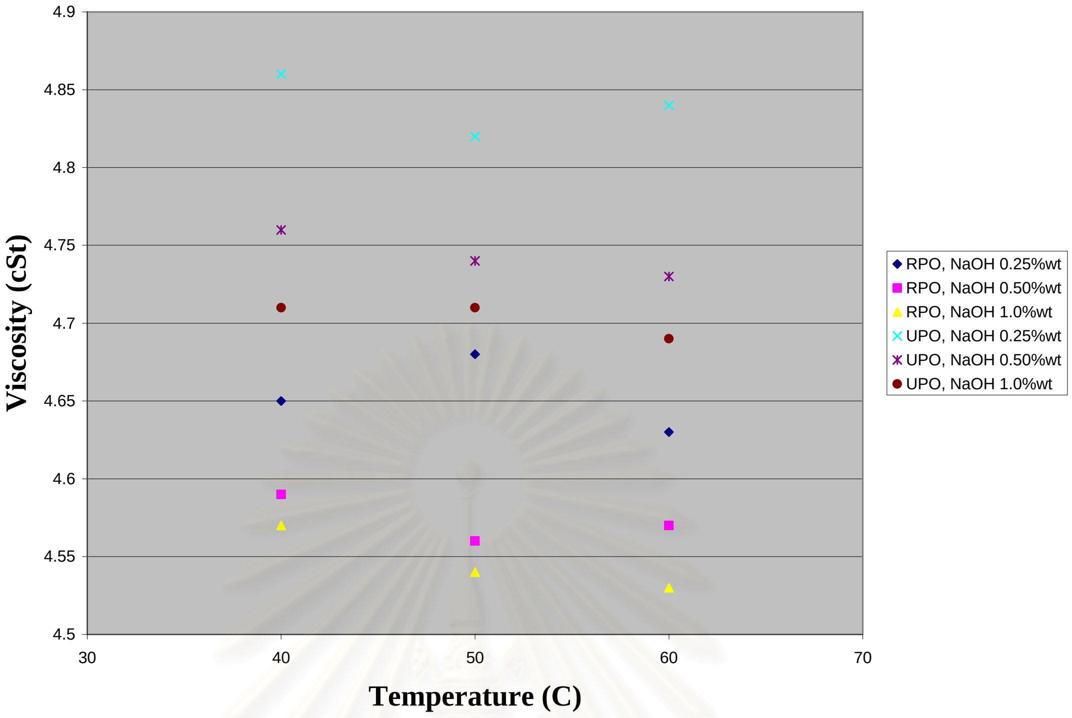


Figure 4.2 Effect of reaction temperature of viscosity

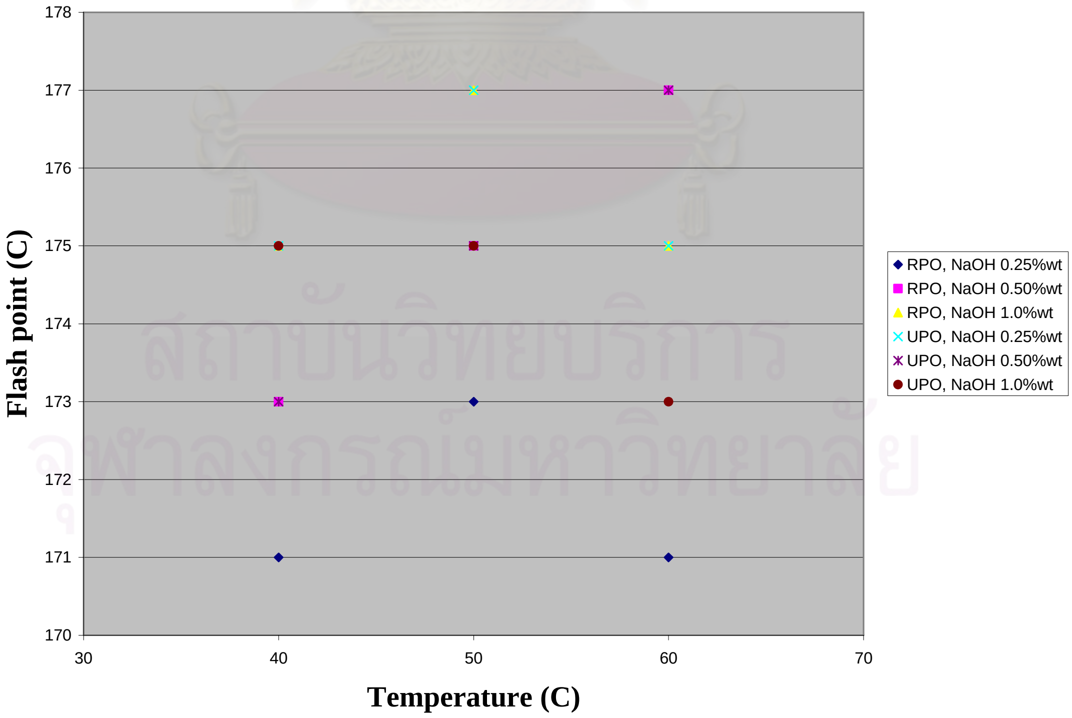


Figure 4.3 Effect of reaction temperature of flash point

The results from Figure 4.1, 4.2, and 4.3 showed that all viscosities at 40˚C are higher than viscosities at 60˚C. One mole of oil can be broken to three moles of methyl esters, so viscosity of methyl esters is lower than oil. It proved that at the temperature of 60˚C the reaction was more completed than temperature of 40˚C. Density and flash point in this study can not be described the effect to the reaction temperature.

- <u>Effect of amount of catalyst</u>

As shown in Table 4.4, the results of density, viscosity, and flash point were shown in Figure 4.4, 4.5, and 4.6, respectively.

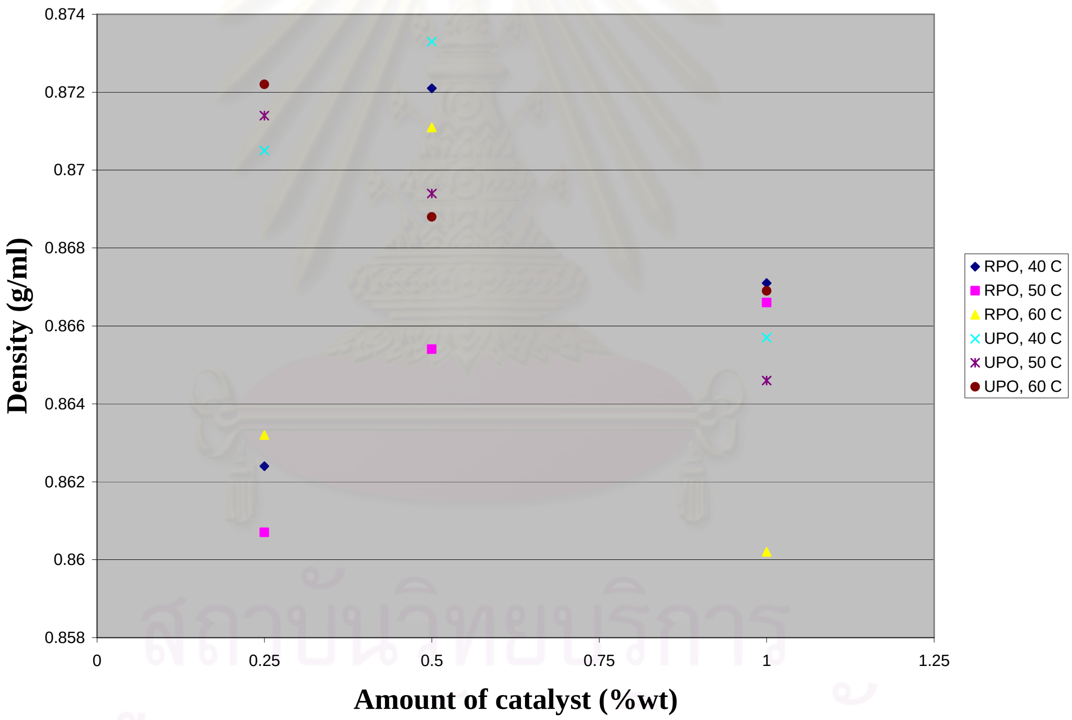


Figure 4.4 Effect of amount of catalyst of density

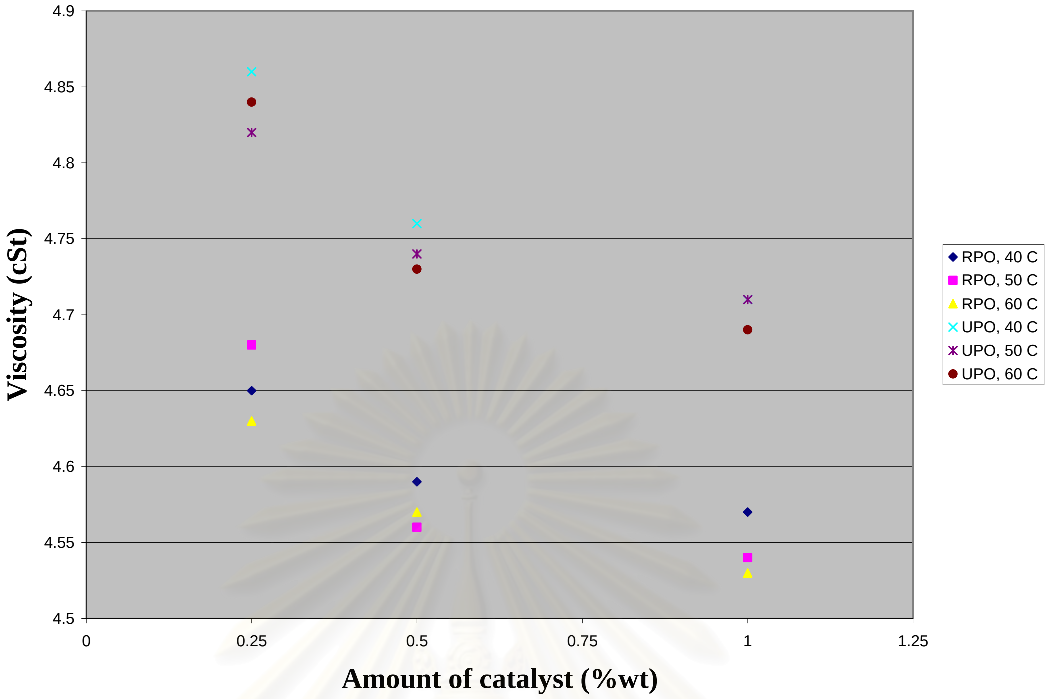


Figure 4.5 Effect of amount of catalyst of viscosity

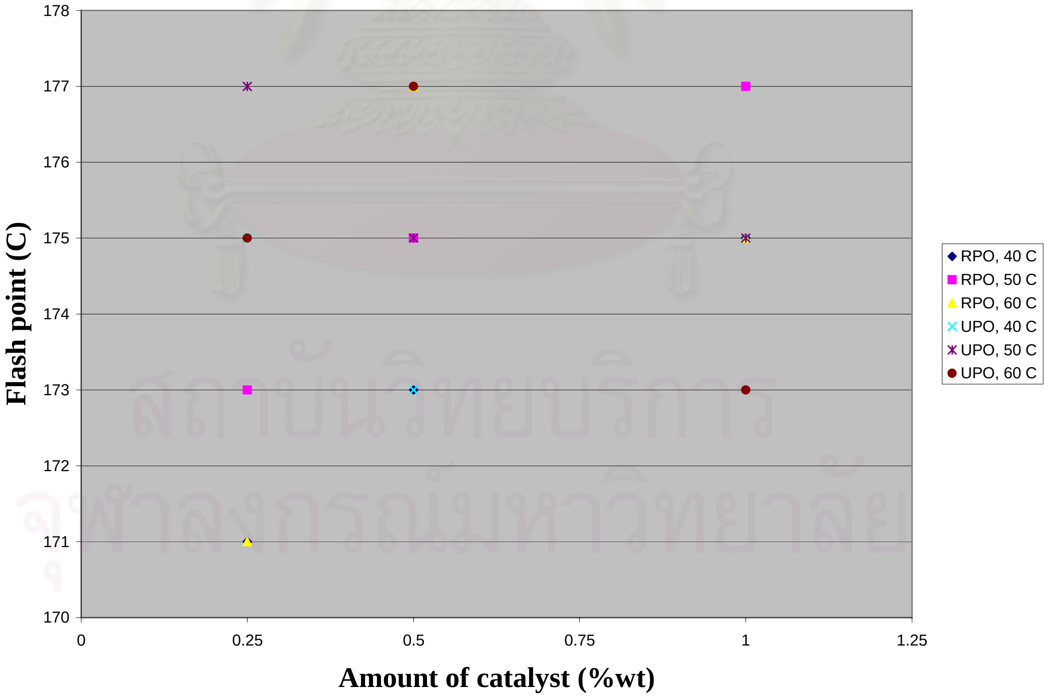


Figure 4.6 Effect of amount of catalyst of flash point

The results shown in Figure 4.4, 4.5, and 4.6 showed that viscosity had an effect on amount of catalyst. Increasing of amount of catalyst from 0.25 to 1.0%wt trend would decrease viscosity.

- Effect of types of palm oil

As shown in Table 4.4, the results of density, viscosity, and flash point were shown in Figure 4.7, 4.8, and 4.9, respectively.

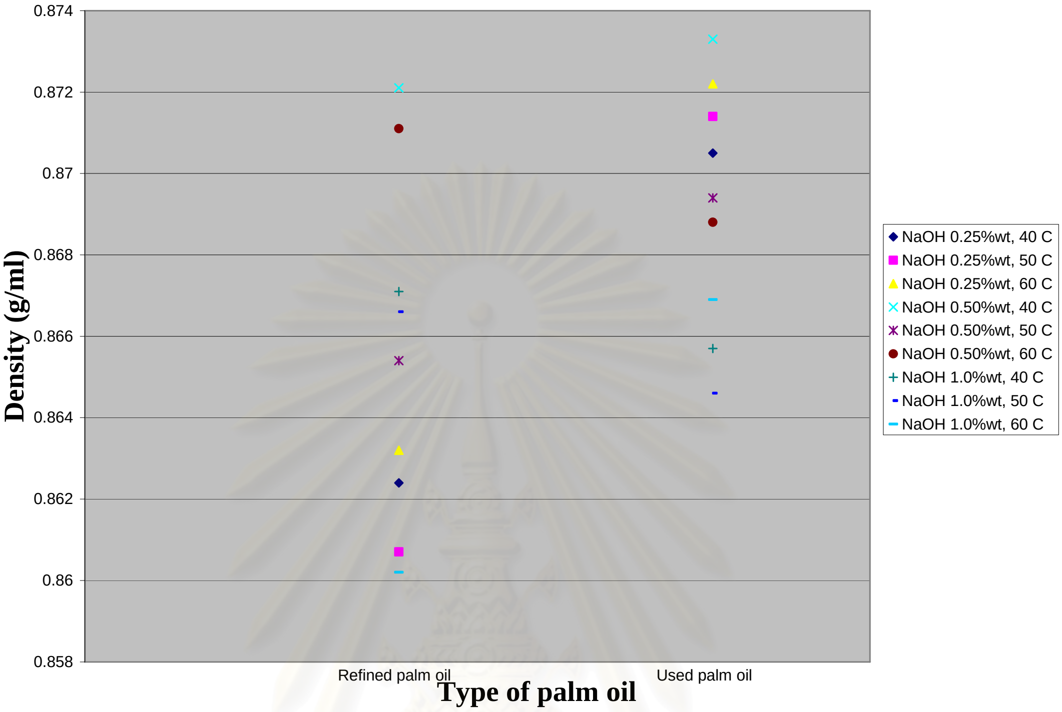


Figure 4.7 Effect of types of palm oil of density

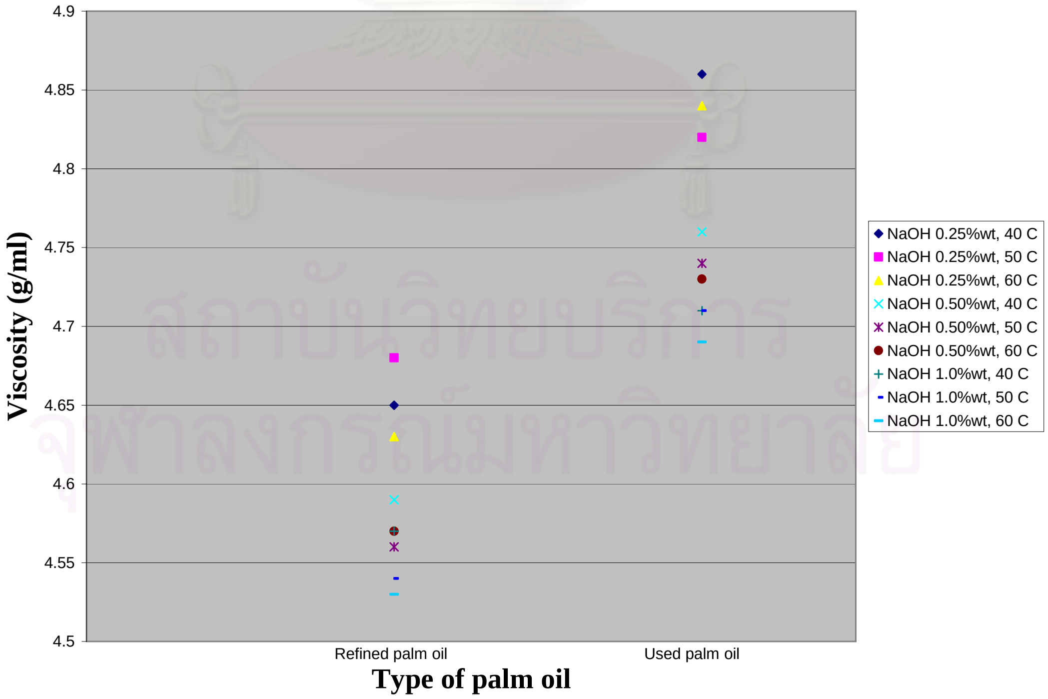


Figure 4.8 Effect of types of palm oil of viscosity

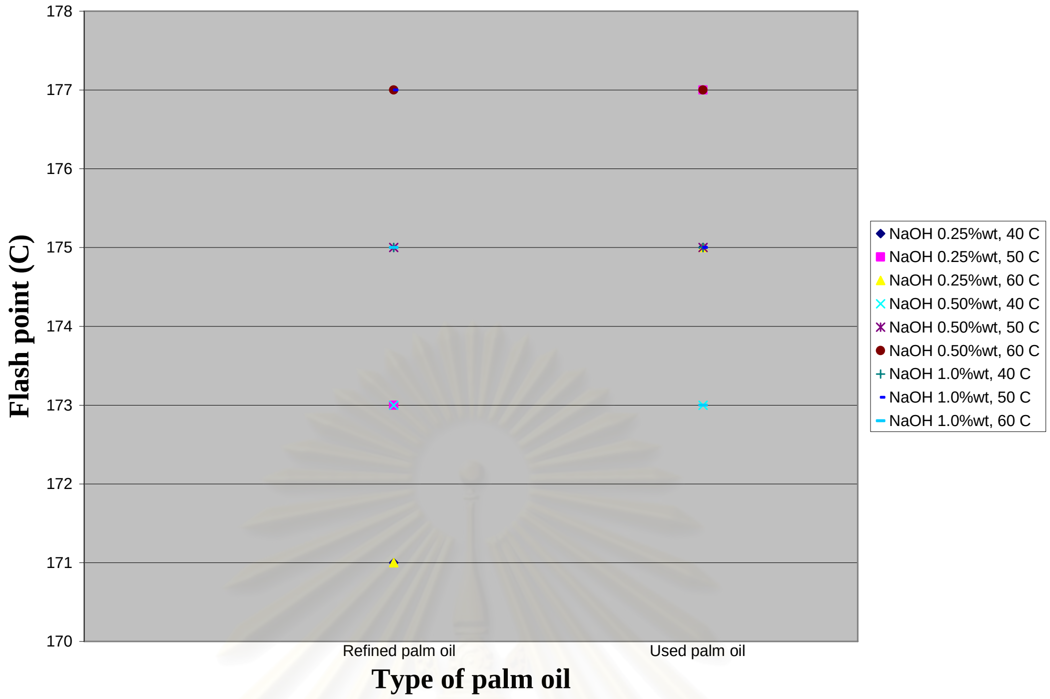


Figure 4.9 Effect of types of palm oil of flash point

The results shown in Figure 4.7, 4.8, and 4.9 showed that viscosities have effect to types of palm oil. Transesterification which used refined palm oil had lower viscosity than used palm oil.

Figure 4.10 Picture of refined palm oil (left), Glycerol (middle), and methyl esters (right)

Figure 4.11 Picture of used palm oil (left), glycerol (middle), and methyl esters (right)

Before reaction

After reaction

Figure 4.12 Picture of CPO before and after reaction

Figure 4.13 Picture of crude palm oil after reaction standing overnight to insure the separation of the methyl ester (biodiesel)

From experimental conditions, there were three parameters to be discussed.

4.2.1 Effect of reaction temperature
4.2.2 Effect of amount of catalyst
4.2.3 Effect of types of palm oil

4.2.1 Effect of reaction temperature

Transesterification can occur at different temperatures. In this study, methanol was used 100%excess from its stoichiometric ratio and all conditions were used as shown in Table 3.2. Results of percentage of yield were shown in Table 4.3.

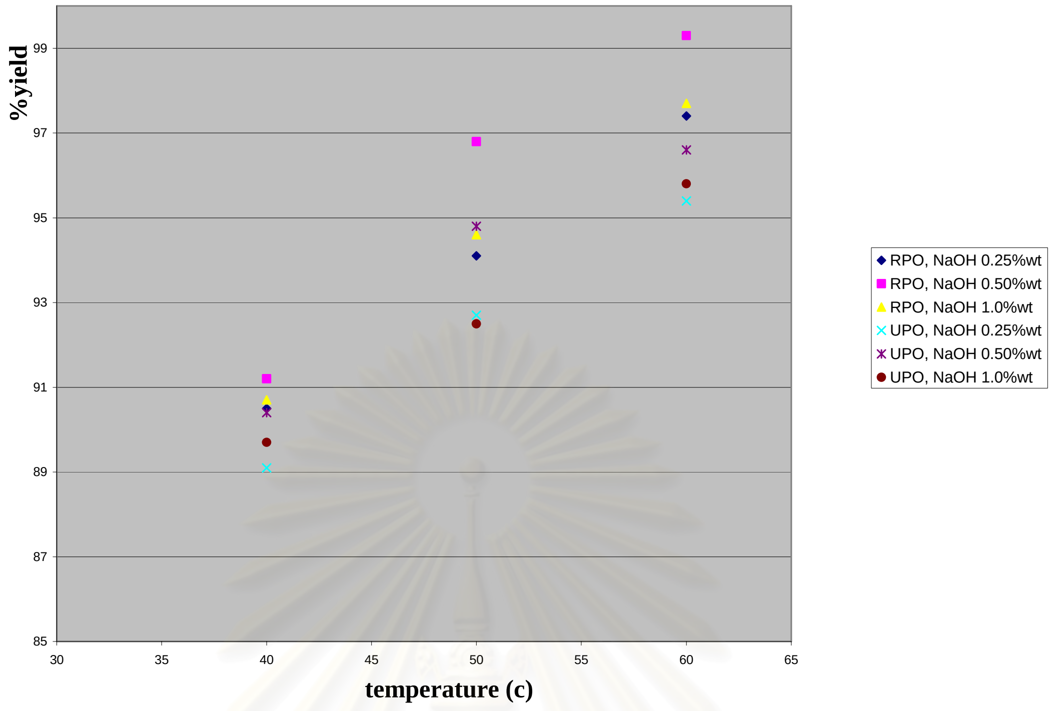


Figure 4.14 Effect of reaction temperature on percentage of yield

Acoording to Figure 4.14, it showed that at 60°C percentage of yield were greater than at 50 and 40°C, respectively.

Previous study of transesterification of soybean oil with methanol (6:1) using 1%NaOH and three different temperatures were used (Freedman et al., 1984). Ester yields were 94, 87, and 64% at temperature of 60, 45, and 32°C, respectively.

It proved that ester yield would decrease when temperature decrease.

4.2.2 Effect of amount of catalyst

The transesterification was carried out by the procedure as described in section 3.3.2. The reaction conditions were set the same as section 4.2.1. Results of percentage of yield were shown in Table 4.3.

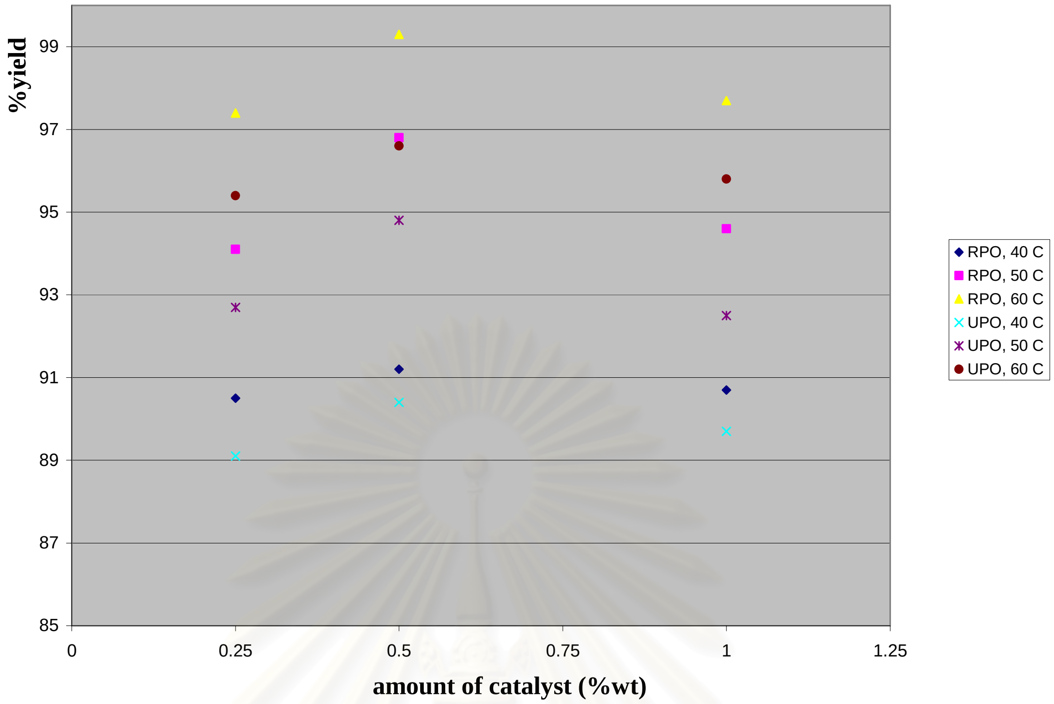


Figure 4.15 Effect of amount of catalyst on percentage of ester yield

As shown in Figure 4.15, when catalyst was increased from 0.25 to 0.5%wt, percentage of yield increased. But percentage of yield decreased when catalyst was 1%wt.

The alkaline catalyst, sodium hydroxide concentration in the range of 0.3-1%wt was used in studying of A.S. Ramadhas et al., 2004. The maximum conversion efficiency was achieved at 0.5%wt of NaOH. Addition of excess amount of catalyst, gave rice to the formation of emulsion, which increased the viscosity and led to the formation of gels (A.S. Ramadhas et al., 2004).

It proved that the suitable amount of catalyst is 0.5%wt for transesterification.

4.2.3 Effect of type of palm oils

Two possible side reactions are saponification or neutralization of the free fatty acid in the vegetable oil. Both of them produced sodium soaps (Gemma Vicente et al., 2003). The reaction conditions are set the same as section 4.2.1. Results of percentage of yield were shown in Table 4.3.

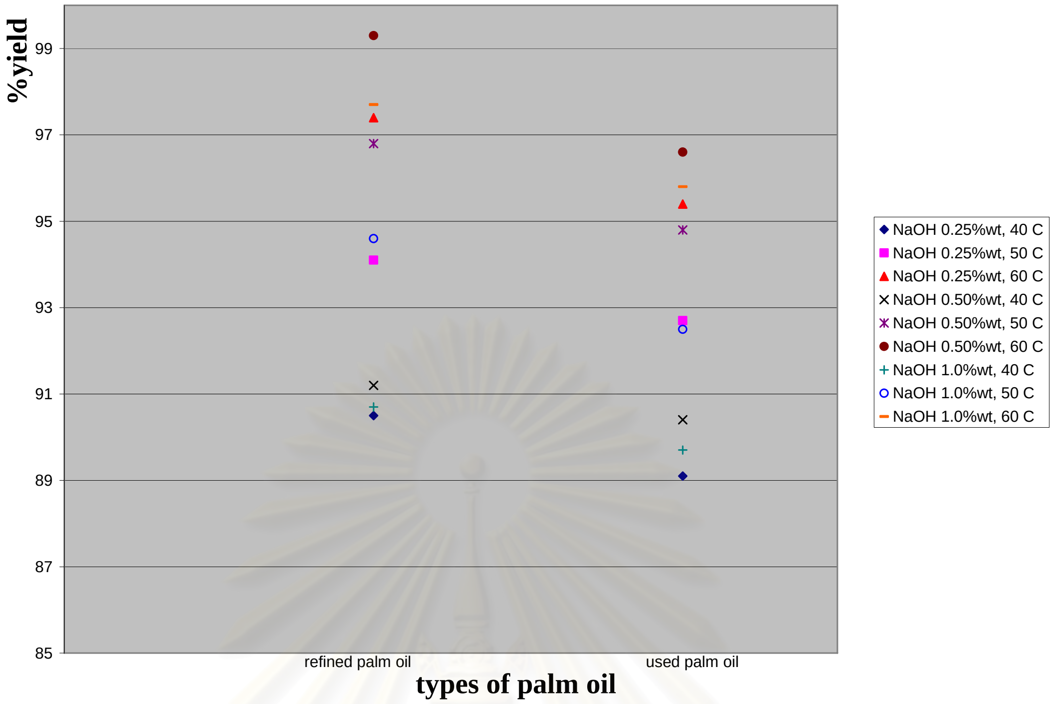


Figure 4.16 Effect of type of palm oils on percentage of ester yield

Each type of palm oil was used in the experiments had different free fatty acid which was shown in section 4.1. The results shown in Figure 4.16 showed that transesterification by using refined palm oil was higher percentage of ester yields than used palm oil. Crude palm oil could not be determined. Owing to their polarity, the soaps dissolved in to the glycerol phase during the separation stage after the reaction. In addition, the dissolved soaps increased the methyl ester solubility in the glycerol, and additional cause of yield lost (Gemma Vicente et al., 2003). It supposed that amount of free fatty acid in oil was increased resulted in percentage of yield decreased.

In this study, percentages of methyl esters were determined to compare with percentages of yields. They were shown in Table 4.5.

Table 4.5 Comparison between %methyl esters and %yields

Oil	**Amount of NaOH as catalyst(%wt of oil)**	**Temperature (°C)**	**%Yield**	**%Methyl ester**
Refined palm oil	0.25	40	90.5	87.12
Refined palm oil	0.25	50	94.1	90.58
Refined palm oil	0.25	60	97.4	90.92
Refined palm oil	0.5	60	99.3	93.72
Refined palm oil	1.0	60	97.7	96.29
Used palm oil	0.25	40	89.1	79.19
Used palm oil	0.25	50	92.7	81.09
Used palm oil	0.25	60	95.4	83.58
Used palm oil	0.5	60	96.6	89.14
Used palm oil	1.0	60	95.8	91.08

According to Table 4.5, it showed that percentage of methyl ester increased when temperature and catalyst amount were increased. On the other hand, percentage of yield decreased when catalyst amount was increased to 1%wt.

4.3 Heterogeneous catalyst

Initially, the mixture of vegetable oil, methanol and solid catalyst will separate into three phase. The reaction is controlled by diffusion and poor diffusion of reactants results in a slow rate (Srivastava and Prasad, 2000). Thus, solvent is needed to increase the contact among reactants and catalyst. In this study, solvent used is THF (tetrahydrofuran). Several studies on heterogeneous catalytic transesterification have examined it at high temperature. Therefore, catalysts for low reaction temperature (60°C) were chosen for investigating in this thesis. After the transesterification, the products were the mixtures of esters, glycerol, methanol, solvent and the spent solid catalyst. The spent catalyst was separated from the products by filtration. After the catalyst removal, the product was condensed to separate excess methanol and solvent, which will result in the methyl esters phase (top phase) and the glycerol phase (bottom phase).

The purity of biodiesel products (methyl esters) was then determined by GC. The percentage of methyl esters were shown in Table 4.6. To confirm this, the chromatograms of methyl esters were shown in Appendix B.

Table 4.6 Percentage of methyl esters

Oil	Catalyst	%Catalyst (by weight of oil)	%Methyl esters(by mass)
Refined palm oil	Dowex	25	20.84
Refined palm oil	Dowex	50	32.96
Refined palm oil	Amberlyst-15	25	29.23
Refined palm oil	Amberlyst-15	50	41.90
Used palm oil	Dowex	25	33.86
Used palm oil	Dowex	50	44.22
Used palm oil	Amberlyst-15	25	44.71
Used palm oil	Amberlyst-15	50	51.95
Crude palm oil	Dowex	25	41.91
Crude palm oil	Dowex	50	47.58
Crude palm oil	Amberlyst-15	25	49.32
Crude palm oil	Amberlyst-15	50	57.89

4.4 Investigating of heterogeneous catalysts for transesterification

This study based on two ion-exchange resin catalysts (Dowex and Amberlyst-15). The experiment conditions were shown in Table 3.3. Temperature, methanol: oil molar ratio, and stirrer speed were set at 60°C, 300:1 (Referring to a previous study showed that suitable methanol: oil molar ratio was 300:1), and 400 rpm respectively. Products can be analyzed only percentage of methyl esters because amount of catalysts have to use 25-50%wt and its cost is very expensive. This study used 10 grams of oils for each batch reaction.

As shown in Table 3.3, there were many parameters which had an effect on percentage of methyl esters. Discussion of results was divided into three sections.

4.4.1 Effect of catalysts between dowex and amberlyst-15
4.4.2 Amount of catalyst for transesterification
4.4.3 Influence of free fatty acid content

4.4.1 Effect of catalysts between dowex and amberlyst-15

Both catalysts were studied during the transesterification of palm oil and methanol at 60°C over time period of 8 hours. For all reactions, the initial molar ratio of reagents was 300:1 (methanol: palm oil) which was the suggested proportion for tranesterification with methanol over ion-exchange resins (Simone C.M. dos Reis et at., 2005). Previous results have shown that higher molar ratios are needed in acid-catalyzed transesterification on account of slower reaction rates (M. Mittelbach et at., 1996). However, in this study, the same reagent molar ratio was maintained for both catalysts for comparison reasons. Resins with two types of structure were studied: One had a gel structure (Dowex) and the other, a macro porous structure (Amberlyst-15). Each experimental batch was set temperature, methanol: oil molar ratio and stirrer at 60°C, 300:1 and 400 rpm, respectively. Dowex and Amberlyst-15 were used as catalysts. Reaction time was 8 hours.

From GC analytical, percentage of methyl esters were shown in Table 4.7.

Table 4.7 Results of percentage of methyl esters

Sample	**%Methyl esters(by mass)**
111	20.84
112	32.96
121	29.23
122	41.90
211	33.86
212	44.22
221	44.71
222	51.95
311	41.91
312	47.58
321	49.32
322	57.89

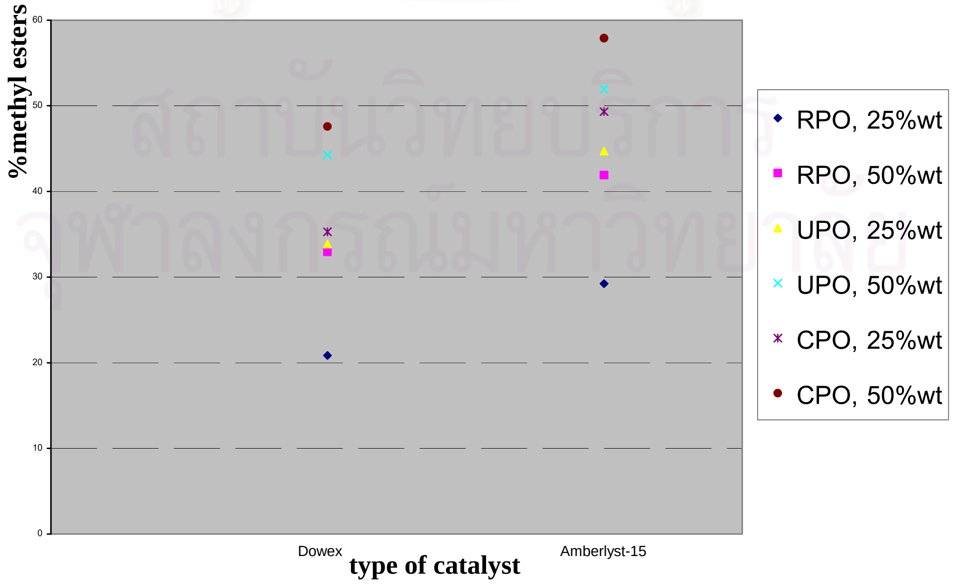


Figure 4.17 Results of transesterification reaction with different resins

The results shown in Figure 4.17 showed that transesterification by using Amberlyst-15 had higher percentage of methyl esters than Dowex, which indicated that percentage of methyl esters depended on the structure of the resins. For dowex (gel resin), a contraction of the gel matrix probably occurs that limits the accessibility of the reactant to active sites. On the other hand, the active sites of Amberlyst-15 are located in the macroporous structure, where they are easily accessible to the reactants (Pouilloux et at., 1999).

4.4.2 Amount of catalyst for transesterification

In the previous study, the reactions were carried out using alcohol/oil molar ratio (300:1) and 1 g of resin in presence of a co-solvent (THF). After the reaction time (8 hours), its conversion was 74% (Simone C.M. dos Reis et at., 2005). It was also mentioned by G.D. Yadav et al., 2002 that the catalyst loading was varied from 50 to 150 kg/m^3 based on the total volume of the reactants. It was found that with an increase in loading the conversion of maleic acid increased in consonance with the proportional increase in the active sites.

For this study the reactions were carried out using amount catalyst as 25%wt and 50%wt (by weight of oil). Each experimental batch was set the same as section 4.3.1. From GC analytical, percentage of methyl esters were shown in Table 4.7. And results of effect of amount of catalyst were shown in Figure 4.18

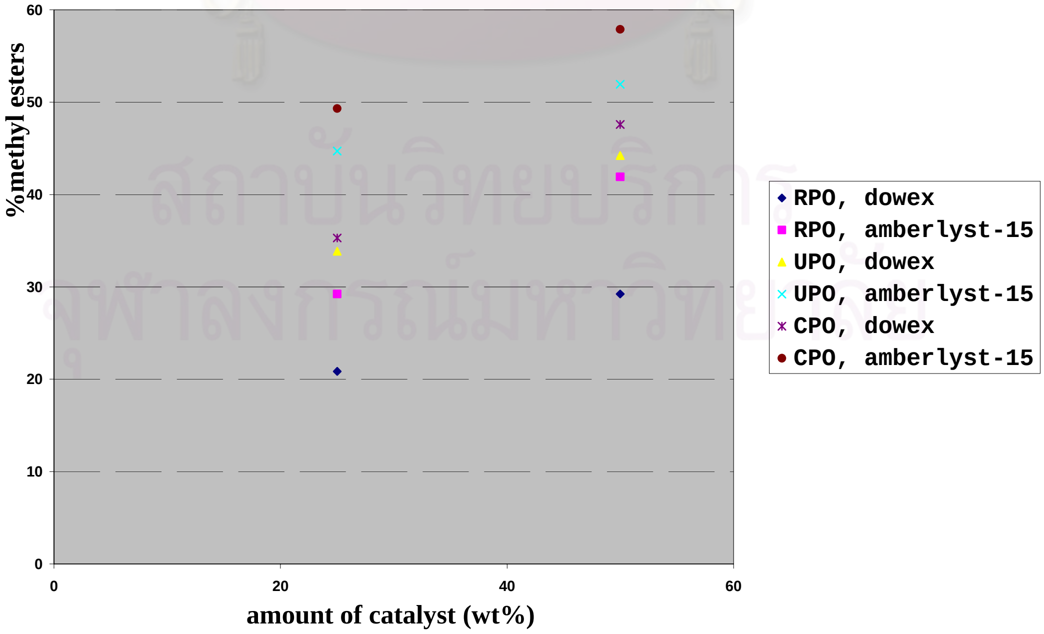


Figure 4.18 Results of transesterification reaction with different amount of catalyst

For Dowex, all conditions percentage of methyl esters from using 50%wt catalyst were higher than using 25%wt catalyst about 10% methyl esters similar to using Amberlyst-15. After amount of catalyst was increased two times, percentage of methyl ester was not being double. It proved that increasing catalysts resulted in percentage of methyl esters increases.

4.4.3 Influence of free fatty acid content

This experiment used three types of palm oil, refined palm oil, used palm oil, and crude palm oil. There were different free fatty acids in each type as shown in Table 4.1. The reaction conditions were set the same as section 4.3.1. From GC analytical, percentage of methyl esters were shown in Table 4.7. The results of influence of type of palm oil of methyl esters were shown in Figure 4.19.

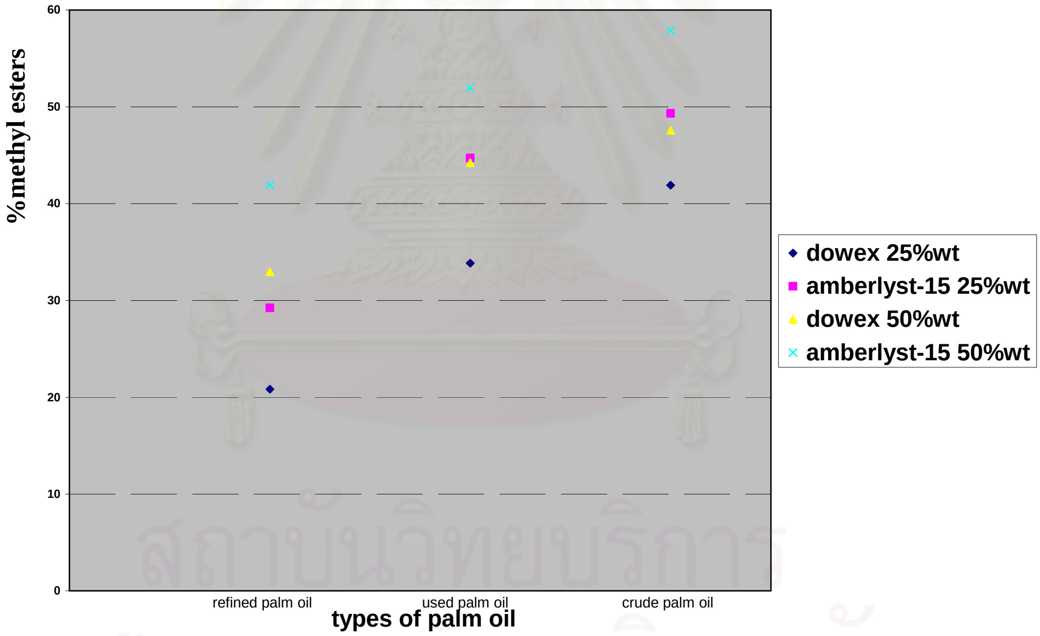


Figure 4.19 Influence of type of palm oil on percentage of methyl esters in transesterification reactions

As the results, percentage of methyl esters of transesterification from crude palm oil > used palm oil > refined palm oil. Free fatty acid content has an influence on the course of the transesterification (Ulf Schuchardt et al., 1998). These result proved that, percentage of methyl esters of transesterification was increased with increasing free fatty acid content.

4.5 Comparison between homogeneous and heterogeneous catalyst

There are many parameters such as the type of catalyst, temperature, free fatty acid content, and purity of the reactants (mainly water content) etc. have influence to percentage of methyl esters of transesterification reaction. From 4.3.3 reported percentage of methyl esters of heterogeneous catalyzed transesterification with different types of palm oil. Homogeneous catalyzed transesterification with 1.0%NaOH at 60°C was occurred for a comparison. The results of percentage of methyl esters were shown in Figure 4.20 as follows.

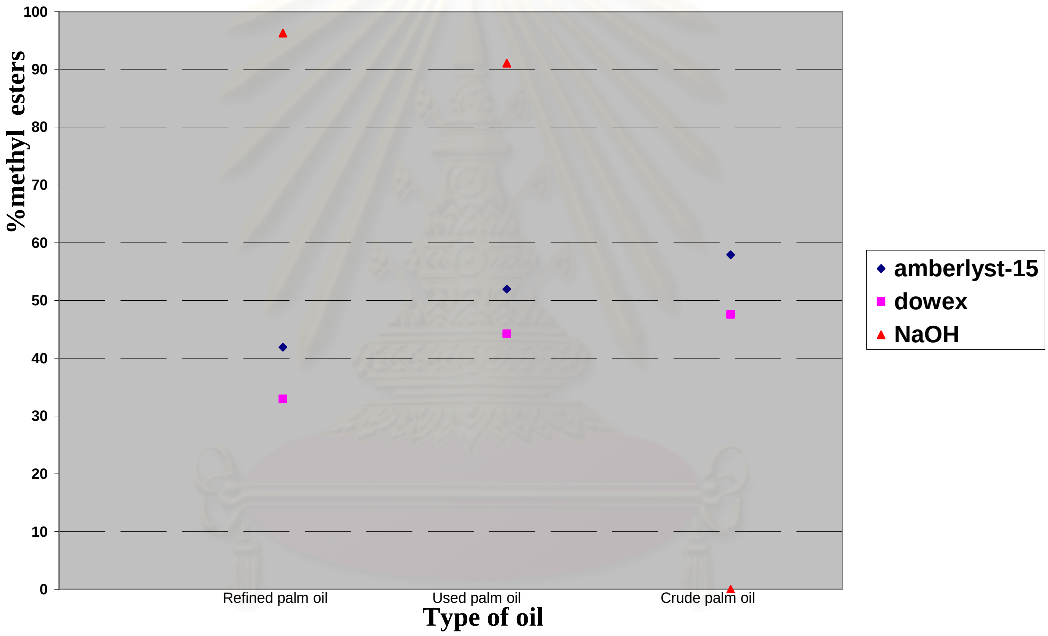


Figure 4.20 Percentages of methyl esters between homogeneous and heterogeneous catalyzed transesterification reactions

As shown, for heterogeneous catalyst, percentage of methyl esters of reactions were increased according the amount of free fatty acid content in oils but increasing amount of free fatty acid content would decrease percentage of methyl esters for homogeneous catalyst.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions are drawn from the study:

1. The study showed that the refined and used palm oils could be used as a material for producing biodiesel for transesterification using homogeneous catalyst.
2. Increasing free fatty acid resulted in a decrease in percentage of yield of methyl esters for transesterification using homogeneous catalyst.
3. Increasing operating temperature tended to increase percentage of yield of methyl esters for transesterification using homogeneous catalyst.
4. Amberlyst-15 gave percentage of methyl esters more than Dowex.
5. Increasing free fatty acid and amount of catalyst resulted in an increase in percentage of methyl esters for heterogeneous catalyzed-transesterifcation reaction.
6. For transesterification using homogeneous catalyst, the optimum condition was refined palm oil using catalyst 1% by weight of oil at 60°C which gives Methyl ester of 96.29%.
7. For transesterification using heterogeneous catalyst, the optimum condition was crude palm oil using Amberlyst-15 50% by weight of oil which gives methyl ester 57.89%.

5.2 Recommendations

1. The heterogeneous catalysts used in the experiment are too expensive and they have to use a lot of amount for reaction.
2. Co-solvent for reaction should be less toxic than tetrahydrofuran.
3. In the experiment, catalysts were broken which effect to percentage of methyl esters.
4. Select others ion-exchange resins for study.

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APPENDICES

APPENDIX A

A-1 Acid Value (Free Fatty Acid Content), AOCS Official Method Cd-3d-63

1. Weigh palm oil 10-20 g. in conical flasks 250 ml.
2. Add mix equal volumes of 96% ethanol and diethyl ether molar ratio 1:1 50 ml.
3. Solution is titrated with 0.5 N sodium hydroxide solution.
4. Titrate while swirling, using phenolphthalein as indicator.

Calculation

Let: Weight (g)of sample = w
Volume (ml)of sodium hydroxide used = v
Normality of sodium hydroxide = N
Molecular weight of the fatty acids = M

$$\text{Acid value} = \frac{56.1Nv}{w}$$

Table A1 Acid value of oils

	Refined palm oil	Used palm oil	Crude palm oil
Weight(g)	10.0056	10.0860	10.0369
Conc.NaOH	0.5 N	0.5 N	0.5 N
V NaOH (ml)	0.4	1.6	10.2
Acid value	**1.12**	**4.45**	**28.51**

% Free fatty acid (oleic acid) = acid value x 0.503

Table A2 Percentage of free fatty acid of oils

	Refined palm oil	Used palm oil	Crude palm oil
% Free fatty acid (oleic acid)	**0.56**	**2.24**	**14.34**

A-2 Saponification Value, AOCS official Method Cd-3b-76

The saponification value is determined by completely saponifying the oil or fat with a known amount of potassium hydroxide, the excess of which is determined by titration.

Reagents

Hydrochloric acid 0.5 N aqueous solution, accurately standardized.
Potassium hydroxide 0.5 N solution in 96% ethanol.
Phenolphthalein indicator 1% in 96% ethanol.

Apparatus

Conical flasks 250 ml, made of alkali-resistant glass, provided with a reflux condenser with a ground joint.

Process

1. Weigh into a 250 ml conical flask about 4 g. filtered fat with an accuracy of 1 mg.
2. Add, accurately measured, 50 ml 0.5 N ethanol potassium hydroxide solution to the cold fat and attach the reflux condenser to the flask.
3. Heat, and as soon as the ethanol boil, occasionally shake the flask until the fat is completely dissolved. Boil the solution for half an hour after the fat is completely dissolved.
4. Add 1 ml phenolphthalein indicator and slowly titrate the hot soap solution obtained with 0.5 N hydrochloric acid.
5. Carry out a blank determination upon the same quantity of potassium hydroxide solution at the same time and under the same conditions.

Calculation

Let; Weight (g)of oil or fat taken = w
Volume (ml)of hydrochloric acid used in test = v_1
Volume (ml)of hydrochloric acid used in blank = v_2
Normality of hydrochloric acid = N

$$\text{Saponification value} = \frac{56.1N(v_2 - v_1)}{w}$$

Table A3 Saponification of oils

	Refined palm oil	Used palm oil	Crude palm oil
Weight (g)	2.0001	2.0005	2.0007
Conc.of HCl(N)	0.5	0.5	0.5
Volume of HCl used in test (ml)	6.7	6.7	7.3
Volume of HCl used in blank (ml)	21.7		
Saponification value	**210**	**210**	**202**

A-3 Molecular weight of the fatty acids

For the determination of the mean molecular weight of the fatty acids present in a fat the following methods may be used;

1. Assuming the fat to consist of a mixture of triglycerides and free fatty acids and fixed and free fatty acids to have the same mean molecular weight, an apparent value for the mean molecular weight of the fatty acids (M) may be calculated:

$$M = \frac{[56108 - 12.67(SV-AV)]}{SV}$$

Where

SV = saponification value of the fat

AV = acid value of the fat

2. The mean molecular weight of the water-insoluble fatty acids (M) is calculated:

$$M = \frac{56108}{\text{SV of fatty acids}}$$

3. In 1 and 2 the unsaponifiable is included in M. The true mean molecular weight of the water insoluble fatty acids is determined by saponification of the fat, extraction of the unsaponifiable matter, separation of the fatty acids and determination of their saponification value:

$$M = \frac{56108}{\text{SV of fatty acids}}$$

Note: The saponification value (S.V), which is related to the molecular weight of the fat, denotes the number of mg. potassium hydroxide which is required to saponify 1 g. of fat, i.e. to neutralize the free fatty acids and the fatty acids combined as glycerides.

Calculation

For this study, the determination of the mean molecular weight of the fatty acids present in a fat the following methods may be used;

1. Assuming the fat to consist of a mixture of triglycerides and free fatty acids and fixed and free fatty acids to have the same mean molecular weight, an apparent value for the mean molecular weight of the fatty acids (M) may be calculated:

Where

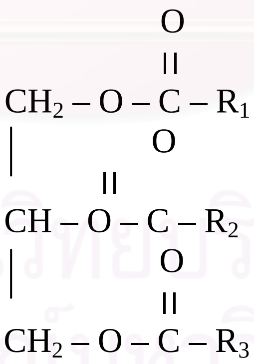
SV = saponification value of the fat
AV = acid value of the fat

$$M = \frac{[56108 - 12.67(SV\text{-}AV)]}{SV}$$

Table A4 Mean molecular weight of the fatty acids

	Refined palm oil	Used palm oil	Crude palm oil
Saponification value	210	210	202
Acid value	1.12	4.45	28.51
Mean molecular weight of the fatty acids	**254.58**	**254.78**	**266.88**

A-4 Calculation molecular weight of palm oil



Triglyceride

R_1, R_2, R_3: carbon chain of the fatty acids

Molecular weight of triglyceride

$$Mw_{TG} = 3R_{aver} + 38$$

Where

Mw_{TG} = molecular weight of triglyceride

R_{aver} = average molecular weight of fatty acid (M)

Table A5 Molecular weight of palm oils

	Refined palm oil	Used palm oil	Crude palm oil
Mean molecular weight of the fatty acids	254.58	254.78	266.88
$Mw_{TG} = 3R_{aver} + 38$	3(254.58)+38	3(254.78)+38	3(266.88)+38
Molecular weight	801.74	802.34	838.64

A-5 Density of palm oils and its methyl esters

For this study densities were determined at 40°C by using pycnometer 10 ml.

Table A6 Density of palm oils and its methyl esters

Palm oil	Weight of pycnometer (g)	Weight of pycnometer + Weight of oil (g)	Weight of oil (g)	Volume of pycnometer (ml)	Density (g/ml)
Refined	17.4741	17.4621	17.4543	10	0.9155
Used	26.6292	26.5862	26.5562	10	0.9124
Crude	9.1551	9.1241	9.1019	10	0.9102
Sample No.	Weight of pycnometer (g)	Weight of pycnometer + Weight of oil (g)	Weight of oil (g)	Volume of pycnometer (ml)	Density (g/ml)
1	17.4736	26.0974	8.6238	10	0.8624
2	17.4665	26.0733	8.6068	10	0.8607
3	17.4823	26.1138	8.6315	10	0.8632
4	17.4442	26.1655	8.7213	10	0.8721
5	17.4953	26.1494	8.6541	10	0.8654
6	17.4468	26.1578	8.7110	10	0.8711
7	17.4563	26.1273	8.6710	10	0.8671

Sample No.	Weight of pycnometer (g)	Weight of pycnometer + Weight of oil (g)	Weight of oil (g)	Volume of pycnometer (ml)	Density (g/ml)
8	17.4399	26.1060	8.6661	10	0.8666
9	17.4668	26.0689	8.6021	10	0.8602
10	17.4557	26.1608	8.7051	10	0.8705
11	17.4094	26.1237	8.7143	10	0.8714
12	17.4561	26.1776	8.7215	10	0.8722
13	17.4705	26.2032	8.7327	10	0.8733
14	17.477	26.1709	8.6939	10	0.8694
15	17.4222	26.1101	8.6879	10	0.8688
16	17.4675	26.1241	8.6566	10	0.8657
17	17.4984	26.1439	8.6455	10	0.8646
18	17.481	26.1503	8.6693	10	0.8669

Table A7 Kinetic viscosity and flash point measurements

Sample No.	Kinetic viscosity (cSt)	Flash point (°C)
1	4.65	171
2	4.68	173
3	4.63	171
4	4.59	173
5	4.56	175
6	4.57	177
7	4.57	175
8	4.54	177
9	4.53	175
10	4.86	175
11	4.82	177
12	4.84	175
13	4.76	173
14	4.74	175
15	4.73	177
16	4.71	175
17	4.71	175
18	4.69	173

APPENDIX B

B-1 Standard calibration curve of methyl esters

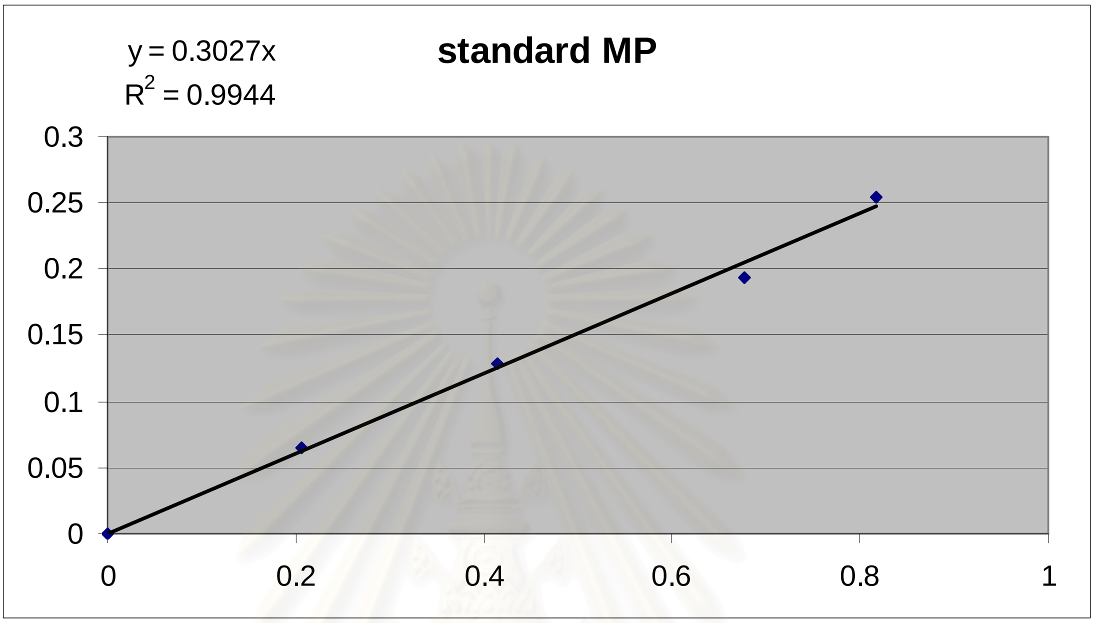


Figure B1-1 Standard calibration curve of Methyl palmitate

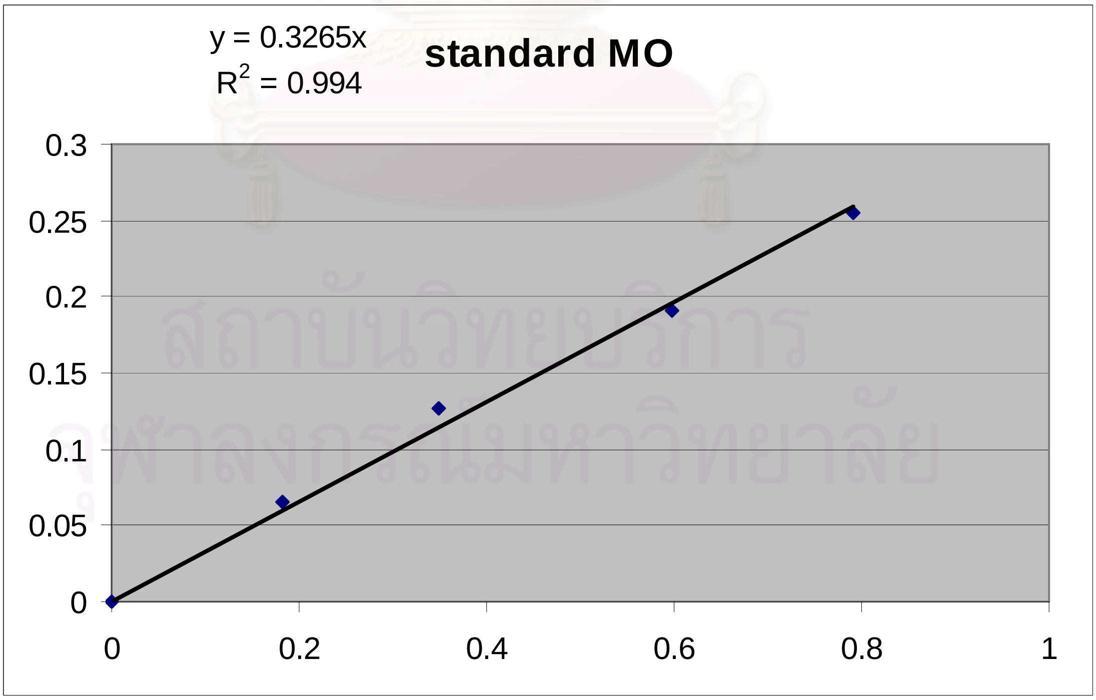


Figure B1-2 Standard calibration curve of Methyl oleate

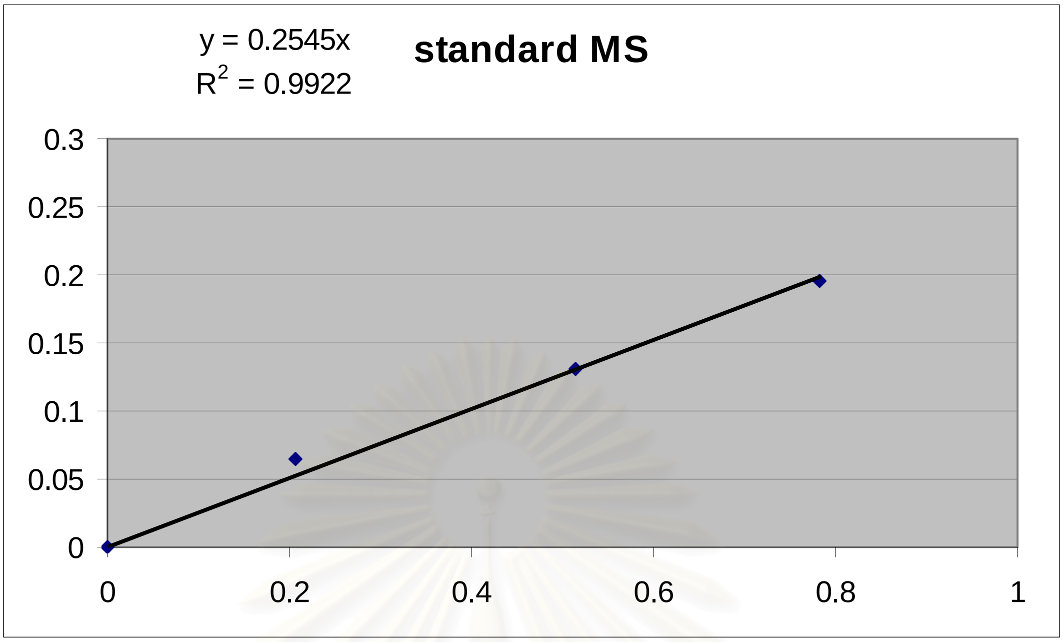


Figure B1-3 Standard calibration curve of Methyl stearate

B-2 GC chromatograms of transesterification reactions

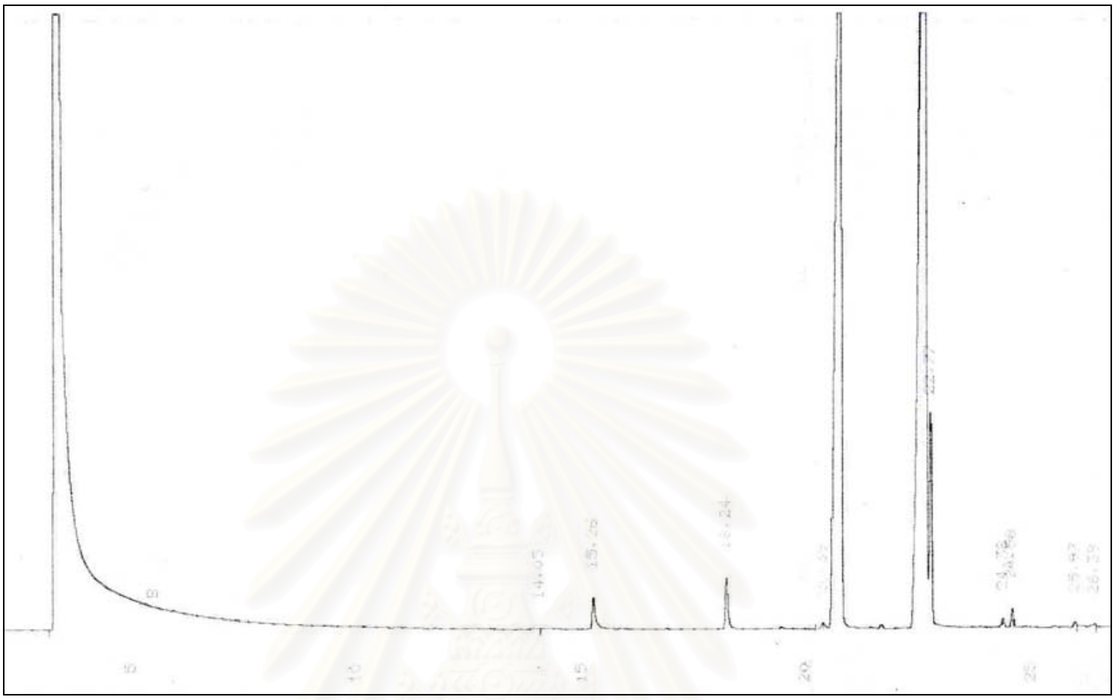
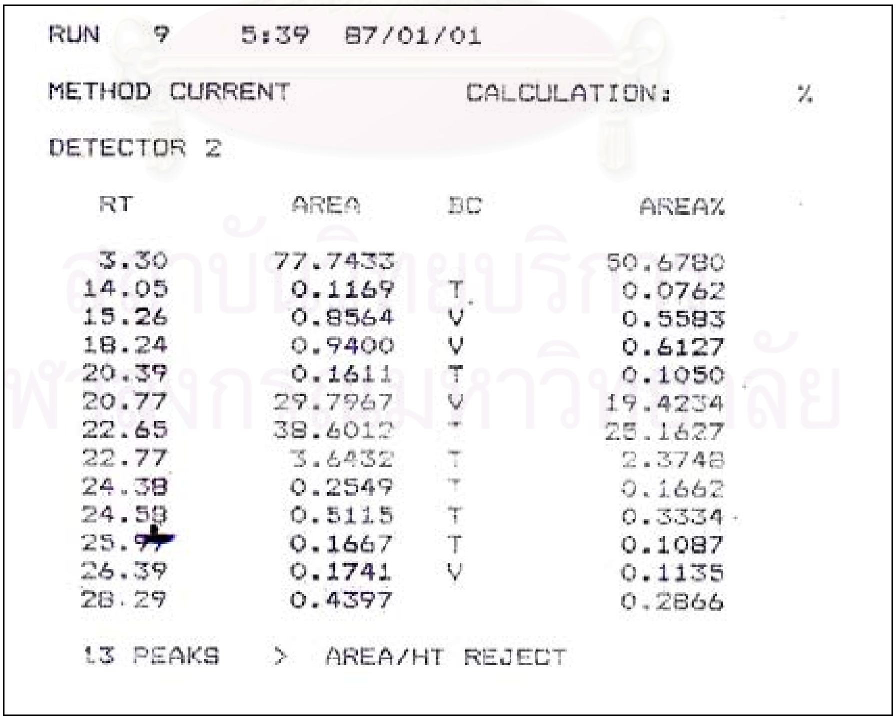


Figure B2-1 Chromatogram of methyl esters, condition: refined palm oil, 0.25wt% of NaOH, 40°C



```
RUN    9     5:39   87/01/01

METHOD CURRENT            CALCULATION:        %

DETECTOR 2

   RT           AREA       BC          AREA%

    3.30       77.7433                50.6780
   14.05        0.1169     T           0.0762
   15.26        0.8564     V           0.5583
   18.24        0.9400     V           0.6127
   20.39        0.1611     T           0.1050
   20.77       29.7967     V          19.4234
   22.65       38.6012     T          25.1627
   22.77        3.6432     T           2.3748
   24.38        0.2549     T           0.1662
   24.58        0.5115     T           0.3334
   25.97        0.1667     T           0.1087
   26.39        0.1741     V           0.1135
   28.29        0.4397                 0.2866

   13 PEAKS    >   AREA/HT  REJECT
```

Figure B2-2 Default report, condition: refined palm oil, 0.25wt% of NaOH, 40°C

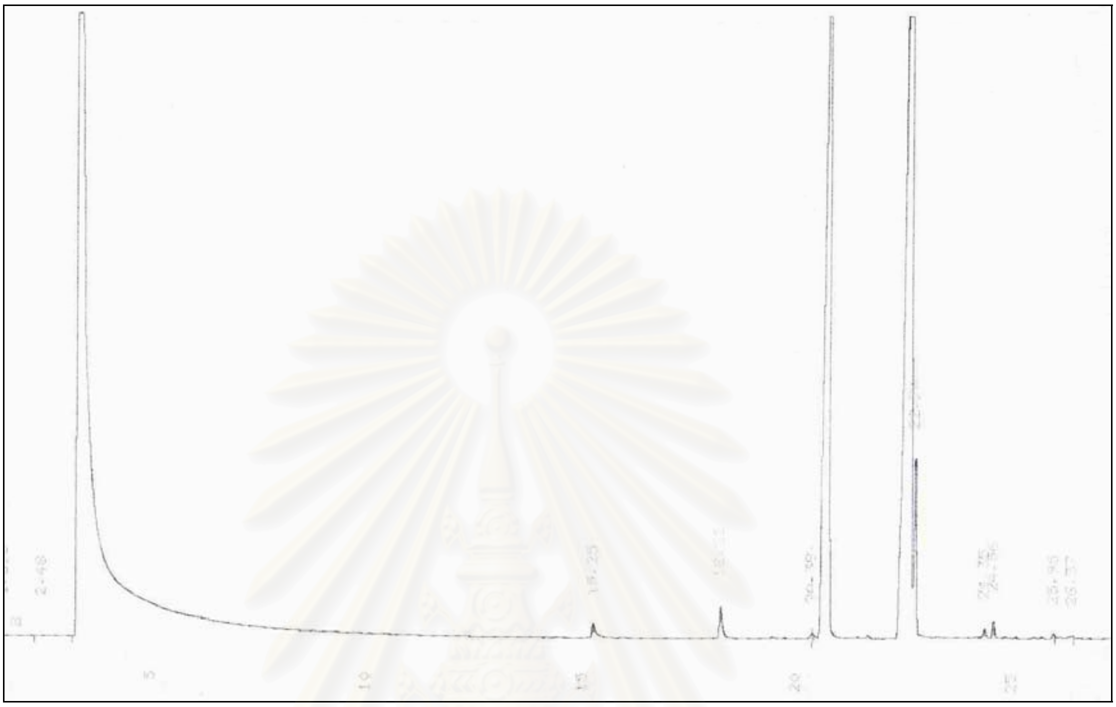
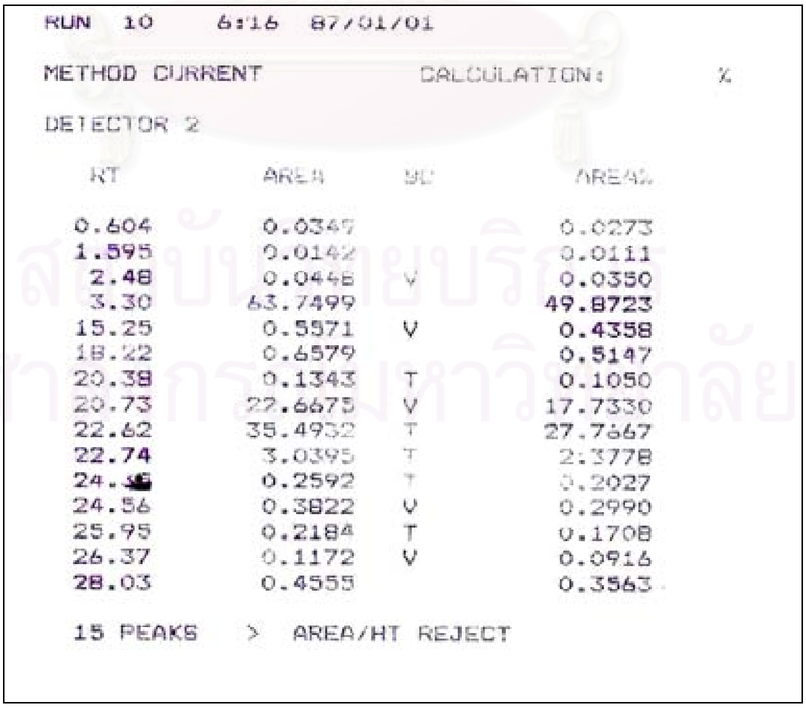


Figure B2-3 Chromatogram of methyl esters, condition: refined palm oil, 0.25wt% of NaOH, 50°C



```
RUN  10     6:16  87/01/01

METHOD CURRENT           CALCULATION:       %

DETECTOR 2

  RT           AREA     BC         AREA%

 0.604        0.0347               0.0273
 1.595        0.0142               0.0111
  2.48        0.0448    V          0.0350
  3.30       63.7499              49.8723
 15.25        0.5571    V          0.4358
 18.22        0.6579               0.5147
 20.38        0.1343    T          0.1050
 20.73       22.6675    V         17.7330
 22.62       35.4932    T         27.7667
 22.74        3.0395    T          2.3778
 24.[illegible]        0.2592    T          0.2027
 24.56        0.3822    V          0.2990
 25.95        0.2184    T          0.1708
 26.37        0.1172    V          0.0916
 28.03        0.4555               0.3563

 15 PEAKS   >  AREA/HT REJECT
```

Figure B2-4 Default report, condition: refined palm oil, 0.25wt% of NaOH, 50°C

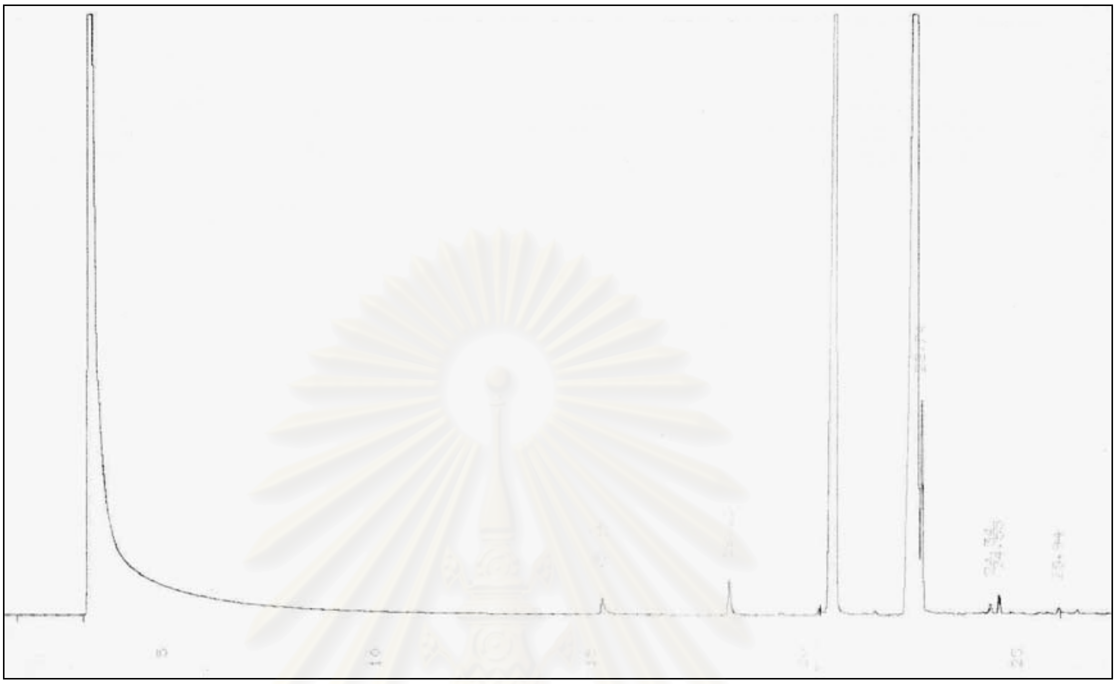
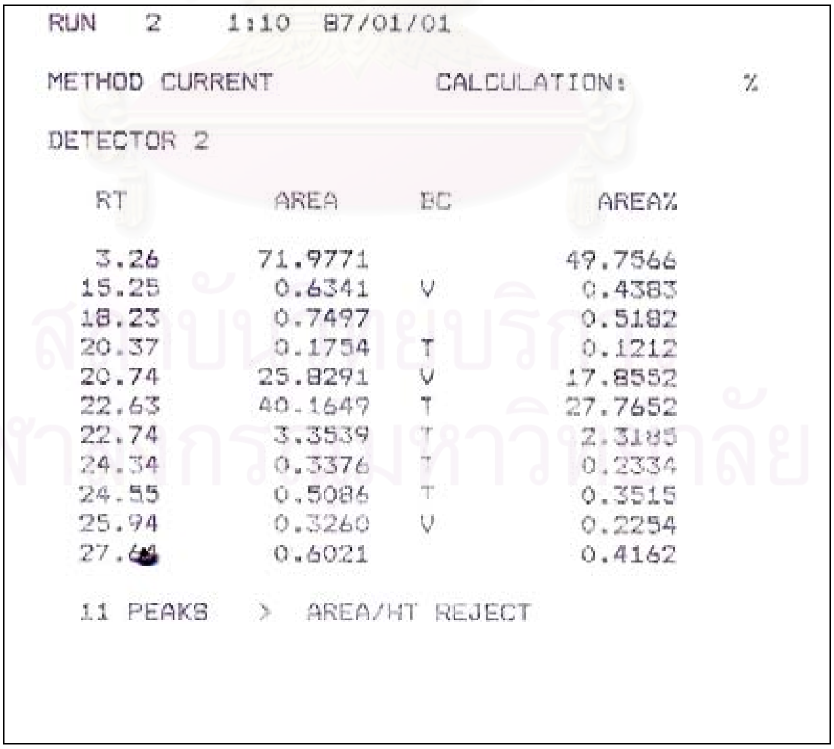


Figure B2-5 Chromatogram of methyl esters, condition: refined palm oil, 0.25wt% of NaOH, 60°C



```
RUN   2    1:10  87/01/01

METHOD CURRENT          CALCULATION:      %

DETECTOR 2

   RT          AREA     BC          AREA%

   3.26       71.9771               49.7566
  15.25        0.6341    V           0.4383
  18.23        0.7497                0.5182
  20.37        0.1754    T           0.1212
  20.74       25.8291    V          17.8552
  22.63       40.1649    T          27.7652
  22.74        3.3539    T           2.3185
  24.34        0.3376    T           0.2334
  24.55        0.5086    T           0.3515
  25.94        0.3260    V           0.2254
  27.6[illegible]        0.6021                0.4162

  11 PEAKS   >  AREA/HT REJECT
```

Figure B2-6 Default report, condition: refined palm oil, 0.25wt% of NaOH, 60°C

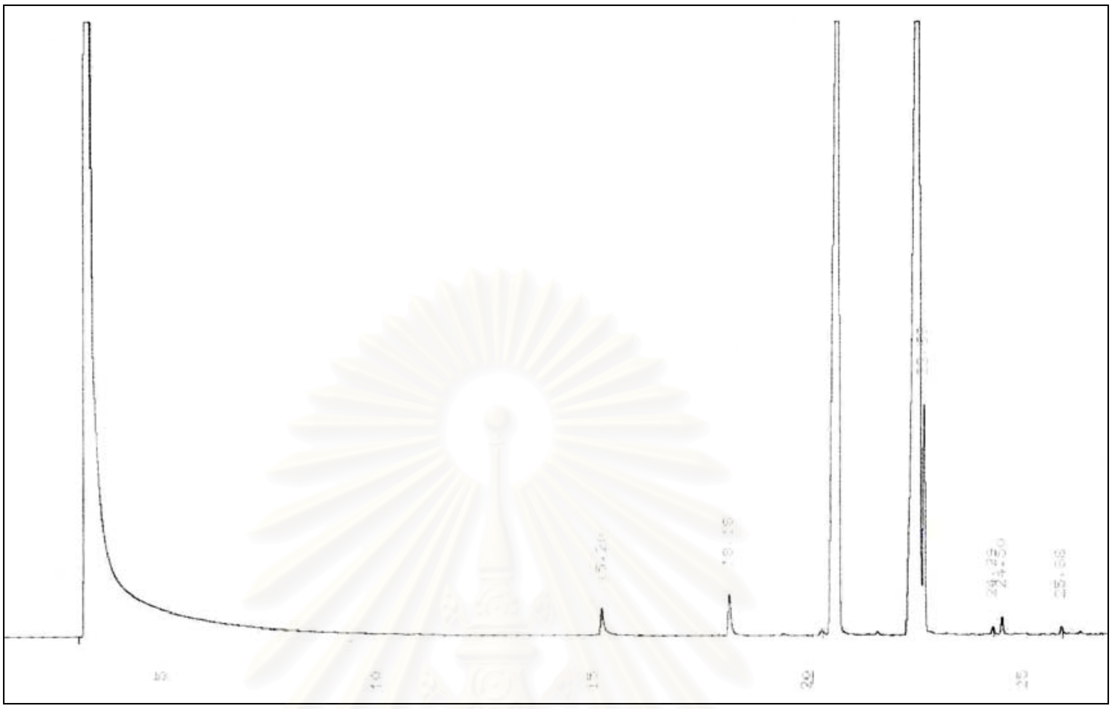
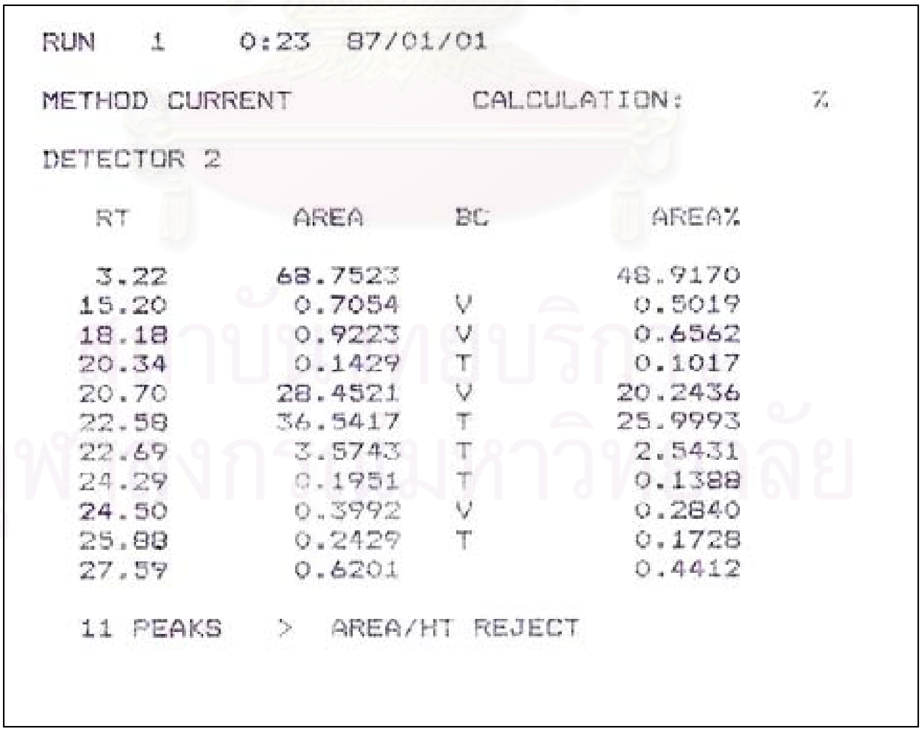


Figure B2-7 Chromatogram of methyl esters, condition: refined palm oil, 0.50wt% of NaOH, 60°C



```
RUN   1     0:23  87/01/01

METHOD CURRENT          CALCULATION:       %

DETECTOR 2

   RT           AREA      BC          AREA%

   3.22       68.7523               48.9170
  15.20        0.7054     V          0.5019
  18.18        0.9223     V          0.6562
  20.34        0.1429     T          0.1017
  20.70       28.4521     V         20.2436
  22.58       36.5417     T         25.9993
  22.69        3.5743     T          2.5431
  24.29        0.1951     T          0.1388
  24.50        0.3992     V          0.2840
  25.88        0.2429     T          0.1728
  27.59        0.6201                0.4412

  11 PEAKS    >   AREA/HT REJECT
```

Figure B2-8 Default report, condition: refined palm oil, 0.50wt% of NaOH, 60°C

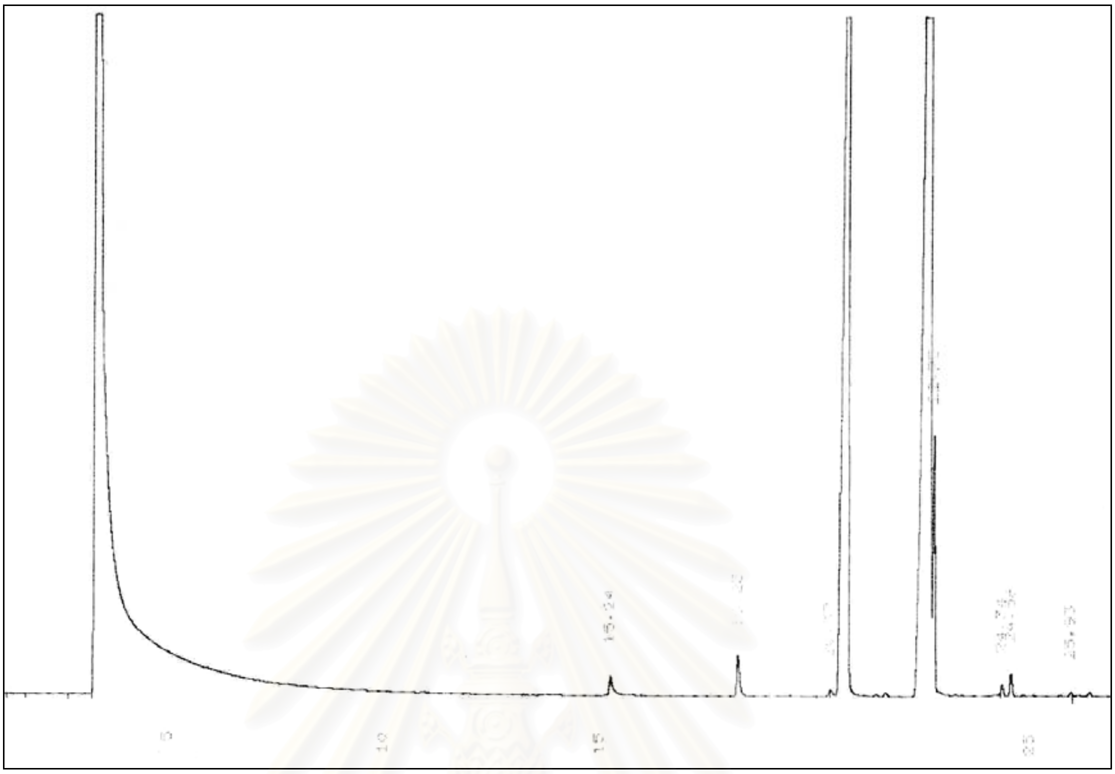
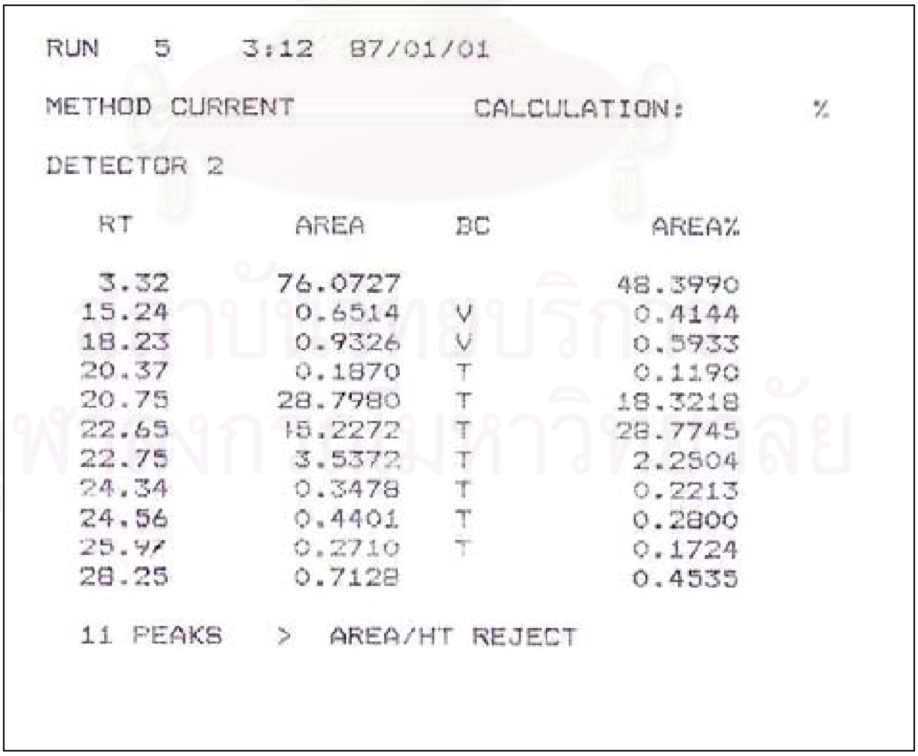


Figure B2-9 Chromatogram of methyl esters, condition: refined palm oil, 1.0wt% of NaOH, 60°C



```
RUN   5    3:12  87/01/01

METHOD CURRENT          CALCULATION:       %

DETECTOR 2

   RT          AREA      BC         AREA%

   3.32      76.0727               48.3990
  15.24       0.6514     V          0.4144
  18.23       0.9326     V          0.5933
  20.37       0.1870     T          0.1190
  20.75      28.7980     T         18.3218
  22.65      45.2272     T         28.7745
  22.75       3.5372     T          2.2504
  24.34       0.3478     T          0.2213
  24.56       0.4401     T          0.2800
  25.97       0.2710     T          0.1724
  28.25       0.7128                0.4535

  11 PEAKS   >  AREA/HT REJECT
```

Figure B2-10 Default report, condition: refined palm oil, 1.0wt% of NaOH, 60°C

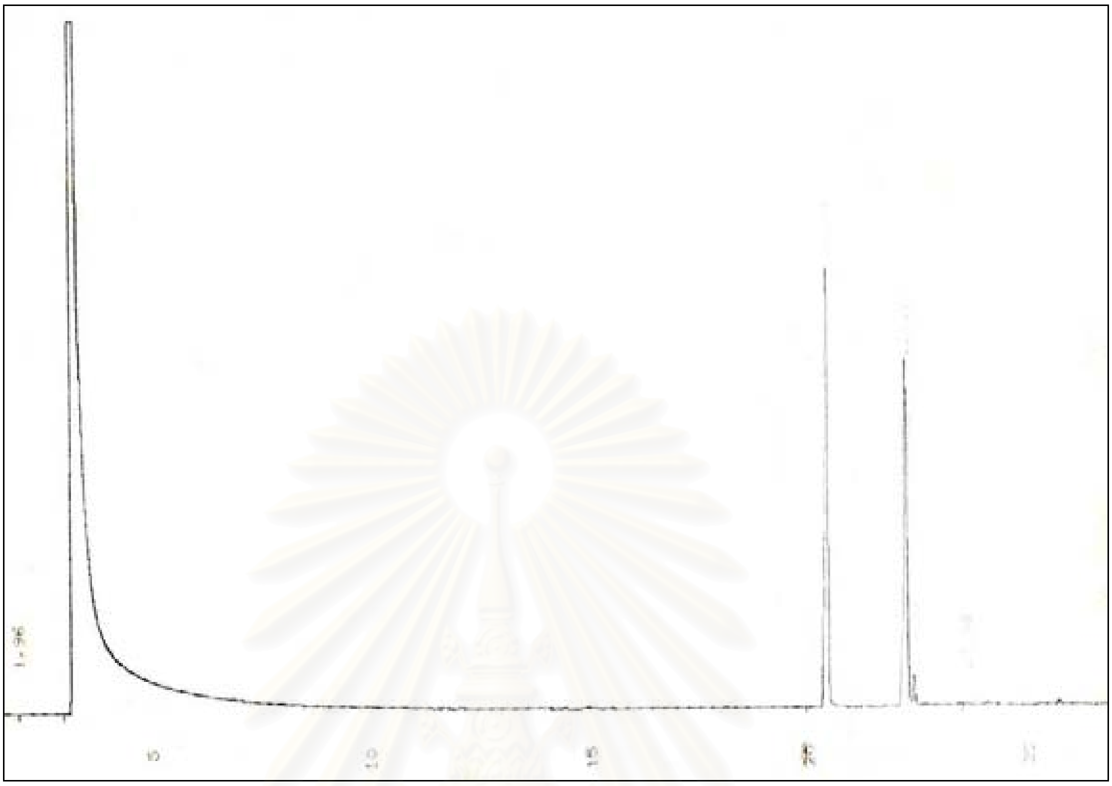
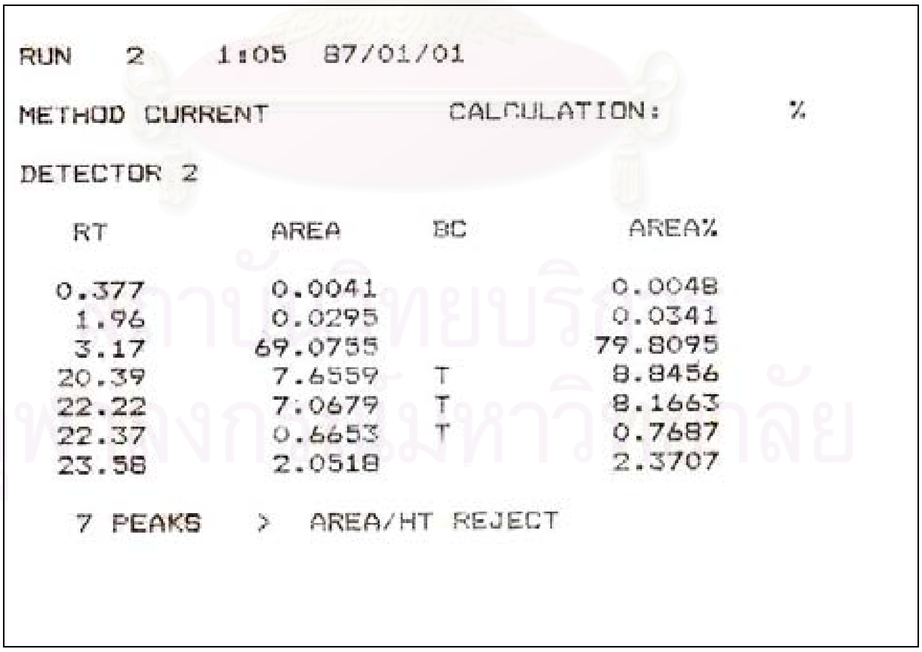


Figure B2-11 Chromatogram of methyl esters, condition: refined palm oil, 25.0wt% of Dowex, 60°C



```
RUN   2    1:05  87/01/01

METHOD CURRENT              CALCULATION:       %

DETECTOR 2

   RT            AREA      BC           AREA%

  0.377          0.0041                 0.0048
    1.96         0.0295                 0.0341
    3.17        69.0755                79.8095
   20.39         7.6559     T           8.8456
   22.22         7.0679     T           8.1663
   22.37         0.6653     T           0.7687
   23.58         2.0518                 2.3707

   7 PEAKS    >   AREA/HT REJECT
```

Figure B2-12 Default report, condition: refined palm oil, 25.0wt% of Dowex, 60°C

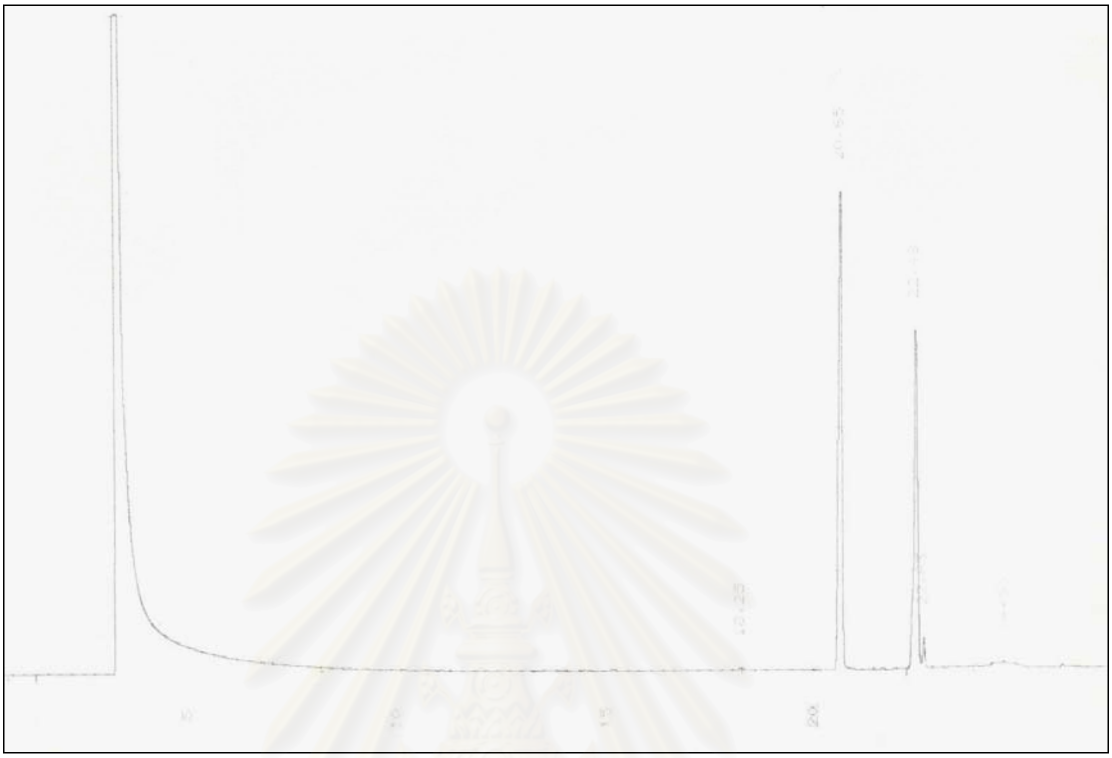
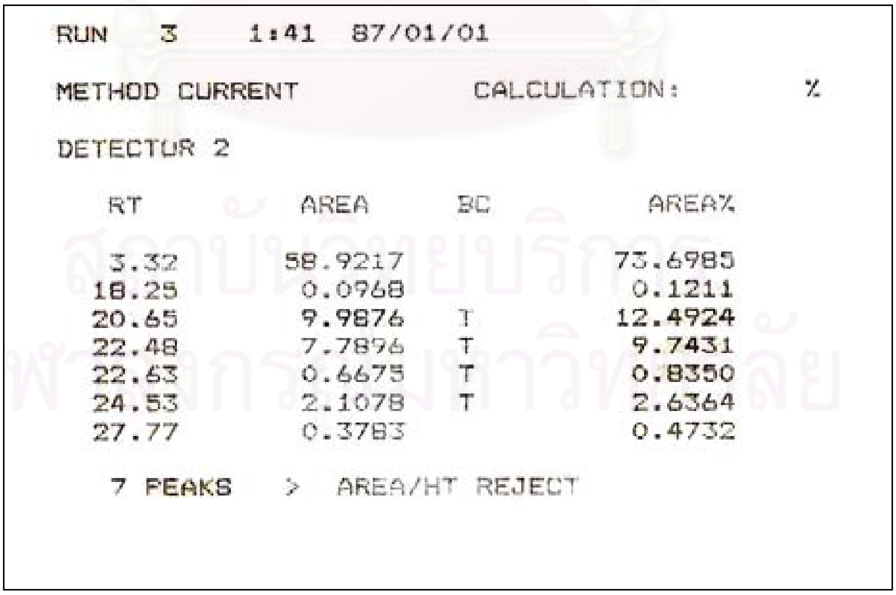


Figure B2-13 Chromatogram of methyl esters, condition: refined palm oil, 25.0wt% of Amberlyst-15, 60°C



```
RUN   3    1:41  87/01/01

METHOD CURRENT           CALCULATION:        %

DETECTOR 2

   RT          AREA       BC          AREA%

   3.32      58.9217                73.6985
  18.25       0.0968                 0.1211
  20.65       9.9876      T         12.4924
  22.48       7.7896      T          9.7431
  22.63       0.6675      T          0.8350
  24.53       2.1078      T          2.6364
  27.77       0.3783                 0.4732

   7 PEAKS    >  AREA/HT REJECT
```

Figure B2-14 Default report, condition: refined palm oil, 25.0wt% of Amberlyst-15, 60°C

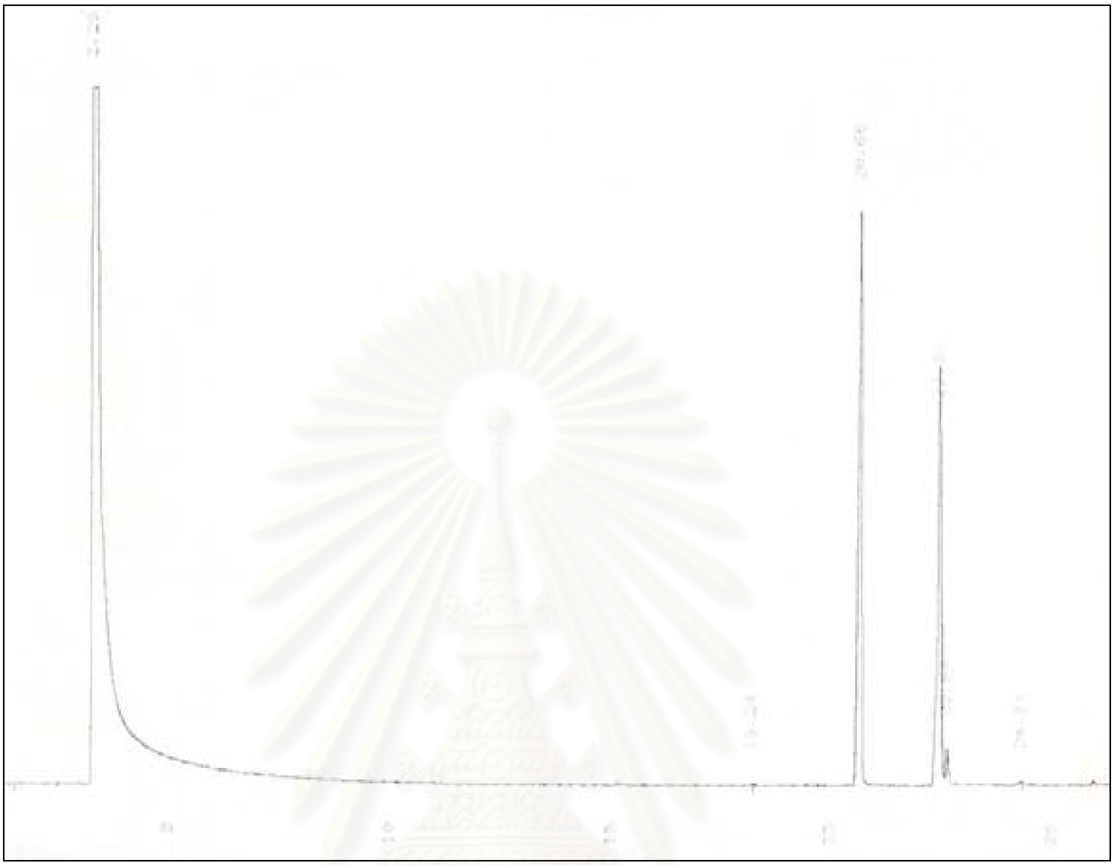
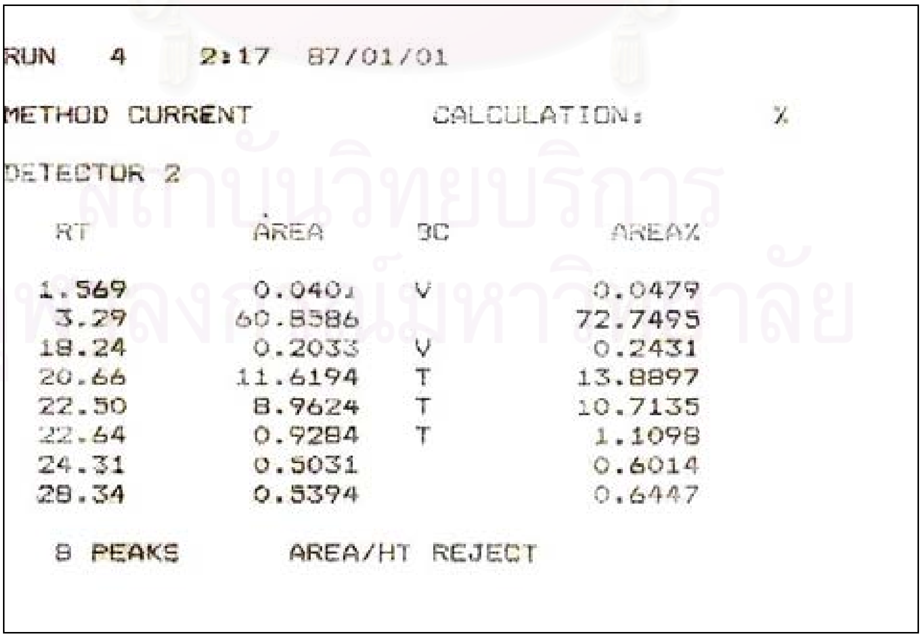


Figure B2-15 Chromatogram of methyl esters, condition: used palm oil, 25.0wt% of Dowex, 60°C



```
RUN    4     2:17  87/01/01

METHOD CURRENT          CALCULATION:        %

DETECTOR 2

   RT          AREA      BC          AREA%

  1.569       0.0401     V           0.0479
   3.29      60.8586               72.7495
  18.24       0.2033     V           0.2431
  20.66      11.6194     T          13.8897
  22.50       8.9624     T          10.7135
  22.64       0.9284     T           1.1098
  24.31       0.5031                 0.6014
  28.34       0.5394                 0.6447

   8 PEAKS        AREA/HT  REJECT
```

Figure B2-16 Default report, condition: used palm oil, 25.0wt% of Dowex, 60°C

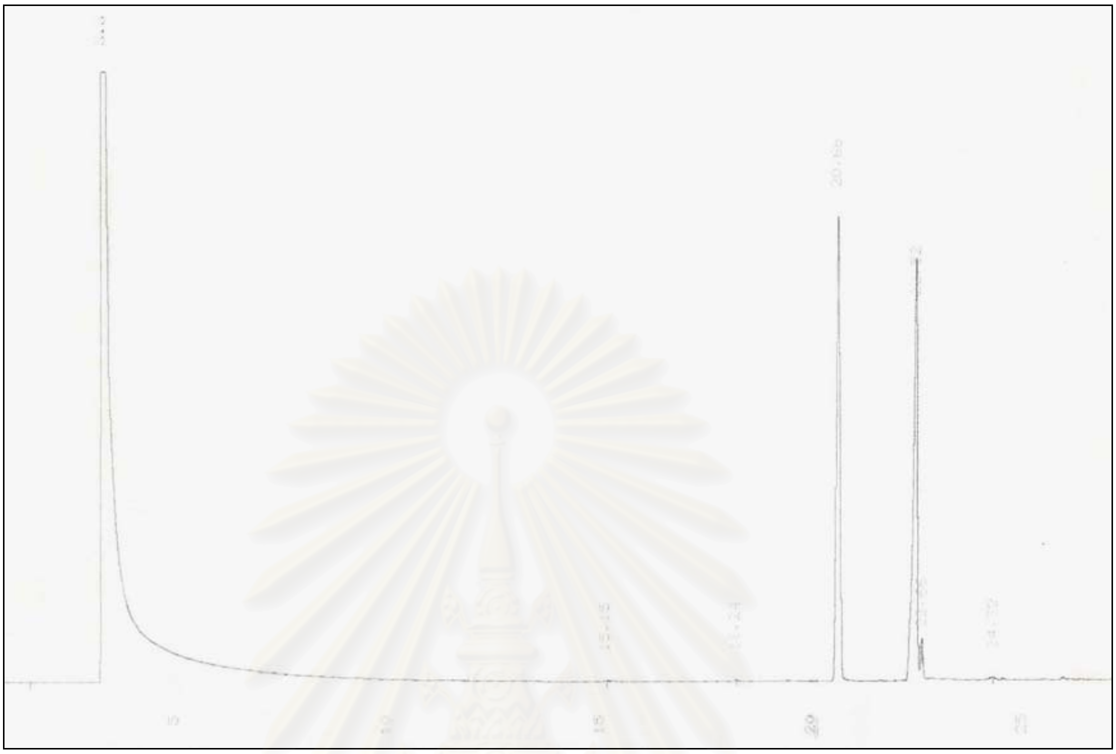
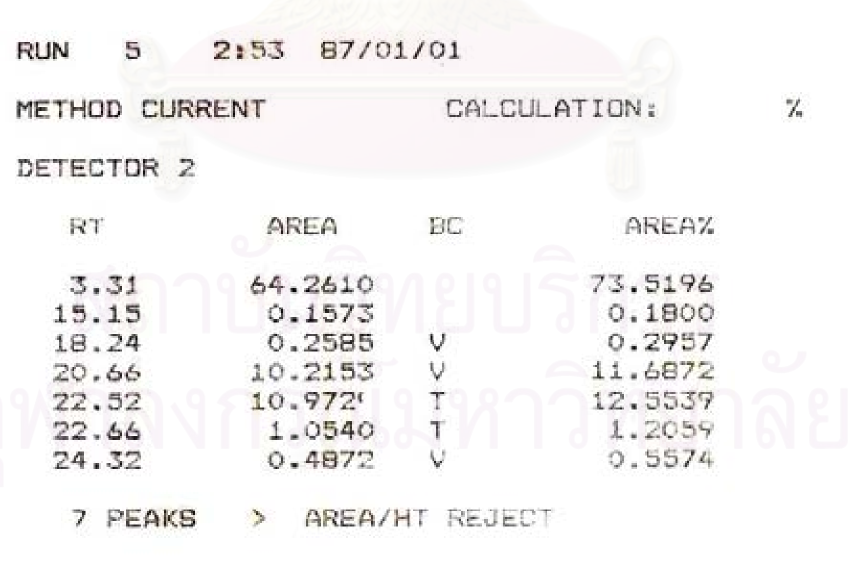


Figure B2-17 Chromatogram of methyl esters, condition: used palm oil, 25.0wt% of Amberlyst-15, 60°C



```
RUN    5     2:53   87/01/01

METHOD CURRENT           CALCULATION:        %

DETECTOR 2

    RT            AREA       BC          AREA%

   3.31        64.2610              73.5196
  15.15         0.1573               0.1800
  18.24         0.2585   V           0.2957
  20.66        10.2153   V          11.6872
  22.52        10.9729   T          12.5539
  22.66         1.0540   T           1.2059
  24.32         0.4872   V           0.5574

    7 PEAKS    >   AREA/HT REJECT
```

Figure B2-18 Default report, condition: used palm oil, 25.0wt% of Amberlyst-15, 60°C

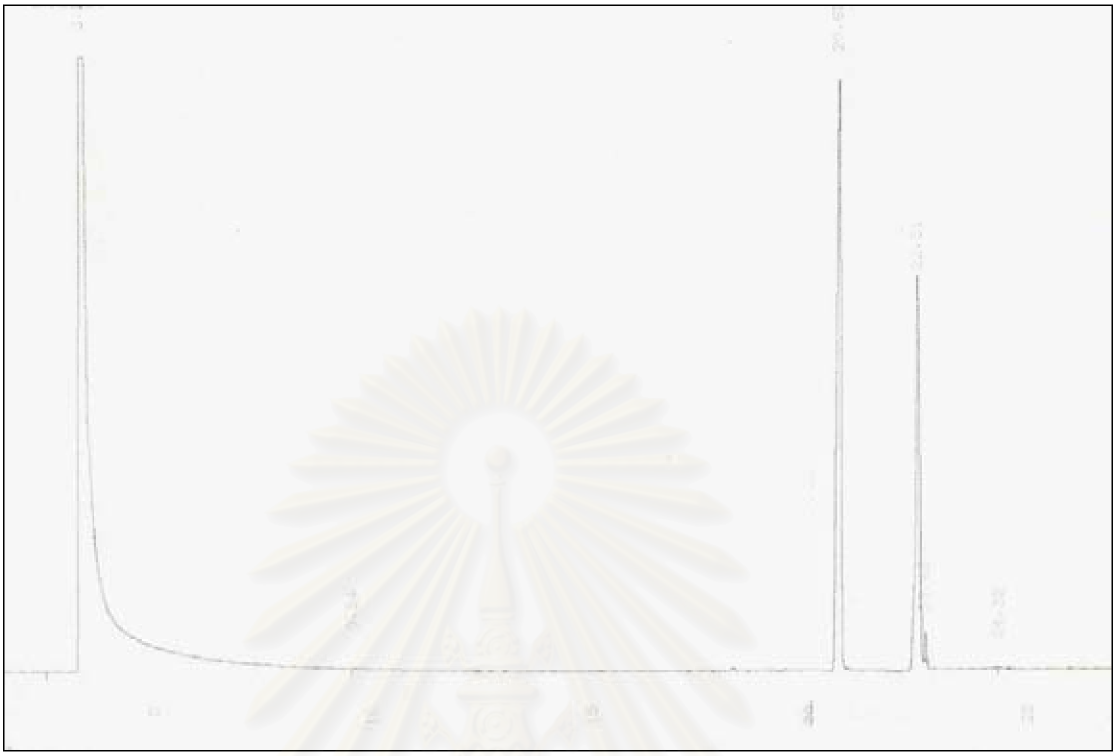
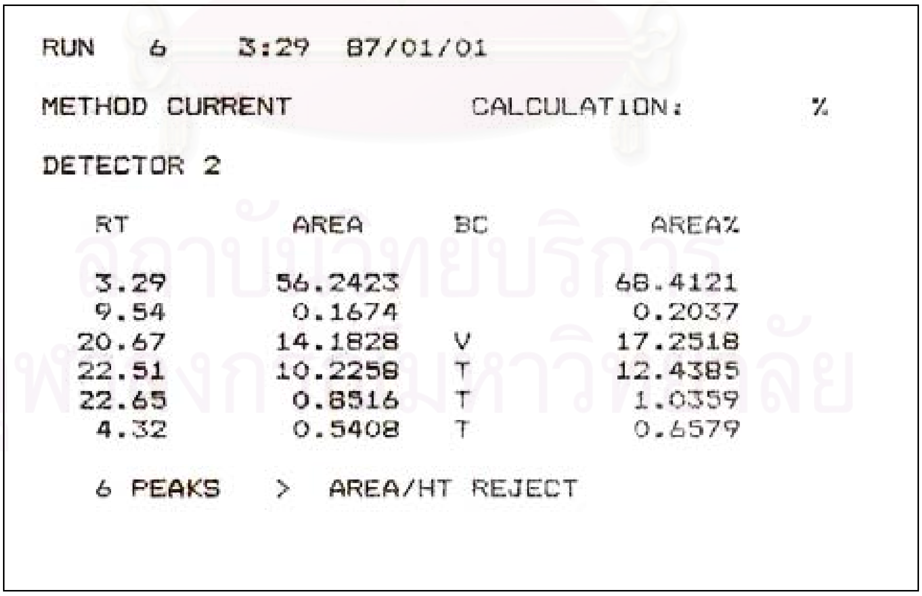


Figure B2-19 Chromatogram of methyl esters, condition: crude palm oil, 25.0wt% of Dowex, 60°C



```
RUN    6     3:29  87/01/01

METHOD CURRENT            CALCULATION:        %

DETECTOR 2

   RT          AREA      BC          AREA%

   3.29      56.2423               68.4121
   9.54       0.1674                0.2037
  20.67      14.1828     V         17.2518
  22.51      10.2258     T         12.4385
  22.65       0.8516     T          1.0359
   4.32       0.5408     T          0.6579

   6 PEAKS    >   AREA/HT REJECT
```

Figure B2-20 Default report, condition: crude palm oil, 25.0wt% of Dowex, 60°C

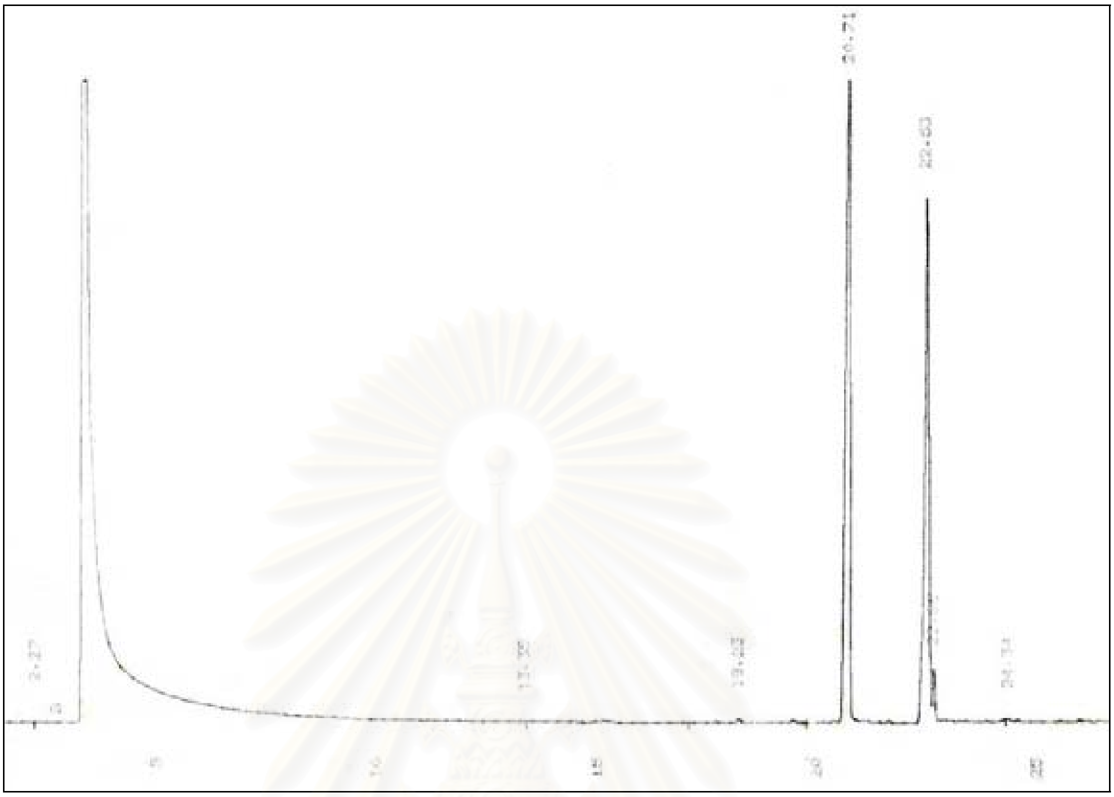
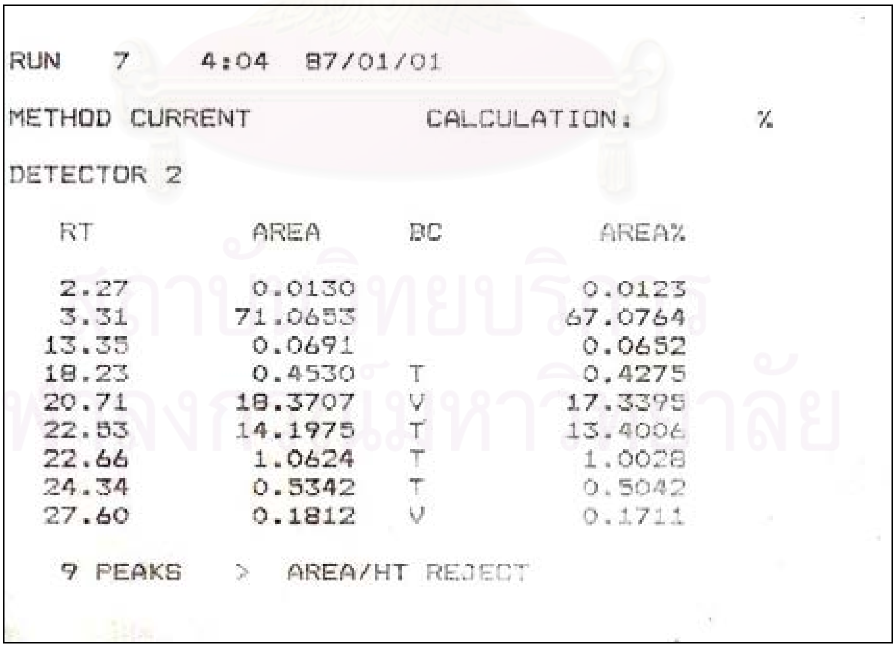


Figure B2-21 Chromatogram of methyl esters, condition: crude palm oil, 25.0wt% of Amberlyst-15, 60°C



```
RUN   7    4:04  87/01/01

METHOD CURRENT          CALCULATION:        %

DETECTOR 2

   RT          AREA      BC          AREA%

   2.27        0.0130                0.0123
   3.31       71.0653               67.0764
  13.35        0.0691                0.0652
  18.23        0.4530    T           0.4275
  20.71       18.3707    V          17.3395
  22.53       14.1975    T          13.4006
  22.66        1.0624    T           1.0028
  24.34        0.5342    T           0.5042
  27.60        0.1812    V           0.1711

   9 PEAKS    >   AREA/HT REJECT
```

Figure B2-22 Default report, condition: crude palm oil, 25.0wt% of Amberlyst-15, 60°C

B-3 Percentage of methyl esters

Procedure

1. Mix 0.5 grams of biodiesel with 1.5 grams of tetrahydrofuran.
2. Suck 0.5 μl of sample to put in gas chromatography

Calculation

1. Bring area of each methyl esters divide with area solvent (X_i).

2. Weight of each methyl esters (Y_i) was calculated by bringing value from 1. put in equation following:

-For methyl palmitate

$$Y_1 = 0.3027 \times X_1$$

X_1 is area of methyl palmitate/area of solvent

-For methyl oleate and linoleate

$$Y_2 = 0.3265 \times X_2$$

X_2 is area of methyl oleate and methyl linoleate/area of solvent

- For methyl stearate

$$Y_3 = 0.2545 \times X_3$$

X_3 is area of methyl stearate/area of solvent

3. Sum Y_1, Y_2, Y_3 which is weight of methyl esters of each experiment.

4. Percentage of methyl ester is weight of methyl ester divide to 0.5 grams.

Table B-3 percentage of methyl esters

Sample No.	Area of solvent	Area of MP	Area of MO+ML	Area of MS	%methyl esters
1	77.7433	29.7967	38.6012	3.6432	87.12
2	63.7499	22.6675	35.4932	3.0395	90.58
3	71.9771	25.8291	40.1649	3.3539	90.92
6	68.7523	28.4521	36.5417	3.5743	93.72
9	76.0727	28.7980	45.2272	3.5372	96.29
10	62.1779	21.7557	27.9128	2.7342	79.19
11	69.7530	22.0036	34.6269	3.3903	81.09
12	74.7938	24.7599	38.3736	3.0946	83.58
15	72.7430	24.8553	40.0853	3.4001	89.14
18	59.4464	21.1656	33.2207	3.0322	91.08
111	69.0755	7.6559	7.0679	0.6653	20.84
112	77.4289	12.7216	14.3656	2.1905	32.96
121	58.9217	9.9876	7.7895	0.6675	29.23
122	85.1827	16.5667	19.0250	2.5903	41.90
211	60.8586	11.6194	8.9624	0.9284	33.86
212	71.5457	14.9571	17.0574	2.1795	44.22
221	64.2610	11.2153	10.9729	1.0540	44.71
222	66.5632	16.9519	17.8388	2.1965	51.95
311	56.2423	14.1828	10.2258	0.8516	41.91
312	57.9113	13.9842	13.7125	1.8278	47.58
321	71.0653	18.3707	17.1975	1.0624	49.32
322	60.3229	16.2235	13.9333	1.7590	57.89

MP is methyl palmitate, ML is methyl linoleate
MO is methyl oleate, MS is methyl stearate

B-4 percentage of yield of methyl esters

Percentages of yield of methyl esters can determine by weighing of the top layer. Equation B-4 defines percentage of yield of biodiesel.

$$\%\text{yield} = \frac{\text{weight of top layer X 100}}{\text{weight of palm oil}} \qquad \text{(B-4)}$$

Table B-4 percentage of yield of methyl esters from homogeneous catalyzed-transesterification

Sample No.	Weight of oil (g)	Weight of top layer (g)	%yield
1	2416	2186	90.5
2	2416	2273	94.1
3	2416	2353	97.4
4	2416	2203	91.2
5	2416	2338	96.8
6	2416	2399	99.3
7	2416	2191	90.7
8	2416	2285	94.6
9	2416	2360	97.7
10	2416	2152	89.1
11	2416	2239	92.7
12	2416	2304	95.4
13	2416	2184	90.4
14	2416	2290	94.8
15	2416	2333	96.6
16	2416	2167	89.7
17	2416	2234	92.5
18	2416	2314	95.8
19	2416	-	-
20	2416	-	-
21	2416	-	-
22	2416	-	-
23	2416	-	-
24	2416	-	-
25	2416	-	-
26	2416	-	-
27	2416	-	-

VITA

Mr. Wattanachai Yaowarat was born on June 21, 1980 in Nan, Thailand. He finished high school in 1998 from Phrae-Piriyalai School. In 2002, he graduated from Faculty of Engineering, King Mongkut’s Institute of Technology Ladkrabang with a Bachelor of Engineering in Chemical Engineering. After the graduation, he pursued his graduate study to a Master of Engineering (Chemical Engineering), Faculty of Engineering, Chulalongkorn University.