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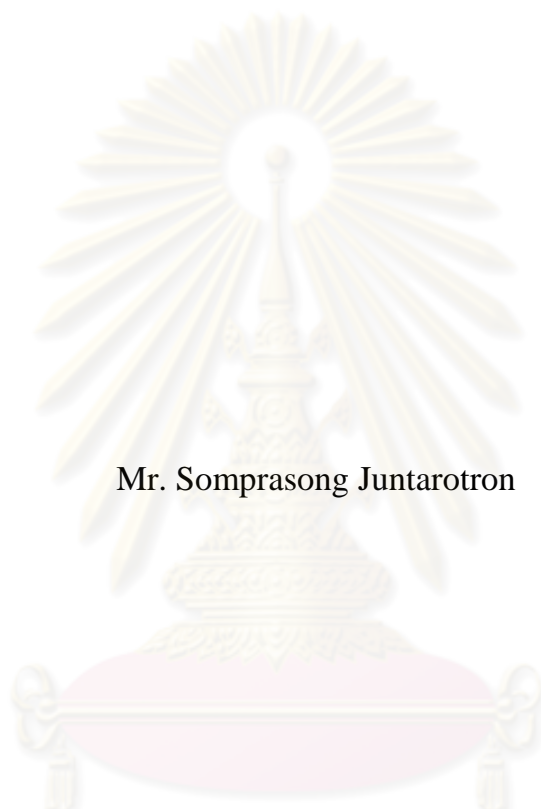
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PRODUCTION OF METHYL ESTERS FROM PALM OLEIN USING
COSOLVENTS



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The objective of this research was to study the production of methyl esters by transesterification reaction of palm olein oil using sodium methylate as an alkaline catalyst with various cosolvents including diethyl ether, tetrahydrofuran, hexane, cyclohexane, butanol and t-butanol were investigated. The experiments were conducted in a batch reactor system, at temperatures of 35 and 65°C, at an ambient pressure and at methanol to oil molar ratio of 6:1. Amount of catalyst used in each experiment was 1% by weight of oil.

The results indicate that percentage of methyl esters in the presence of cosolvents was higher than the absence cosolvents. Butanol was the most effective cosolvents giving methyl esters concentration of 98% at a temperature of 65°C.

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CHAPTER I

INTRODUCTION

Alkyl esters can be produced from transesterification reaction between vegetable oils or animal fat and alcohol. This reaction is catalyzed by homogeneous or heterogeneous catalyst. The products of this reaction are desirable alkyl esters and the by-product is glycerol. Methyl esters are used extensively as intermediates in manufacture of emulsifiers, textile treatments and other applications. Raw materials for producing methyl esters are provided from renewable natural resources such as oil palm, rapeseed, soybean, sunflower, cotton seed, coconut, canola, Jatropha, and animal fat such as beef tallow and pork lard. Choice of vegetable oil for Thailand is palm oil which has high productivity and low cost when compared to the other vegetable oils.

Transesterification reaction between oils and alcohol is a reversible reaction which the ratio for transesterification reaction requires three moles of alcohol for one mole of triglyceride to produce three moles of alkyl ester and one mole of glycerol. However, in order to shift the equilibrium to the right, an excess of alcohol is used in alkyl ester production to ensure that the oils will be completely converted to esters. Feedman et al. (1984) studied the effect of molar ratio of methanol to oil from 1:1 to 6:1. The reactions were conducted at 60°C for 60 minutes. They found that the optimum value of the methanol to oil molar ratio to produce methyl esters were 6:1.

Transesterification reaction is commonly carried out in the presence of homogeneous alkaline or acid catalysts. Acid catalyzed transesterification is usually slower than alkaline catalyzed reaction and requires higher temperatures. The commonly basic homogeneous catalysts are potassium hydroxide (KOH), sodium hydroxide (NaOH) and sodium methoxide

(CH_3ONa). Gemma et al. (2003) compared these three catalysts in transesterification reaction conducted at reaction temperature of $60\text{ }^\circ\text{C}$ with methanol to oil molar ratio of 6:1 and 1% of alkaline catalyst by weight of oil. The results indicated that CH_3ONa gave the highest amount of products.

The previous studies reported that the transesterification reaction could generally occur slowly. The main problem of the lower rate of transesterification is that the reaction mixture is not homogeneous system because of their chemical structures. The problem of immiscibility is that the probability and rate of collisions of molecules become lower. This leads to longer reaction time and higher capital investments. Therefore, the additional cosolvents enhance the miscibility of the phase, resulting in a homogeneous system and a faster reaction rate. Boocock et al. (1996) studied the transesterification reaction using tetrahydrofuran as cosolvent to homogeneous oil and methanol at room temperature with the ratio of methanol to oil 6:1 and 1% of NaOH by weight of oil as a catalyst. The results showed that the cosolvent can give yield methyl esters 87% within 10 minutes, which led to a very fast reaction and less energy used. Moreover, the previous studies had indicated that the product could be generated in the room temperature as well. Therefore, this study will focus on the use of cosolvent in transesterification reaction at reaction temperature of $65\text{ }^\circ\text{C}$ and $35\text{ }^\circ\text{C}$.

In this study, methyl esters were produced from palm olein oil with methanol, and sodium methylate (CH_3ONa) was used as catalyst. The experiments were conducted at 35 and $65\text{ }^\circ\text{C}$ by using various types of cosolvent.

CHAPTER II

THEORY AND LITERATURE REVIEWS

Methyl esters are compound of ester has that structure CH_3COOR when R depends on the type of FFA such as palmitic acid, stearic acid and oleic acid etc. When palmitic acid reacts with methanol, the product is methyl palmitate, when stearic acid reacts with methanol, the product is methyl stearate and when oleic acid reacts with methanol, and the product is methyl oleate. The present methyl esters can be converted to other products such as alkanolamine, isopropyl ester, fatty alcohol and sucrose polyester etc. Furthermore, methyl esters can be used in surfactant industry and fuel gas is biodiesel. Methyl esters can be produced from vegetable oils, animal fat and waste cooking oils. The vegetable oils used for producing methyl esters have many types such as palm oil, soybean oil, coconut oil, sunflower oil and rapeseed oil etc. This research will focus on palm oil because of its abundance in Thailand.

2.1 Palm Oil

The palm fruit is the source of both palm oil and palm kernel oil. Palm oil is extracted from palm fruit flesh and palm kernel or seed oil. They consist of fatty acids esterified with glycerol just like any ordinary fat. Both are high in saturated fatty acids. Saturated fat, also found in coconut oil, beef fat, and milk fat are correlated with an increased incidence of atherosclerosis and coronary heart disease. The palm oil gives its name to the 16 carbon, saturated fatty acid palmitic acid found in palm oil; furthermore, monosaturated oleic acid is a constituent of palm oil, as shown in Table 2.1.

Table 2.1 Fatty Acid composition of palm oil and other vegetable oils

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

2.2 Cosolvents

Transesterification of vegetable oils with methanol is two phase reaction system, and the reaction occurs in the methanol phase (Fadi Ataya, 2007). Because the nonpolar oils phase and the polar methanol phase are immiscible. Although the miscibility of the two phases can be enhanced by increasing the temperature, it increases the mutual solubility of the two phases (Muniyappa, 1996). Increasing the stirring intensity favors conversion (Noureddini, 2004), which is an energy-consumptive process. Boocock et al. (1996) suggested that an additional cosolvent could enhance the miscibility of the phases and speed up the reaction rate because of the disappearance of interphase mass transfer resistance in the heterogeneous two phase of reaction system.

The selection of cosolvents could be considered from these important factors, namely, small molecular weight, having relatively low boiling point or close to that of methanol which would be advantageous in the separation of methanol and cosolvents from oils for further reuse. The common cosolvents are mentioned with details below.

Ethers are compound consisting of oxygen atom attached to 2 alkyl or aryl groups such as diethyl ether, dimethyl ether, tert-butyl methyl ether. There are also cyclic ethers such as tetrahydrofuran, 1,4 dioxane which has higher

boiling point compared with non-cyclic ethers. They also have greater solubility because of the higher ability to form hydrogen bond. The interesting properties of ethers are their structures which are similar to water and alcohol, they are polar molecule and inert to react and do not react to common base and acid in comparably low temperature. As a result, ethers are the best choice as cosolvent to facilitate the mixing of palm oil and methanol.

Alkanes are saturated hydrocarbon compound that is inert to initiate chemical reaction. They could not react to base and acid. Even though they are non-polar, several studies had reported that they could be dissolved in methanol such as hexane and heptane. The boiling points of alkanes are lower than ethers with the same range of molecular weight. Consequently, alkanes could be potential cosolvent that could improve efficiency of palm oil and methanol mixing.

Alcohols, such as t-butanol which is a branched chain alcohol, could be dissolved in water better than straight chain could. They are also able to dissolve in methanol and glycerin which are non-toxic and cheap solvent. They are popular as cosolvents of reaction in which enzymes are used to accelerate the reaction because they do not react to substrate. Lipase could not react to tertiary alcohols.

2.3 Transesterification

Transesterification or alcoholysis is the reaction of alcohol and vegetable oils or animal fat to produce alkyl ester of fatty acid. This process has been widely used to reduce the high viscosity of triglyceride. The general equation of transesterification is shown in Figure 2.1. The stoichiometry required three moles of alcohol and one mole of triglyceride to produce three moles of alkyl ester and one mole of glycerol. In practice, this ratio is usually increased to 6:1 that reaction is reversible. Excess of alcohol is used in reaction to shift the equilibrium to the right side (products).

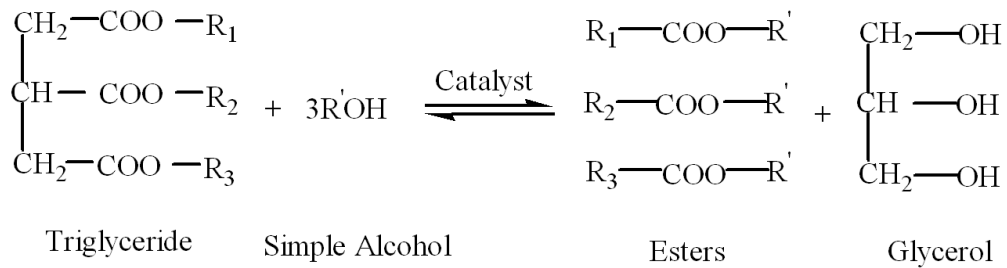
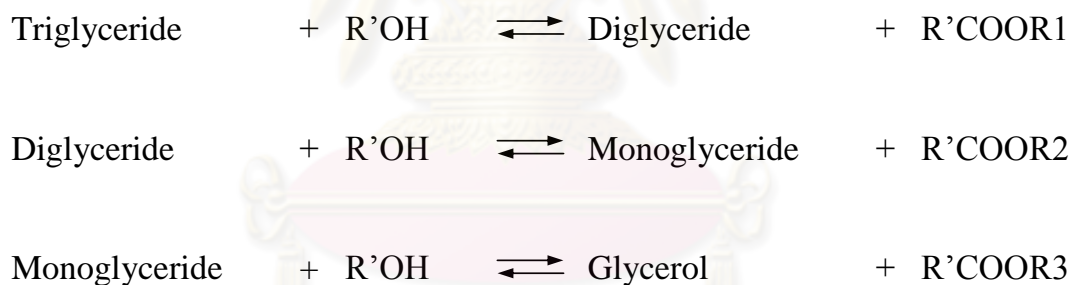


Figure 2.1 Transesterification equation

Transesterification reaction shown in Equation 2.1 is indeed the overall reaction for three stepwise reactions with intermediate formation of diglyceride and monoglyceride (Equation 2.2.). In the first reaction, triglyceride reacts with alcohol to produce diglyceride, and then in the second reaction, diglyceride reacts with alcohol to form monoglyceride. Finally, in the third reaction, monoglyceride reacts with alcohol to give glycerol.



Equation 2.2 Transesterification of triglycerides: three consecutive and reversible reactions. R₁, R₂, R₃ and R' represent alkyl groups

Transesterification can be catalyzed by many types of catalysts including:

1. Homogeneous catalysts
2. Heterogeneous catalysts

2.4 Transesterification using homogeneous catalysts

2.4.1 Alkaline catalysts transesterification

Alkaline catalysis is by far the most commonly used reaction type for biodiesel production. The main advantage of this form of catalysis over acid catalyzed transesterifications is high conversion under mild conditions in comparatively short reaction times (Freedman et al. 1986). So, it was estimated that under the same temperature conditions and catalyst concentrations methanolysis might proceed about 4000 times faster in the presence of an alkaline catalyst than in the presence of the same amount of an acidic equivalent. However, from a chemical standpoint, the active species with both types of catalyst are methoxide ions. Methoxide ions from methanol react with hydroxyl ions from added alkaline hydroxides in the second situation. Once formed, the methoxide ions are strong nucleophiles and attack the carbonyl moiety in glyceride molecules to produce the alkyl esters. The application of an alkaline catalyst in the transesterification of vegetable oil is shown that limited because the free fatty acid in vegetable oil with alkaline catalyst (KOH, NaOH) forms soap.

Freedman et al. (1984) studied transesterification of vegetable oil with methanol in which the molar ratio of methanol to oil was varied from 6:1 to 1:1. The reactions were conducted at temperature of 60°C for 60 minutes. The results indicated that at a 6:1 molar ratio, a 98 % conversion to the ester was obtained. As the molar ratio decreased to the theoretical ratio of 3:1, the percentage of ester decreased to 82%. They suggest that for maximum conversion to the ester a 6:1 ratio should be used. Ratios which are greater than 6:1 do not increase yields (already at 98-99%), complicate ester and glycerol recovery and add costs to alcohol recovery.

Boocock et al. (1996) studied transesterification of vegetable oil with methanol which prepared the methoxide base catalyzed methanolysis of soybean oil at 40°C to form methyl esters proceed approximately 15 minutes more slowly than butanolysis at 30°C. They found that a two phase reaction in methanolysis occurs only in the methanol phase which causes the slow reaction rate. Thus, Tetrahydrofuran (THF) was used as a cosolvent which makes both the oil and methanol miscible in which methanolysis speeds up and occurs as fast as butanolysis.

Gemma Vicente et al. (2003) compared catalysts for biodiesel production which is homogeneous basic catalysts. A comparison is made of different basic catalysts (sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide) for methanolysis of sunflower oil. The reaction were carried out in a batch stirred reactor at temperature of 65°C, 6:1 methanol to oil molar ratio. They found that biodiesel purity was near 100 wt.% for all catalysts. However, nearly 100 wt. % biodiesel yields were only obtained with the methoxide catalysts. Because sodium or potassium hydroxide was the catalyst, there were yield losses due to molecule of water generated from reaction when hydroxide (OH) group dissolved in methanol that can generate soap in the reaction and inhibit the separation of ester from the glycerol.

Weiyang Zhou et al. (2003) studied the methyl esters synthesis from used soybean oils by transesterification reaction, using basic catalysts such as KOH at four different molar ratio of alcohol to oil (6:1, 20:1, 25:1, 60:1). The use of tetrahydrofuran (THF) as cosolvent, the effect of various parameters such as the variation in oil quality, alcohol type (methanol, ethanol, butanol), the molar ratio of methanol to oil, amount of alkaline catalyst, time and temperature of reaction on the yield, and the properties of esters were studied. The optimum conditions, developed for the production of good methyl esters from used soybean oil, were as follows: for methanolysis and butanolysis, the

corresponding values 0.6 and 2% wt, respectively. The use of 1.4 % wt KOH led to ethanolysis equilibrium within 6-7 min at 23°C rather than 15 min when only 1% wt was used. At 60°C, equilibrium was reached within only 2 min.

Ji-Yeon Park et al. (2009) studied the transesterification of vegetable oils with methanol which was carried out in a batch reactor by using KOH as a catalyst, 60°C of reaction temperature and 60 minute reaction time. Fatty acid methyl esters (FAME) were used as the cosolvent, does not require additional separation after the reaction because it is the end product of the reaction. When the molar ratio of oil to methanol was 1:6 at 0.8 wt.% of KOH oil. The reaction mixture was made miscible within a short period of time. As the amount of FAME and catalyst, as well as the temperature, increased, the production rate of FAME increased. Because the introduction of FAME as the cosolvent used to increase the reaction rate was very successful.

Guoqing Guan et al. (2009) studied transesterification of sunflower oil with methanol using alkaline catalysts such as 1 % wt KOH. The experiments were carried out at 25 °C in the presence of several cosolvents, dimethyl ether (DME), diethyl ether (DEE), tert-butyl methyl ether (TBME) and tetrahydrofuran (THF). The minimum cosolvents to methanol molar ratio required for the complete dissolution of methanol and sunflower oil were determined. Experimental results showed that DME was the highest among those for the tested ethers. DME produced the best results for the transesterification, in which the nearly 97 % methyl esters concentration were obtained at 10 min. Moreover, they found that excessive addition of cosolvent into the reaction system decreased the transesterification rate, due to a dilution effect on the reagents. When the cosolvent to methanol molar ratio was lower than the minimum ratio, the oil conversion decreased because of the immiscibility of the oil and methanol.

In transesterification with alkaline catalyst, sodium methoxide, sodium hydroxide, potassium methoxide and potassium hydroxide can be used. The

alkaline catalysts are the most popular and widely used in commercial scale. However, the main problem of transesterification reaction is that the reactants are not readily miscible. Addition of cosolvents enhances the miscibility of the phases. So, it can allow the transesterification reaction to proceed efficiently. Choose a cosolvent with a boiling point near of the alcohol used. An important factor in the transesterification with alkali catalysts is the moisture because it can react with the fatty acid and following the saponification reaction, which produce soap. The soap consumes the catalyst, reduces the efficiency of the process, increases the viscosity, and makes it difficult to separate glycerol.

2.4.2 Acid catalysts transesterification

One limitation in the alkali 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. However, acid catalyzed transesterifications are usually far slower than alkali catalyzed reactions and require higher temperatures and pressures as well as higher amounts of alcohol. Transesterification can be catalyzed by Bronsted acids, such as sulfonic acid, sulfuric and hydrochloric acids.

Widyan et al. (2002) studied a comparison of the catalytic activities of HCL and H₂SO₄ for the transesterification of waste palm oil. Compared to HCL, H₂SO₄ was 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.

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

Fadi Ataya et al. (2007) studied and found that transesterification of canola oils with methanol was carried out in a batch reactor by using 3wt% sulfuric acid as a catalyst, 20°C of reaction temperature and 24 hours reaction time, 6:1 methanol to oil molar ratio. Three experimental conditions: the quiescent two phase reaction, the agitated two phase reaction and the agitated single phase reaction were tested. Tetrahydrofuran (THF) was used as the cosolvent which makes single phase reaction. They found that for the two phase reaction, the reaction appears to occur at the interface of the two phases. For the single phase medium, where no mass-transfer resistance occurred, and for the two phases agitated reaction, a mass-transfer coefficient was calculated and was found to be the first order of magnitude smaller than the kinetic rate constant for the single-phase reaction.

Guoqing Guan et al. (2009) studied a comparison of the catalytic activities of p-toluenesulfonic acid (PTSA), benzenesulfonic acid, and sulfuric acid for transesterification using vegetable oils with methanol, which dimethyl ether (DME) was used as a cosolvent to produce a homogeneous solution. P-toluenesulfonic acid (PTSA) showed highest catalytic activity. The reaction rate was greatly improved by addition of DME as a cosolvent because of disappearance of mass transfer resistance between the two phases. The yield of methyl esters reaches 97.1% when 4% wt of p-toluenesulfonic acid (PTSA)

based on the oil weight was used at 80°C with a reaction time 2 hours in the presence of DME.

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

2.5 Transesterification 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 into higher production cost. The synthesis of fatty acid methyl esters need to involve continuous processing in a flow system, have as few reaction steps as possible, limit the number of separation processes, and ideally use a robust heterogeneous catalyst (such as metal oxides). The appropriate solid catalysts could be easily incorporated into a packed bed continuous flow reactor, simplifying product separation and purification and reducing waste generation. Therefore, it is of interest to investigate the possibility to replace the homogeneous catalyst by solid catalysts in transesterification reactions.

Kim et al. (2004) studied the production of biodiesel from soybean oil using heterogeneous catalyst (Na/NaOH/ γ -Al₂O₃). The reaction was carried out at temperature of 60°C in a stainless steel batch reactor, 9:1 methanol to oil molar ratio and n-hexane was used as cosolvent and a reaction of 2 hours. Both the sodium aluminate formed by loading on γ -Al₂O₃, and the ionization of

sodium originate the strong basic strengths. The reaction conditions for the system were optimized to maximize the biodiesel production yield.

A utilization of a cosolvent was found to be inevitable for transesterification of vegetable oil to biodiesel. Among the cosolvents tested, 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 -Al₂O₃ heterogeneous base catalyst showed almost the same activity under optimized reaction conditions compared to the conventional homogeneous NaOH catalyst.

Sanjib et al. (2005) studied and found that the transesterification of *Pongamia pinnata* oils with methanol was carried out in a batch reactor by using solid acid catalysts viz. Hb-Zeolite, Montmorillonite K-10 and ZnO, 120°C of reaction temperature and 24 hours reaction time. Tetrahydrofuran (THF) was used as the cosolvent. ZnO gave a good conversion of 83 %, while Hb-Zeolite and Montmorillonite K-10 gave low conversions of 59% and 47% respectively.

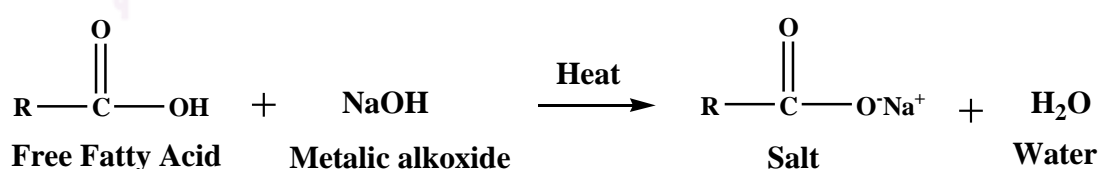
Huaping et al. (2006) studied biodiesel produced by the transesterification of vegetable oils is promising alternative fuel to diesel because of the limited resources of fossil fuel and environmental concerns. An environmentally benign process was developed for the production of biodiesel from *Jatropha curcas* oil using a heterogeneous solid super base catalyst, calcium oxide. The results showed that the base strength of calcium oxide was more than 26.5 after dipping in an ammonium carbonate solution followed by calcination. A study for optimizing the reaction conditions for the transesterification of *Jatropha curcas* oil was performed. Under the optimum conditions of catalyst calcination temperature of 900°C, reaction temperature of 70°C, reaction time of 2.5 h, catalyst dosage of 1.5%, and methanol/oil molar ratio of 9:1, Tetrahydrofuran (THF) was used as the cosolvent, and the oil conversion was 93%. The purification of the as-synthesized biodiesel with

decalcifying agents to eliminate the remaining calcium was investigated. Citric acid showed good performance for the decalcification. The properties of the refined biodiesel accorded with the domestic and foreign standards.

Transesterification using heterogeneous catalysts can be used. However, there still appear to be some problems with this technique and finding a suitable catalyst that is active and selective. The important barrier for using heterogeneous catalyst is that the price of heterogeneous is much higher than price of acid or base catalyst resulting in higher production cost of methyl esters.

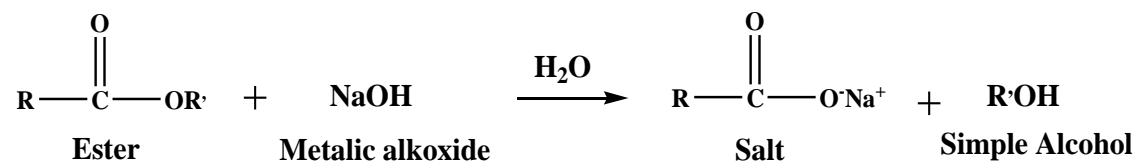
2.6 Saponification

The production of soap, sometimes called alkaline hydrolysis, converts triglyceride to glycerol and a mixture of salts of long-chain carboxylic acids. As it can be seen from Equation 2.3 and Equation 2.4, the reaction can be carried out with an ester (i.e. triglycerides) or with carboxylic acids (i.e. free fatty acid). However, the production of fatty acids is an intermediate step when triglycerides are directly used for saponification. The commercial production of soap is usually conducted in two phases. The first phase is the conversion of lipids into free fatty acid by boiling with aqueous sodium hydroxide until hydrolysis is completed and then adding sodium chloride to precipitate the soap (Solomon, 1996).



Equation 2.3 Saponification reaction from free fatty acid

Or

**Equation 2.4** Saponification reaction from alkyl ester

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER III

EXPERIMENTAL AND ANALYTICAL METHOD

The preparations of the experimental 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 reaction of vegetable oil and the last section refers to an analytical method and errors of the experiments.

3.1 Material

3.1.1 Palm olein oil

Vegetable oil used in this studied was palm olein oil. The palm olein oil was a commercial grade available in supermarket.

3.1.2 Chemical

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

Table 3.1 All chemicals used in the research

Name	Source	Purity
Methanol	Fisher Scientific	98% (industrial grade)
Ethanol	Fisher Scientific	98% (industrial grade)
Iso-Propanol	Fisher Scientific	99.99% (analytical reagent grade)
Toluene	Ajax Chemicals	99.8% (analytical reagent grade)
Sodium Hydroxide	Ajax Chemicals	98% (analytical reagent grade)
Potassium Hydroxide	Ajax Chemicals	85% (analytical reagent grade)
T-butanol	Ajax Chemicals	95% (analytical reagent grade)
Sodium Methylate	ACROS	N/A
Sulfuric Acid	J:T Baker	95% (analytical reagent grade)
Hydrochloric Acid	J:T Baker	36.5-38%
Heptane	QREC	99%
Diethyl Ether	QREC	99.5%
Tetrahydrofuran	QREC	99.9%
Hexane	QREC	99%
Cyclo Hexane	QREC	99.5%
Butanol	QREC	99.5%
Mix Fatty Acids	RESTEK	99.5%+
Methyl Esters		

3.2 Equipment

3.2.1 Transesterification of palm olein oil

All experiments were carried out in a 250 ml round-bottom flask. The flask was connected to a reflux condenser and was heated in a water bath as shown in Figure 3.1. The reaction was carried out at a temperature of 65°C and 35°C, oil to methanol molar ratio of 6:1. Samples were taken at 2, 4, 6, 8, 10, 20, 30, 40, 50 and 60 minutes.

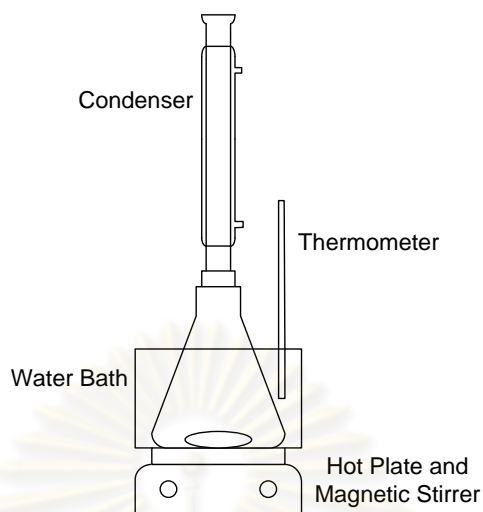


Figure 3.1 Condenser and hot plate magnetic stirrer set

3.3 Methodology

3.3.1 Characterization of palm olein oil

Palm olein oils were analyzed for density at 40 °C, Free fatty acids content (AOCS Ca 5A-40), Acid value (AOCS Cd-3D-63) and Saponification value (AOCS Cd-3b-76).

3.3.2 Basic catalyzed process

1. Heat palm olein oil at 100°C to eradicate moisture.
2. Prepare catalyst for experiment.
 - 2.1 The molar ratio of methanol to oil of 6:1 is put in the flask.
 - 2.2 The concentration of basic catalyst used is 1% of oil weight
 - 2.3 Mix the catalyst, sodium methyrate and methanol.
3. Determine the volume of cosolvents that were required for the creation of one phase.
 - 3.1 Cosolvents were added slowly to this mixture, followed by thorough shaking of the flask.

3.2 Determine amount of cosolvents that transformed the milky, non homogenous solution to a clear.

4. The reaction was starting at 65°C and 35°C under stirring at constant.

3.3.3. Separation step

At the end of reaction, the reaction products were carried out to separating funnel and those products was separated into two phases; crude methyl esters in the upper phase and crude glycerol in the bottom phase. Vacuum distillation was used to remove methanol from both phases of reaction product. Samples were taken from both phases and were kept for analysis to determine the amount of residue catalyst, and methanol. Crude methyl esters were purified by washing techniques, which the water presence is eliminated by heating above 100°C to boil off water.

3.4 Analytical method

3.4.1 Residue basic catalysts (AOCS Cc 17-79)

To determine residue basic catalyst in sample, a simple titration procedure can be used to measure the amount of catalyst. The basic consists of the phase to be analyzed with a 0.1 normal solution of hydrochloric acid to the phenolphthalein end point.

3.4.2 Methyl esters analysis

The analysis of standards and the products formed was carried out on Variance 8700 gas chromatography (GC) at Hazardous Laboratory, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. A non-polar capillary column (Carbowax M20) with an internal diameter of 0.32 mm, length of 30 m and film thickness of 0.25 m and flame ionization detector (FID) was used. Helium was used as a carrier gas with

pressure 10 psig. The injector and detector were set at 300°C, respectively. The column temperature was programmed with an initial temperature 80 °C for 5 min, heating at 20°C/min to 230°C, then holding on 5 min to a final temperature of 230°C. Methyl decanoate was chosen as an internal standard and heptane was solvent. Therefore, the type of methyl esters were compared, retention time of each methyl esters, with methyl esters standard in Figure 3.2 and Table 3.2.

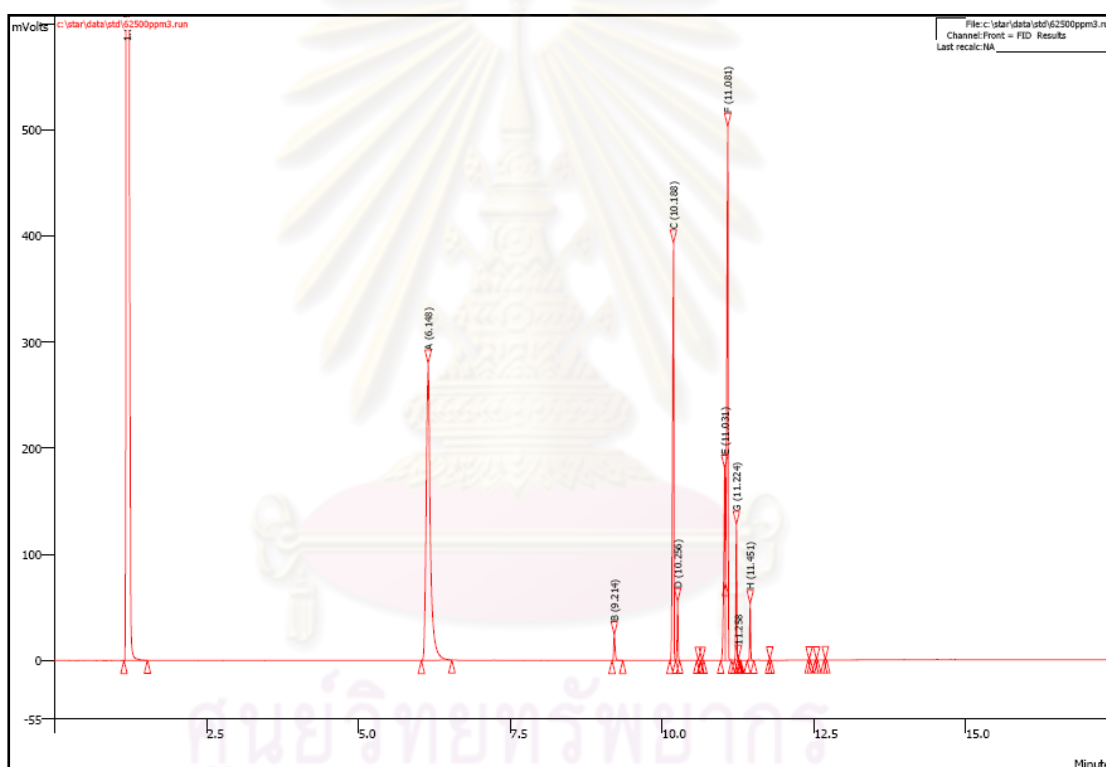


Figure 3.2 GC chromatogram of methyl esters

Table 3.2 Retention time of methyl esters in GC chromatogram

Retention time (min)	Peak of sample
1.190	N-Heptane
6.148	Methyl Decanoate
9.214	Methyl Myristate
10.118	Methyl Palmitate
10.256	Methyl Palmitoleate
11.031	Methyl Stearate
11.081	Methyl Oleate
11.224	Methyl Linoleate
11.458	Methyl Linolenate

The concentration of methyl esters and fatty acid is defined as a ratio of weight of methyl esters or fatty acid, which was determined by using gas chromatography (GC) to weight of sample as shown in Equation 3.1.

$$\% \text{Methyl Esters} = \frac{\text{Weight of Methyl Esters}}{\text{Weight of Sample}} \times 100 \quad (3.1)$$

By; weight of methyl esters calculate from response factor determined by GC

3.4.3 Experimental and Analytical Error

In this section, the experiments were conducted to verify repeatability, an average, and a standard deviation value of the experiment. In Equation 3.2 and Equation 3.3 define an average value and percent deviation respectively.

$$\text{Average value, } \bar{X} = \frac{\sum x}{n} \quad (3.2)$$

$$\text{Standard deviation from average value} = \sqrt{\frac{\sum (X - \bar{X})^2}{n}} \quad (3.3)$$

CHAPTER IV

RESULTS AND DISCUSSIONS

This chapter presents experimental results and discussions of production of methyl esters from palm olein oil via transesterification using various cosolvents using a sodium methylate (CH_3ONa) as a catalyst. The presence of various cosolvents such as n-Hexane, Cyclohexane, Tetrahydrofuran (THF), Diethyl ether (DEE), n-Butanol and t-Butanol on palm oil conversion were investigated in a batch reactor system. All experiments were conducted at an ambient pressure, a methanol to oil ratio of 6:1, and temperature of 35°C and 65 °C. The reaction products were analyzed by gas chromatography (GC) in order to determine percentage of methyl esters. Results and discussions are presented in six parts.

4.1 Characterization of palm olein oil

4.2 Dissolution of cosolvents

4.3 Non-catalytic transesterification reaction

4.4 Transesterification reaction without cosolvent

4.5 Transesterification reaction using cosolvent

4.6 Comparison of cosolvent

4.1 Characterization of palm olein oil

Vegetable oil used in this research is commercial grade palm olein oil. It is light yellow liquid at room temperature. The palm olein oil was characterized for its properties; free fatty acid, acid value, saponification value and molecular weight. Table 4.1 shows the properties of palm olein oil. The quantity of free fatty acids is an effective function in production of methyl

esters. The results show that free fatty acids value of palm olein oil was 0.2% which palm olein oil indicted difficultly with soap formation. Maher et al. (2006) studied the effect of free fatty acid on yield of methyl ester in tranesterification reaction. They concluded that free fatty acid (FFA) value lower than 3% is needed which effect to cause difficult soap formation. The molecular weight of palm olein oil was calculated based on acid value and saponification value which the molecular weight of palm olein oil is 850.76 g/mole.

Table 4.1 Properties of Palm Olein Oil

Properties	Palm olein oil
Free fatty acid, %	0.2
Acid value, mg KOH/g	0.7
Saponification value, mg KOH/g oil	197.82
Molecular weight, g/mole	850.76

The fatty acid composition was performed by gas chromatography (GC). The results are shown in Table 4.2. It shows that the major fatty acids components in palm olein oil are oleic, palmitic, and linoleic acids. The total percentage of saturated fatty acid is 42.34% and the remaining 57.86 % is unsaturated fatty acid. The molecular weight of palm olein oil was calculated based on acid by fatty acids composition equal to 850.76 g/mole. This molecular weight equals molecular weight that was calculated by the acid value and saponification value.

Table 4.2 Fatty acid composition in palm olein

Fatty acid	Structure ^a	Palm Olein Oil (%Composition)
Myristic	14:0	1.03
Palmitic	16:0	37.66
Stearic	18:0	3.66
Total Saturated fatty acid		42.34
Palmitoleic	16:1	0.18
Oleic	18:1	45.15
Linoleic	18:2	12.28
Linolenic	18:3	0.25
Total Unsaturated fatty acid		57.86
Molecular Weight (g/mol)		850.76

^axx:y indicates x carbon in fatty acid chain with y double bonds

4.2 Dissolution of cosolvents

The main problem of transesterification reaction is that the reactants are immiscible. The addition cosolvents enhance the miscibility of phase.

Therefore, the amount of cosolvents that homogeneous miscibility between methanol and palm olein oil were determined. All experiments using amount of cosolvents as shown in the Table 4.3.

Table 4.3 The amount of cosolvents required for the complete dissolution of methanol and palm olein oil

Cosolvents	Volume (ml)	Mass (g)
Diethyl ether	50	44
Tetrahydrofuran	55	39
Hexane	160	105
Cyclo hexane	217	169
Butanol	37	30
T-butanol	42	33

All experiments use catalyst and triglyceride in constant volumes. However, the volume of each cosolvent was used not equal. Therefore, it affects and changes the concentration of triglyceride and catalyst. The concentration of triglyceride and catalyst of each cosolvent is shown in Table 4.4. It shows that the concentration of triglyceride and catalyst decreased when cosolvent was added.

Table 4.4 The concentration of triglyceride and catalyst of each cosolvent

Cosolvents	Concentration of triglyceride (mol/l)	Concentration of catalyst (mol/l)
No-cosolvent	0.823	0.129
Diethyl ether	0.539	0.084
Tetrahydrofuran	0.597	0.094
Hexane	0.391	0.061
Cyclo hexane	0.328	0.051
Butanol	0.645	0.102
T-butanol	0.606	0.095

4.3 Non-catalytic transesterification reaction

4.3.1 Non-catalytic transesterification reaction

The effect of non-catalytic transesterification reaction is shown in Table 4.5. Samples were collected at 10, 20, 30, 40, 50 and 60 minutes. It shows that methyl esters did not occur without catalyst at temperature of 35 °C and 65°C. This result is in agreement with previous reports for transesterification in literatures. Berrios et al. (2007) studied a non-catalytic transesterification reaction of sunflower oil. The experiments were carried out at 60°C. They found that non-catalytic transesterification reaction did not occur at low temperature. Cao et al. (2004) conducted experiments to produce methyl esters from soybean oil in supercritical methanol. The experiments were carried out with non-catalytic at temperature of 450°C and pressure of 14700 psi. They found that methyl esters were obtained to 99% in 10 min. This indicated that non-catalytic transesterification reaction did not occur at temperature of 35 and 65°C.

Table 4.5 Effect of non-catalytic transesterification reaction at temperature of 35 and 65°C

Time (min)	Methyl esters (%wt)	
	35°C	65°C
10	N/D	N/D
20	N/D	N/D
30	N/D	N/D
40	N/D	N/D
50	N/D	N/D
60	N/D	N/D

*N/D = not detected

4.3.2 Effect of cosolvents and non-catalytic transesterification reaction

Effect of cosolvents and non-catalytic transesterification reaction is shown in Table 4.6. The results show that methyl esters did not occur when cosolvents were added. However, a non-catalytic transesterification reaction occurs only at a supercritical state. Cao et al. (2005) studied the transesterification of soybean oil in supercritical methanol. Propane was used as cosolvent. The experiments were carried out at temperature of 280°C and pressure of 12.8 MPa. At this temperature and pressure is at its supercritical state. Methanol to oil molar ratio of 24:1 was used in their study. They found that methyl esters were obtained to 98% in 10 min. So, this indicated that non-catalytic transesterification reaction could not occur when cosolvents were added at temperature of 35°C and 65°C.

Table 4.6 Effect of cosolvents and non-catalytic transesterification reaction at temperature of 35 °C and 65°C

Time (min)	Methyl esters (% wt)	
	35°C	65°C
10	N/D	N/D
20	N/D	N/D
30	N/D	N/D
40	N/D	N/D
50	N/D	N/D
60	N/D	N/D

*N/D = not detected

4.4 Transesterification reaction without cosolvents

In each experiment, transesterification reaction of palm olein oil with methanol was performed in a batch reactor using sodium methylate as catalyst. The amount of catalyst is 1 % by weight of palm olein oil. Samples were taken at 2, 4, 6, 8, 10, 20, 30, 40, 50 and 60 minutes. When each of experiment was completely performed in specific time, then the products were analyzed to determine the amount of glycerol, residue catalyst of each phase and percentage of methyl esters.

4.4.1 The effect of catalytic transesterification reaction

In the previous work, Joana et al. (2008) studied effect of amount of sodium methylate as catalyst to the reaction by varying in rang 0.2-1.2% by weight of the oil. The reaction was carried out with 6:1 molar ratio of methanol to oil at temperature of 65°C and 60 minutes of reaction time. They found that the highest concentration of methyl esters were generally obtained using catalyst concentration 1% by weight of the oil. So, amount of catalyst used in this work was 1 % by weight of palm olein oil.

The effect of reaction temperature and time is shown in Figure 4.1. The results in Figure 4.1 show that percentage of methyl esters increased when the reaction time increased. Percentage of methyl esters would increase rapidly in the 20 first minute and thereafter was almost constant.

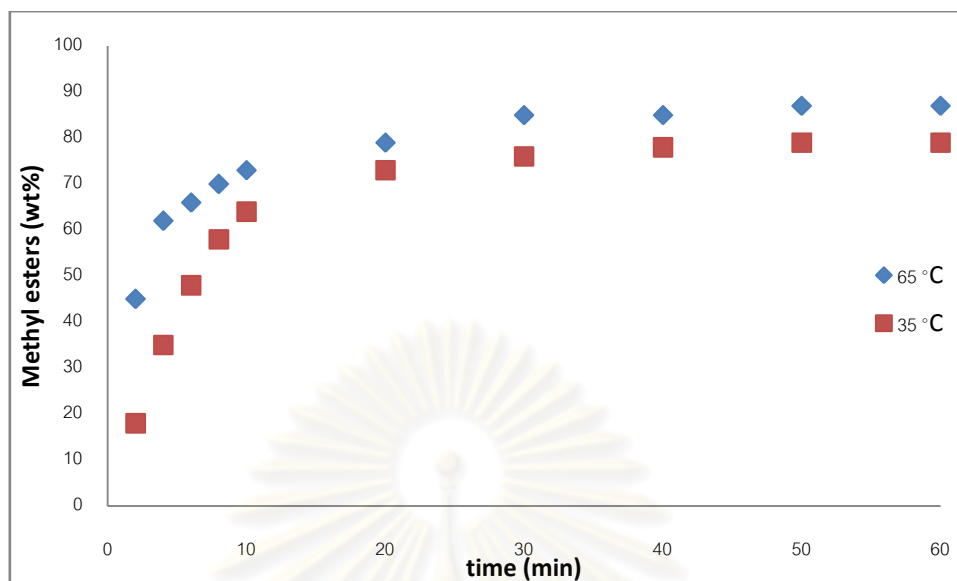


Figure 4.1 Effect of reaction temperature and time on percentage methyl esters in reaction products

Percentage of methyl esters were increased from 76% to 85% when temperature is increased from 35 °C to 65°C. This result is in agreement with previous reports for transesterification in literatures. Jeong et al. (2004) studied the effect of temperature on transesterification reaction of rapeseed oil using a methanol to oil molar ratio of 1:6 and 1% KOH as a catalyst. They found that percentage of methyl esters are 87% and 83% at temperature of 60 °C and 45°C respectively. Freedman et al. (1998) reported the effect of temperature on transesterification of refined soybean oil using a methanol to oil molar ratio of 1:6 and 1% NaOH for 1hour. They found that percentage of methyl esters increased from 64% to 87% when temperature increased from 32 °C to 60°C. Therefore, indicated that percentage of methyl esters increased when the reaction time and temperature increased.

A study of the kinetics of transesterification will provide parameters that can be used to predict the extent of the reaction at any time under particular conditions. There have been a few attempts to develop kinetic models for transesterification reaction of palm oil and methanol, such as Darnoko et al.

(2000), Leevijit et al. (2004). They found that the reaction rate of transesterification was 2nd order reaction.

The second order rate equation has the following form,

$$-r_A = \frac{dC_A}{dt} = kC^2_{TG}$$

where k is the rate constant. Integration this equation obtains

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C^2_A} = k \int_0^{tr} dt$$

or

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

A plot of $(1/C_A - 1/C_{A0})$ versus t gives a straight line through the origin for rate of equation. Figure 4.2 shows the fitting of the experimental data obtained at temperature of 35 °C and 65°C. The straight line was determined to fit the data in order to adopt the second order rate equation. Summary of the rate constant for each temperature could be evaluated from the slope of each line in Figure 4.2.

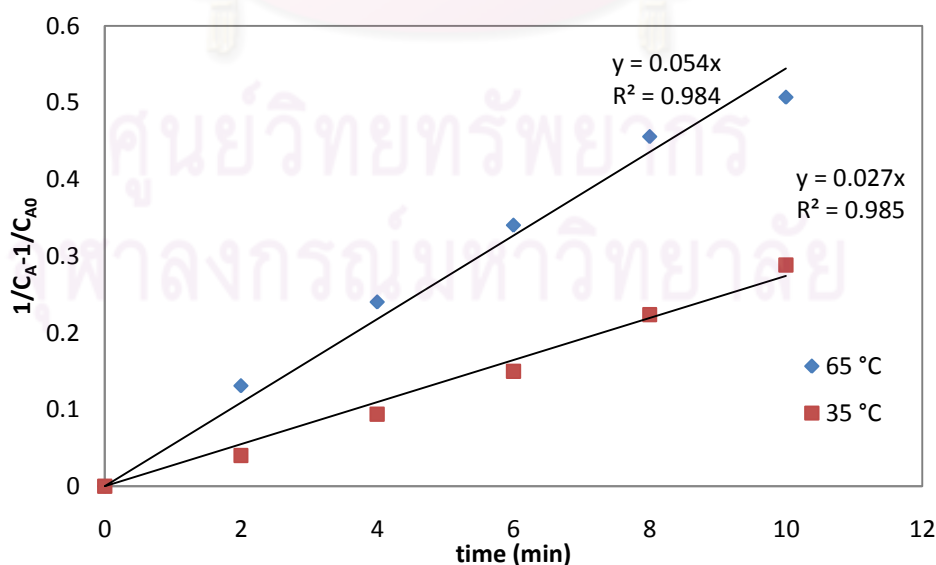


Figure 4.2 Determination of the kinetic constants at temperature of 35 °C and 65°C

The rate constant and its corresponding correlation coefficient obtained at temperature of 35 °C and 65°C are shown in table 4.7. The result found that rate constant increases when increases temperature. This indicated that the reaction at temperature of 65°C is greater than the reaction at temperature of 35°C.

Table 4.7 Reaction rate constant of palm olein, transesterification at different temperature

Temperature (°C)	k [L/(mol·min)]	R ²
35	0.027	0.985
65	0.052	0.984

The influence of temperature on the specific reaction rate was determined by Arrhenius equation.

$$k = Ae^{-\frac{E}{RT}}$$

Arrhenius type relationship of the form could describe the relationship between the kinetic constant and the temperature and the activation energy of the reaction (E). The activation energy was determined from the slope of ln k and 1/T as shown in Figures4.3. The activation energy of tranesterification reaction of palm olein oil was 2.3kJ/mol.

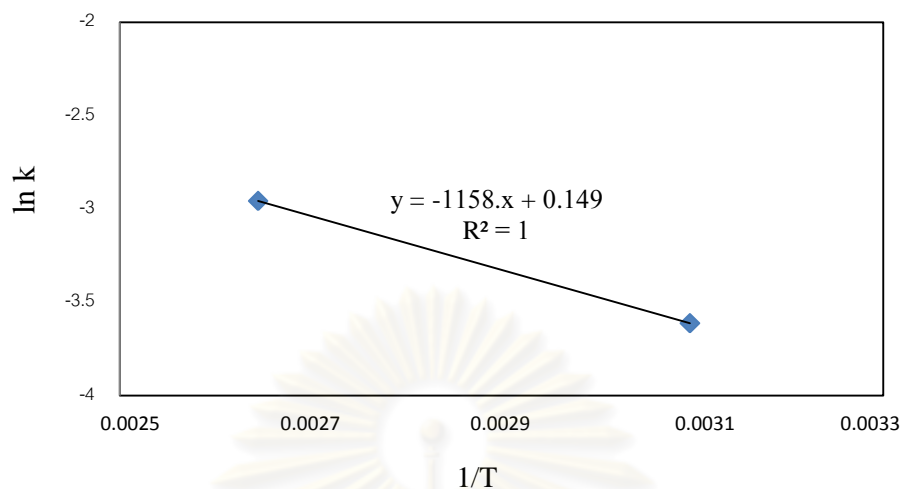


Figure 4.3 Determination of the activation energy at temperature of 35 °C and 65°C

4.4.2 Amount of glycerol

Amount of glycerol and percentage of methyl esters are shown in Table 4.8. The results in Table 4.8 show that amount of glycerol increased when the reaction time and reaction temperature increased. Amount of glycerol would increase when percentage of methyl esters increased both at temperature of 35 °C and 65°C. Moreover, amount of glycerol would increase continuously when reaction time increased due to reaction is not yet reached equilibrium.

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Table 4.8 Amount of glycerol and the percentage of methyl esters

Time (min)	35°C		65°C	
	Glycerol (g)	Methyl esters (% wt)	Glycerol (g)	Methyl esters (% wt)
10	4.1	64.46	7.2	72.26
20	5.9	73.5	9	78.24
30	8.6	76.14	11.2	82.47
40	9.2	78.5	12	85.96
50	9.8	79.07	12.2	87.09
60	10.3	80.21	12.5	87.87

Table 4.9 shows the amount of moles of glycerol and methyl esters from transesterification reaction. From table 4.9, it is found that the molar ratio of glycerol to methyl esters is approximately 1:3 in every experiment which is consistent with stoichiometry in transesterification reaction which gives 1 mole of glycerol and 3 moles of methyl esters. Darnoko et al. (2000) studied this effect in the transesterification of palm oil. They noted that increasing of methyl esters concentration was followed by increasing of glycerol. This indicated that increasing of percentage of methyl esters was followed by increasing of glycerol.

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Table 4.9 The amount of moles of Glycerol and Methyl esters from transesterification reaction

Time (min)	35°C		65°C	
	Glycerol	Methyl esters	Glycerol	Methyl esters
10	0.044	0.138	0.078	0.241
20	0.064	0.198	0.097	0.271
30	0.093	0.289	0.121	0.387
40	0.1	0.32	0.130	0.416
50	0.106	0.029	0.132	0.426
60	0.111	0.037	0.135	0.445

4.4.3 Distribution of residue catalyst in reaction products

The percentage of residue catalyst was calculated by weight of input catalyst. The results are shown Table 4.10. Experimental results show that residue catalyst dissolved in both phase of reaction products. However, free fatty acids were affected by amount of residue catalyst. Amount of catalyst must be neutralized free fatty acids in palm olein oil. Approximately 4% of catalyst is required to neutralize free fatty acid in palm olein oil. Therefore, only 96% of residue catalyst remained in transesterification reaction. Amount of residue catalyst in glycerol phase was higher than in methyl esters phase. Moreover, residue catalyst increases with amount of glycerol. Catalyst is dissolved well in polar chemical compounds. It can be explained that the component of glycerol phase are polar chemical compounds. A similar phenomenon was also observed by Narawut (2007) which studied the transesterification of palm olein oil with methanol. The reaction was carried out with 6:1 molar ratio of methanol to oil at temperature of 65°C for two hours. He found that amount of residue catalyst in glycerol phase were higher than in methyl esters phase due to residue catalyst is dissolved well in polar

chemical compound. So, the results indicated that amount of residue catalyst in glycerol phase was higher than in methyl esters phase.

Table 4.10 Percentage of residue catalyst by weight of input catalyst in each phase of reaction products of basic catalyzed transesterification

Time (min)	Percent of residue catalyst by weight of input catalyst (% wt)			
	glycerol phase		methyl esters phase	
	35°C	65°C	35°C	65°C
10	29	44	66	51
20	34	54	61	42
30	48	65	47	31
40	52	69	43	27
50	55	71	41	25
60	57	73	39	23

4.5 Transesterification reaction using cosolvents

The results shown in Figure 4.4 indicated that percentage of methyl esters increase when cosolvents were added to the reaction system. Butanol is the most effectively cosolvents. The reaction proceeds faster and reaches its maximum equilibrium percentage of 98% of methyl esters within 20-30 minutes. The percentage change of methyl esters obtained by adding cosolvents caused a two phase reaction to become a single phase reaction.

Cosolvents molecule consists of both polar and non polar parts. The polar part can be dissolved with methanol while non polar part can be dissolved with oil. So, cosolvent can help mixing well between polar and non polar layers of this reaction. In a two-phase reaction, methanol and palm olein oil are

immiscible. Therefore, the transesterification reaction is a mass transfer control with the poor diffusion between phases. In a single phase reaction, there is no interface between phases. Therefore, there would not be limitation resulting from inter-phase mass transfer. This result is in agreement with previous reports for transesterification in literatures. Chatri et al. (2007) studied the production of biodiesel fuel from transesterification of palm stearin and methanol. The reaction was carried out with 6:1 molar ratio of methanol to oil at 65°C using 1 wt% potassium hydroxide as catalyst and tetrahydrofuran(THF) as cosolvents. They found that using THF as cosolvents presented higher percentage of methyl esters compared to reaction without cosolvents. Methyl esters in palm stearin can be increased up to 95.74% when using THF as cosolvent. Haixian et al. (2008) studied influence of hexane as cosolvent on transesterification with methanol to oil molar ratio of 9:1 at temperature of 60 °C. They found that percentage of methyl esters were obtained to 95.4% in 60 min. This indicated that that percentage of methyl esters increase when cosolvents were added to the reaction system

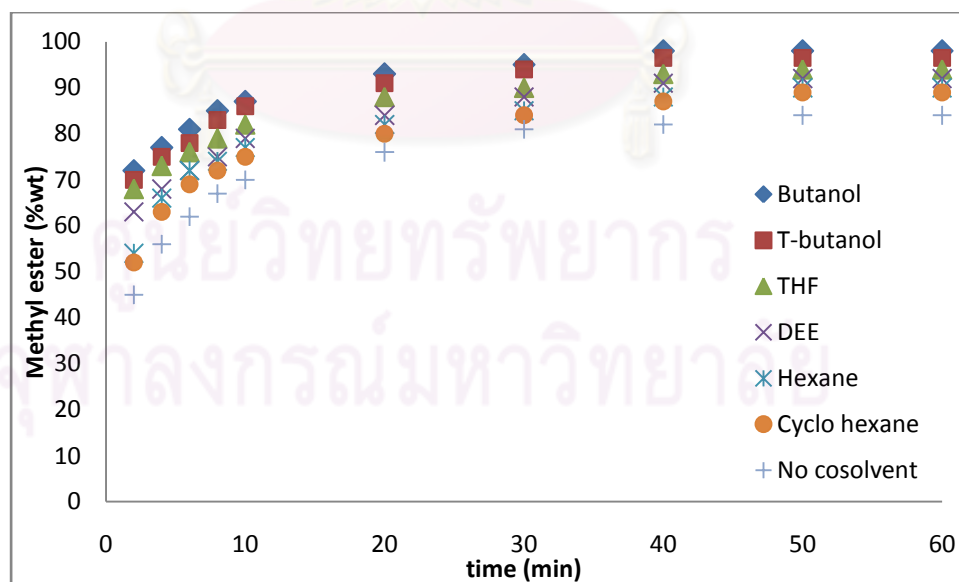


Figure 4.4 Effect of reaction time in the presence of various cosolvents, reaction temperature of 65°C, Methanol to oils molar ratio of 6:1

4.5.1 Transesterification reaction using ether as cosolvents

Ether used in this work comprising tetrahydrofuran (THF) and diethyl ether (DEE) having different chemical structures. THF has a cyclic ether structure while DEE has a symmetric ether structure.

4.5.1.1 Effect of reaction temperature and time

The results are shown in Figure 4.5 and 4.6. It can be seen that using ether as cosolvents was higher percentage of methyl esters in the product compare to the reaction without cosolvents at the same condition reaction due to ether will assist in the mixing of methanol and oil in the same phase.

Percentage of methyl esters would increase rapidly at the reaction time in range of 2 to 20 minutes and thereafter would be almost constant when using ether as cosolvents. Moreover, at 35°C when THF was used as cosolvent, percentage of methyl esters was higher than using DEE as cosolvent at same reaction time. According to Figure 4.5, the maximum percentage of methyl esters reached 91.5% and 87.3% when using THF and DEE as cosolvents, respectively at 60 minutes reaction time.

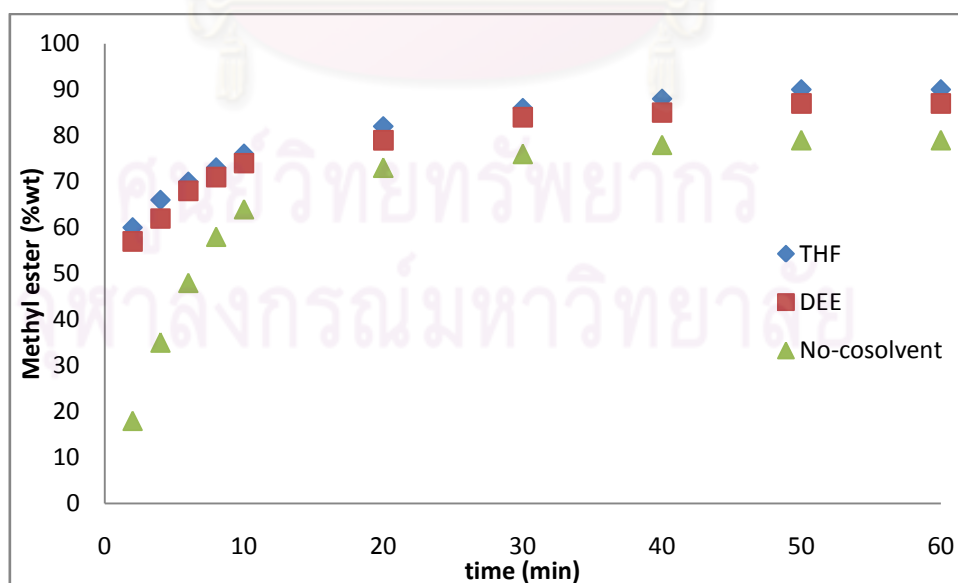


Figure 4.5 Effect of reaction time on percentage of methyl esters in reaction using THF and DEE as cosolvents temperature of 35°C

Figure 4.6 illustrated similar trend at temperature of 35°C. The maximum percentage of methyl esters reached 94.57% and 91.55% when using THF and DEE as cosolvents respectively at 60 minutes reaction time. However, at 65°C reaction temperature, percentages of methyl esters were higher than percentage at temperature of 35°C in both using of THF and DEE as cosolvents. Guan et al. (2009) studied transesterification of sunflower oil by varying of cosolvents. The reaction was carried out with 6:1 molar ratio of methanol to oil at temperature of 25°C. They found that THF presented percentage of methyl esters higher than using DEE as cosolvent at the same reaction time. Chatri et al. (2007) studied influence of cosolvents to the reaction by varying 3 solvents such as THF, tert-butyl methyl ether (TBME) and DEE. The result shows that THF was the most effective cosolvents and percentage of methyl esters of palm stearin was increased up to 95.74% with the help of THF.

This indicated that using THF as cosolvent presented higher percentage of methyl esters compared to the reaction using DEE as cosolvent at the same reaction time.

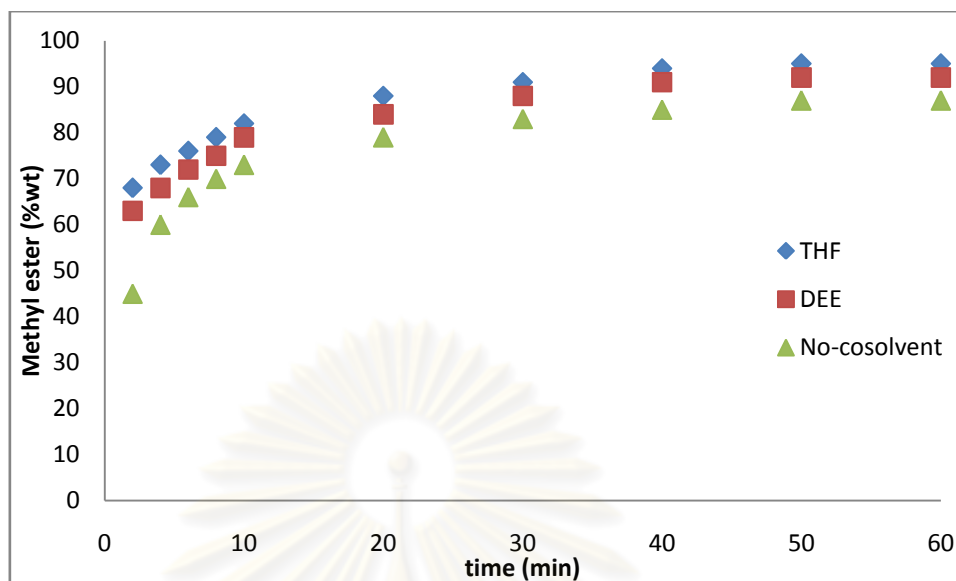


Figure 4.6 Effect of reaction time on percentage of methyl esters in reaction using THF and DEE as cosolvents at temperature of 65°C

4.5.1.2 Amount of glycerol from transesterification reaction using ether as cosolvents

In this section, amount of glycerol from transesterification reaction using cosolvents in the group of ether would be discussed. The results in Table 4.11 show that amount of glycerol increased when reaction time and reaction temperature increased. According to Table 4.10, when cosolvents was not used, it was found that amount of glycerol was lower than using ether as cosolvents. This result is consistent with percentage of methyl esters which was lower when cosolvents were not used. However, using THF as cosolvent was glycerol higher than using DEE as cosolvent at the same condition reaction due to THF presents higher percentage of methyl esters than using DEE. As a result, it indicated that increasing of glycerol presents increasing of percentage of methyl esters.

Table 4.11 Amount of glycerol from transesterification reaction using ether as cosolvents

Time (min)	Amount of glycerol (g)					
	Tetrahydrofuran		Diethyl ether		No-cosolvent	
	35°C	65°C	35°C	65°C	35°C	65°C
10	7.2	8.2	6.9	7.9	4.1	7.2
20	8.1	10.6	7.8	10.3	5.9	9
30	9.7	11.8	9.5	11.6	8.6	11.2
40	10.6	12.3	10.4	12.1	9.2	12
50	10.8	12.9	10.6	12.6	9.8	12.2
60	11.1	13.1	10.8	12.9	10.3	12.5

4.5.1.3 Distribution of catalyst in reaction products

Distribution of catalyst in each phase is shown in Table 4.11 and 4.12. In Table 4.11, it can be seen that residue catalyst dissolved in phase of glycerol increased by time resulting from amount of glycerol increased over time increased. However, it was found that residue catalyst dissolved in phase of glycerol decreased when cosolvents in ether group was used. Using THF as cosolvent, residue catalyst dissolved in glycerol phase was higher than using DEE as cosolvent at the same reaction condition. As THF used as cosolvent, residue catalyst dissolved in glycerol was approximately 25% and 36% at temperature of 35°C and 65°C, respectively, at 60 minutes reaction time. While using of DEE as cosolvent, residue catalyst dissolved in glycerol was approximately 18% and 33% at temperature of 35°C and 65°C, respectively, at 60 minutes.

Table 4.12 Residue catalyst in glycerol phase of reaction products using ether as cosolvents

Time (min)	Percent of residue catalyst by weight of input catalyst in glycerol phase (% wt)					
	Tetrahydrofuran		Diethyl ether		No-cosolvent	
	35°C	65°C	35°C	65°C	35°C	65°C
10	10	14	10	12	29	44
20	12	20	11	17	34	54
30	18	25	12	19	48	65
40	21	32	14	25	52	69
50	23	35	15	30	55	71
60	25	36	18	33	57	73

In Table 4.13, it can be seen that using ether as cosolvents presented higher dissolving of catalyst in methyl phase than without cosolvents. It causes higher percentage of methyl esters when cosolvents were used. This is because of substantial dissolving of catalyst in methyl esters phase presents higher percentage of methyl esters. However, it was found that residue catalyst dissolved in phase of methyl esters decreased by time due to increasing of catalyst dissolved in glycerol phase.

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Table 4.13 Residue catalyst in methyl esters phase of reaction products using ether as cosolvents

Time (min)	Percent of residue catalyst by weight of input catalyst in methyl esters phase (%wt)					
	Tetrahydrofuran		Diethyl ether		No-cosolvent	
	35°C	65°C	35°C	65°C	35°C	65°C
10	85	83	86	84	66	51
20	83	76	85	79	61	42
30	76	71	83	77	47	31
40	75	64	82	71	43	27
50	72	61	81	66	41	25
60	70	60	77	63	39	23

4.5.2 Transesterification reaction using alkane as cosolvents

Alkane used in this work comprising hexane and cyclo hexane having different chemical structures. Hexane, it has a straight chain alkane structure while cyclo hexane, it has a cyclo hexane structure.

4.5.2.1 Effects of reaction temperature and time

The results in Figure 4.7 and 4.8 indicate that percentage of methyl esters increased when the reaction time increased. Figure 4.7 and 4.8 was observed similar trend. It can be clearly seen that using alkane as cosolvents gave a higher percentage methyl esters compared to the reaction without cosolvents at the same reaction time due to alkane will assist in the mixing of methanol and oil into the one phase giving a high percentage of methyl esters. However, using hexane as cosolvent percentage of methyl esters was higher than using cyclo hexane as cosolvent at the same reaction time and temperature.

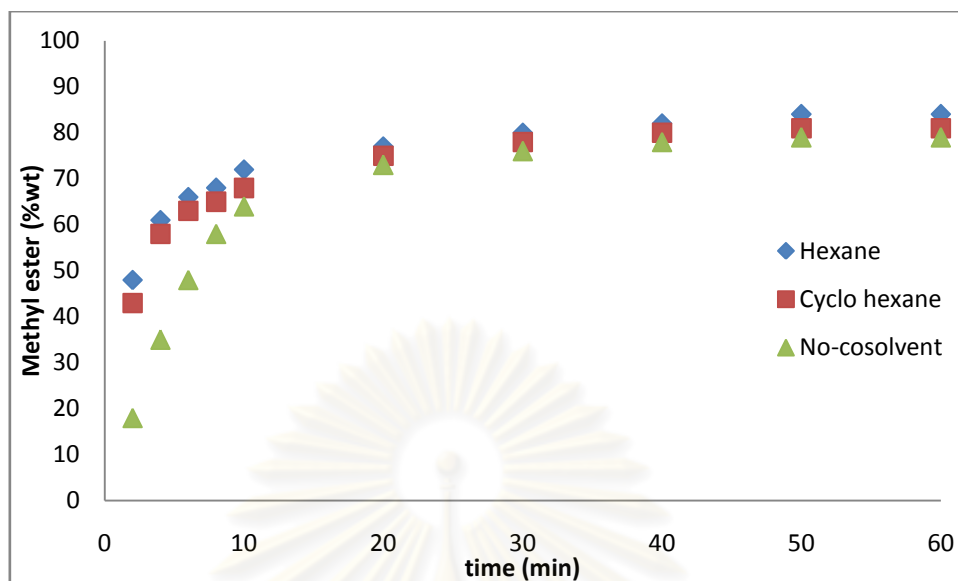


Figure 4.7 Effect of reaction time on percentage methyl esters using hexane and cyclo hexane as cosolvents at temperature of 35°C

The maximum percentage of methyl esters were 90.56 and 88.65% when using hexane and cyclo hexane as cosolvents respectively at temperature of 65°C. Transesterification reaction is shown to be straggly dependent of temperature. The effect of temperature showed that at temperature of 65°C providing the methyl esters more than at temperature of 35°C.

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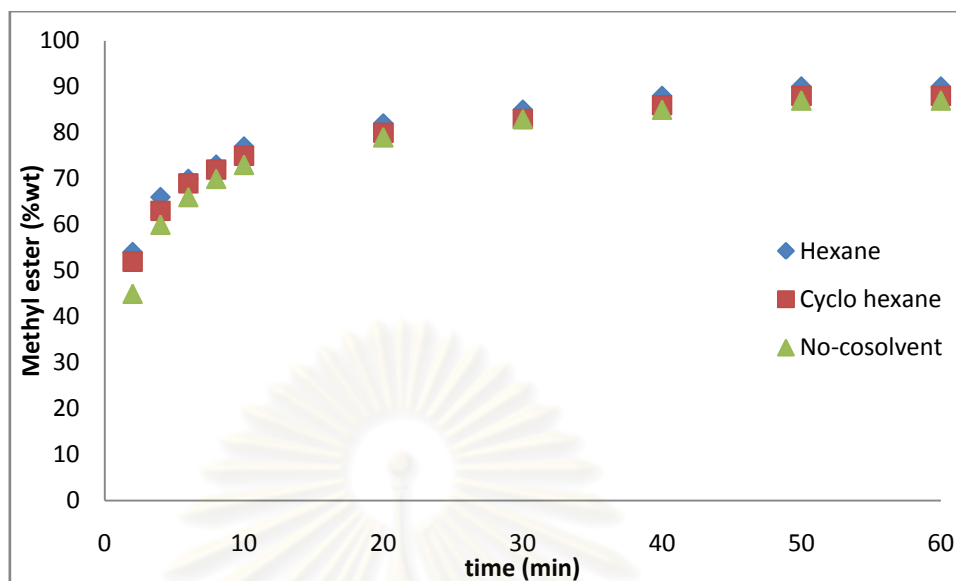


Figure 4.8 Effect of reaction time on percentage methyl esters using hexane and cyclo hexane as cosolvents at temperature of 65°C

4.5.2.2 Amount of glycerol of transesterification reaction using alkane as cosolvents

In this section discussed the amount of glycerol from transesterification reaction using cosolvents in the group of ether. The results in table 4.14 show that amount of glycerol increased when the reaction time increased. According to Table 4.14, when cosolvent was not used, it was found that amount of glycerol is lower than using alkane as cosolvents. However, using hexane as cosolvent was glycerol higher than using cyclo hexane as cosolvent at the same condition reaction. Therefore, consistent with percentage of methyl esters, using hexane as cosolvent get percentage of methyl esters higher than using cyclo hexane as cosolvent.

Table 4.14 Amount of glycerol of transesterification reaction using alkane as cosolvents

Time (min)	Amount of glycerol (g)					
	Hexane		Cyclo hexane		No-cosolvent	
	35°C	65°C	35°C	65°C	35°C	65°C
10	7.0	7.9	6.8	7.4	4.1	7.2
20	7.9	10.4	7.8	9.8	5.9	9
30	9.5	11.3	9.3	10.8	8.6	11.2
40	10.4	12.1	10.1	11.8	9.2	12
50	10.5	12.4	10.3	12.1	9.8	12.2
60	10.8	12.6	10.4	12.3	10.3	12.5

4.5.2.3 Distribution of residue catalyst in reaction products

Distribution of catalyst in each phase is shown in Table 4.15 and 4.16. Residue catalyst dissolved in phase of glycerol increased when increasing reaction time because amount of glycerol increased catalyst is more soluble due to the same polarity of glycerol and catalyst. However, it was found that residue catalyst dissolved in phase of glycerol decreased when cosolvents in alkane group was used. For the use of hexane as cosolvent, catalyst dissolved in glycerol approximately 0.43 and 0.58 gram at temperature of 35 and 65°C of reaction temperature respectively at reaction time of 60 minutes. While using of cyclo hexane as cosolvent, residue catalyst dissolved in glycerol approximately 0.35 and 0.56 grams at reaction temperature of 35 and 65°C respectively at reaction time of 60 minutes. On the other hand, residue catalyst dissolved in the phase of methyl esters decreased with increasing reaction time.

Table 4.15 Residue catalyst in glycerol phase of reaction products using alkane as cosolvents

Time (min)	Percent of residue catalyst by weight of input catalyst in glycerol phase (% wt)					
	Hexane		Cyclo hexane		No-cosolvent	
	35°C	65°C	35°C	65°C	35°C	65°C
10	6	12	5	10	29	44
20	14	20	12	18	34	54
30	2	30	18	29	48	65
40	28	41	23	42	52	69
50	36	49	33	52	55	71
60	43	58	35	56	57	73

Table 4.16 Residue catalyst in methyl esters phase of reaction products using alkane as cosolvents

Time (min)	Percent of residue catalyst by weight of input catalyst in methyl esters phase (% wt)					
	Hexane		Cyclo hexane		No-cosolvent	
	35°C	65°C	35°C	65°C	35°C	65°C
10	90	84	90	86	66	51
20	83	76	84	78	61	42
30	76	66	78	67	47	31
40	68	55	73	54	43	27
50	60	45	63	44	41	25
60	54	39	61	40	39	23

4.5.3 Transesterification reaction using alcohol as cosolvents

Alcohol used in this work comprising butanol and t-butanol having different chemical structures. Butanol has a straight chain alcohol structure and t-butanol has a branched chain alcohol structure.

4.5.3.1 Effects of reaction temperature and time

The results in Figure 4.9 and 4.10 show that percentage of methyl esters increased when the reaction time increased. According to Figure 4.6 and 4.7, transesterification reaction is shown to be straggly dependent of temperature. When using butanol as cosolvent the reaction temperature increases from 35°C to 65°C, the reaction proceeds faster and reaches its maximum equilibrium percentage methyl esters of 98% within 20-30 minutes, when at lower temperature the maximum equilibrium percentage methyl esters of 93%. The effect of temperature showed that at temperature of 65°C providing the methyl esters more than at 35°C.

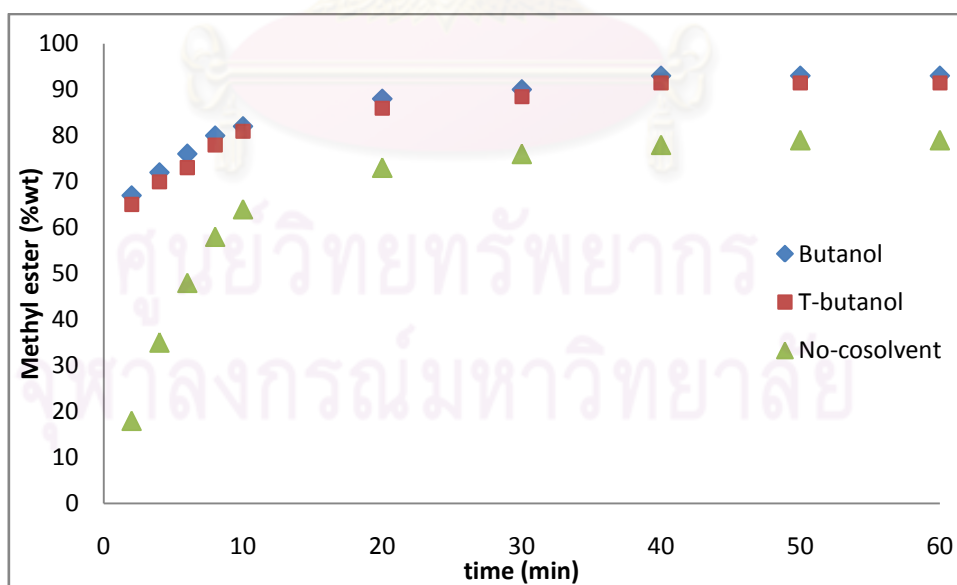


Figure 4.9 Effect of reaction time on percentage methyl esters using butanol and t-butanol as cosolvents at temperature of 35°C

From Figure 4.7, the maximum percentage of methyl esters reached 98.88 and 97.67% when using butanol and t-butanol as cosolvents respectively at reaction time of 60 minutes. In addition, using alcohol as cosolvents gave a higher percentage of methyl esters in the product compared to the reaction without cosolvent at the same reaction time. Owing to butanol and t-butanol, the mutual oil-methanol solubility could be increased, resulting in an increase of percentage of methyl esters.

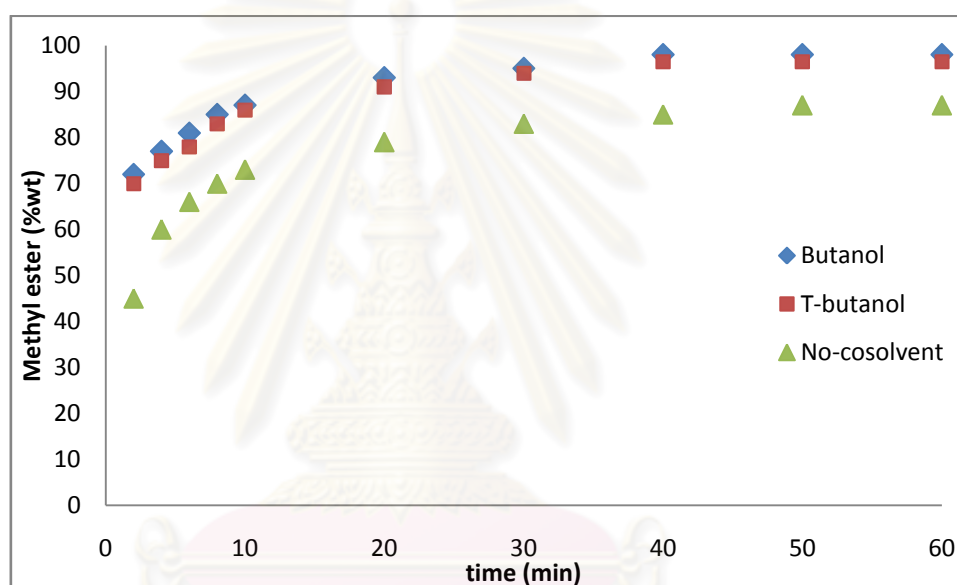


Figure 4.10 Effect of reaction time on percentage methyl esters using butanol and t-butanol as cosolvents at temperature of 65°C

4.5.3.2 Amount of glycerol of transesterification reaction using alcohol as cosolvents

When alcohol was used as cosolvents, it was found that glycerol phase and methyl phase was not separated. Therefore, quantity of glycerol would be determined by using water as solvent because glycerol could be dissolved in water. This part then can be separated from methyl esters phase. Amount of glycerol are shown in Table 4.17. Amount of glycerol increased when the reaction time increased. According to Table 4.17, when cosolvents was not used, it was found that amount of glycerol is lower than using alcohol

as cosolvents. However, using butanol as cosolvent was higher than using t-butanol as cosolvents at the same condition reaction. In addition, consistent with percentage of methyl esters, using butanol as cosolvent get percentage of methyl esters higher than using t-butanol as cosolvent. Residue catalyst could not be analysed when using butanol as cosolvent due to glycerol was dissolved homogeneously in methyl esters phase.

Table 4.17 Amount of glycerol of transesterification reaction using alcohol as cosolvents

Time (min)	Amount of glycerol (g)					
	Butanol		T-butanol		No-cosolvent	
	35°C	65°C	35°C	65°C	35°C	65°C
10	8.2	9.4	7.9	9.2	4.1	7.2
20	9.8	11.9	9.7	11.7	5.9	9
30	10.4	12.9	10.2	12.6	8.6	11.2
40	11.3	13.2	11.0	12.9	9.2	12
50	11.3	13.3	11.1	13.1	9.8	12.2
60	11.3	13.3	11.1	13.1	10.3	12.5

4.6 Comparison of cosolvents

This experiment is considered the effect of decreasing of stirring speed on transesterification reaction. The results in Table 4.18 show that decreasing of stirring speed will decrease percentage of methyl esters in case of the reaction without cosolvents. This result is agreement with previous report for transesterification in literatures. Ma et al. (1999) studied the effect of mixing on the transesterification of beef tallow with methanol at an alcohol to oil molar ratio of 6:1 with NaOH as a catalyst at a reaction temperature of 80°C. It indicated that mixing increased the reaction area between the immiscible reactants, thereby improving the initiation of the reaction. This will increase reaction surface for methanol, catalyst and oil resulting in faster reaction rate.

Mass transfer limitations were evident when little mixing occurred, whereas with increased mixing the diffusion limitations that represent a barrier to interfacial transport were minimized. On the other hand, percentage of methyl esters decreased quite little when decreasing of stirring speed both at the reaction time of 10 and 20 minutes when added cosolvents. Because added cosolvents, there is no interface between phases. Therefore there can be no limitations due to interphase mass transfer. As the result, it indicated that decreasing of stirred speed have more effect to the absence cosolvents than the presence cosolvents.

Table 4.18 Effect of stirring speed

Cosolvents	Percentage of methyl esters (% wt)			
	10 min		20 min	
	stirring	decreasing of stirring	stirring	decreasing of stirring
No-cosolvent	60.31	46.47	66.70	53.98
THF	73.94	72.36	75.63	75.22
DEE	72.11	70.78	74.61	73.67
Hexane	66.92	65.23	73.23	72.51
Cyclo hexane	64.37	64.05	71.51	70.02
Butanol	75.02	74.27	78.07	77.73
T-butanol	73.14	73.87	76.12	75.35

Effect of cosolvents in each type that reactant had equal concentration. The experiments were carried out at methanol to oil molar ratio of 6:1 and reaction temperature of 65°C. Samples were taken at 10 and 20 minutes. The results are shown in Table 4.19. It can be seen that percentage methyl esters of cosolvents in each type was not equal when using equal concentration

of reactant. Thus, types of cosolvent effected to reactions when using in equal volume. The results show that butanol was the most effective cosolvent and percentage methyl esters decreased from 78.07% to 72.45% with reaction time of 20 minutes when using cosolvents volume increased. This indicates that excessive addition of cosolvents into the reaction system decreased the percentage of methyl esters due to a dilution effect on the reactant. This result is in agreement with previous reports for transesterification in literature. Guan et al. (2009) studied transesterification of sunflower oil with methanol. The reaction was carried out with 6:1 molar ratio of methanol to oil and various cosolvents in a group of ether by using equal volume. They found that a conversion is not equal. These cosolvents dimethyl ether could be considered as effective cosolvents in methyl esters production. All results indicated that the types of cosolvents has affect on the transesterification reaction.

Table 4.19 Effect of cosolvents when using in equal volume

Cosolvents	Percentage of methyl esters (% wt)	
	10 min	20 min
THF	65.34	67.23
DEE	62.78	64.34
Hexane	61.92	70.23
Cyclo hexane	64.37	71.51
Butanol	66.12	72.45
T-butanol	64.32	71.64

CHAPTER V

CONCLUSIONS

5.1 Conclusions

The conclusions of the present research are as followed:

1. Addition of cosolvents during production of methyl esters from palm olein oil results is higher methyl esters content in product sample.
2. When butanol is used as cosolvent, product sample shows the highest methyl esters content of 98 %
3. Alcohols are better cosolvents than ethers, while alkanes give lowest methyl esters content.

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APPENDICES

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APPENDIX A

EXPERIMENTAL AND DATA ANALYSIS

A-1 Free Fatty Acids, AOCS Official methods Ca 5a-40

Reagents

1. Ethyl alcohol, 95%. The alcohol must give a definite, distinct and sharp end point with phenolphthalein and must be neutralized with alkali to a faint, but permanent pink color just before using.
2. Phenolphthalein indicator solution 1% in 95% alcohol.
3. Sodium hydroxide solution accurately standardized. Table A.1 for the appropriate normality of the expected free fatty acid concentration range in the sample.

Procedure

1. Sample must be well mixed and entirely liquid before weighing; however, not heat the sample more than 10°C over the melting point.
2. Use Table A.1 to determine the sample weight for various ranges of fatty acids. Weigh the designated sample size into an oil sample bottle or Erlenmeyer flask.
3. Add the specified amount of hot neutralized alcohol and 2 ml of indicator.
4. Titrate with standard sodium hydroxide, shaking vigorously until the appearance of the first permanent pink color of the sample. The color must persist for 30 seconds.

Table A-1 Free fatty acid range, alcohol volume and strength of alkaline

FFA range (%)	Sample (g)	Alcohol (ml)	Strength of alkali
0.0 to 0.2	56.4 ± 0.2	50	0.1 N
0.2 to 1.0	28.2 ± 0.2	50	0.1 N
1.0 to 30.0	7.05 ± 0.05	75	0.25 N
30.0 to 50.0	7.05 ± 0.05	100	0.25 or 0.1 N
50.0 to 100	3.525 ± 0.001	100	0.1 N

Calculations

- The percentage of free fatty acids in most types of fats and oils is calculated as oleic acid, although in coconut and palm kernel oils it is frequently expressed as lauric acid and palm oil in terms palmitic acid.

$$\text{Free fatty acid as oleic, \%} = \frac{\text{ml of alkali} \times \text{N} \times 28.2}{\text{mass, g of sample}}$$

$$\text{Free fatty acid as lauric, \%} = \frac{\text{ml of alkali} \times \text{N} \times 20.0}{\text{mass, g of sample}}$$

$$\text{Free fatty acid as palmitic, \%} = \frac{\text{ml of alkali} \times \text{N} \times 25.6}{\text{mass, g of sample}}$$

- The free fatty acids are frequently expressed in terms of acid value instead of percentage free fatty acids. The acid value is defined as the number of milligrams of KOH necessary to neutralize 1 g of sample.

A-2 Acid Value (Free fatty acids content), AOCS Official Method Cd-3d-63

- Weigh of sample 10-20 g. in conical flasks 250 ml.
- Add mix equal volumes of 95% ethanol and iso-propanol molar ratio 1:1 50 ml.
- Solution is titrated with 0.1 N potassium hydroxide solutions.
- Titrate while swirling, using phenolphthalein as indicator.

Calculation

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

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

A-3 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

1. Hydrochloric acid 0.5 N aqueous solution accurately standardized.
2. Potassium hydroxide 0.5 N solution in 95% ethanol.
3. Phenolphthalein indicator 1% in 95% 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 1mg.
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 HCl.
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 (in g.) of oil or fat taken	=	w
Volume (in ml.) of hydrochloric acid used in test	=	v ₁
Volume (in ml.) of hydrochloric acid used in blank	=	v ₂
Normality of hydrochloric acid	=	N

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

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

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

Note: The saponification value (SV), 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.

A-4 Calculation molecular weight of palm olein oil

Saponification value of palm fatty acid, AOCS official Method Cd-3b-76

Calculation

Saponification value of palm fatty acid, AOCS official Method Cd-3b-76

Calculation

Let; Weight (in g.) of oil or fat taken	=	w
Volume (in ml.) of hydrochloric acid used in test	=	v ₁
Volume (in ml.) of hydrochloric acid used in blank	=	v ₂
Normality of hydrochloric acid	=	N

$$\text{Saponification Value} = \frac{56.1N(v_2 - v_1)}{W}$$

$$SV = \frac{(56.1 \times 0.485)(22 - 7.6)}{1.98}$$

$$S.V.=197.82$$

Where

SV = saponification value of the fat

AV = acid value of the fat

The mean molecular weight of the fatty acids (M) may be calculated:

$$MW = \frac{[56108 - 12.67 (197.82 - 0.7)]}{197.82}$$

$$MW = 270.92$$

Mean Molecular weight of triglyceride

$$M.MW = (3) (MW) + 38$$

$$M.MW = (3) (270.92) + 38$$

$$M.MW = 850.76$$

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APPENDIX B

CALCULATION OF RESIDUE CATALYSTS, CONCENTRATION OF METHYL ESTERS

B-1 Residue catalysts (titrimetric method), AOCS Recommended Practice Cc 17-79

Apparatus

1. Erlenmeyer flask 500 ml.
2. Buret 10 ml, graduated in 0.05 ml units.

Reagents

1. Acetone containing 2% water, prepared by adding 20 ml distilled water to 980 ml of reagent grade acetone.
2. Hydrochloric acid (HCL) approximately 0.01 N, accurately standardized.

Procedure

1. Dissolve sample in 100 ml of containing 2% distilled water. The amount of sample will depend on the expected level of catalyst. Use 0.5 g of crude glycerol, 5g of sample for crude methyl esters.
2. Add 2 ml of 1% phenolphthalein indicator (in isopropyl alcohol).
3. Titrate with 0.1 N hydrochloric acid until you get the phenolphthalein color change (red to clear). This indicates that you have neutralized the free catalyst in sample.

Calculations

Now, the amount of HCL added during the first titration tells us how much free catalyst is in the sample.

$$\text{weight \% of catalyst} = \frac{Q \times 0.1 \times M}{1000 \times W} \times 100$$

Where

Q = ml of HCL or KOH titrate

M = molecular weight of catalyst

W = grams of sample

This gives the amount of free catalyst in the sample, done here assuming the catalyst was CH₃ONa. You can substitute the appropriate molecular weight for other catalysts (KOH = 56.1, NaOH = 40.0, CH₃ONa = 54.03)

B-2 Response factor of methyl esters and fatty acid

The response factor is defined as

$$\text{Response Factor} = \frac{\text{Area of methyl esters} \times \text{g of internal standard in solution}}{\text{Area of internal standard} \times \text{g of methyl esters}}$$

Response factor calculations are based on the data from the chromatogram of standard methyl esters and fatty acids.

$$\text{Response Factor of methyl myristate} = \frac{39614 \times 0.1075}{1369050 \times 0.00279}$$

$$\text{Response Factor of methyl myristate} = 1.11$$

$$\text{Response Factor of methyl palmitate} = \frac{612724 \times 0.1075}{1369050 \times 0.00419}$$

$$\text{Response Factor of methyl palmitate} = 1.15$$

$$\text{Response Factor of methyl palmitoleate} = \frac{60824 \times 0.1075}{1369050 \times 0.00042}$$

Response Factor of methyl palmitoleate = 1.14

$$\text{Response Factor of methyl stearate} = \frac{301793 \times 0.1075}{1369050 \times 0.00195}$$

Response Factor of methyl stearate = 1.21

$$\text{Response Factor of methyl oleate} = \frac{836435 \times 0.1075}{1369050 \times 0.00572}$$

Response Factor of methyl oleate = 1.15

$$\text{Response Factor of methyl linoleate} = \frac{135218 \times 0.1075}{1369050 \times 0.00097}$$

Response Factor of methyl linoleate = 1.09

$$\text{Response Factor of methyl linolenate} = \frac{55774 \times 0.1075}{1369050 \times 0.00041}$$

Response Factor of methyl linolenate = 1.05

B-3 Analysis of methyl esters

Analysis of methyl esters and free fatty acids in product by used gas chromatography (GC). The retention time of each methyl esters are different. Therefore, for find the type of methyl esters by compare retention time of each methyl esters with methyl esters standard. The retention time are shown in Table B-1.

Table B-1 Retention time of methyl esters in Gas Chromatogram

Number of peak	Retention time (min)	Peak of sample
1	1.190	N-Heptane
2	6.160	Methyl Decanoate
3	9.226	Methyl Myristate
4	10.199	Methyl Palmitate
5	10.264	Methyl Palmitoleate
6	11.033	Methyl Stearate
7	11.084	Methyl Oleate
8	11.234	Methyl Linoleate
9	11.458	Methyl Linolenate

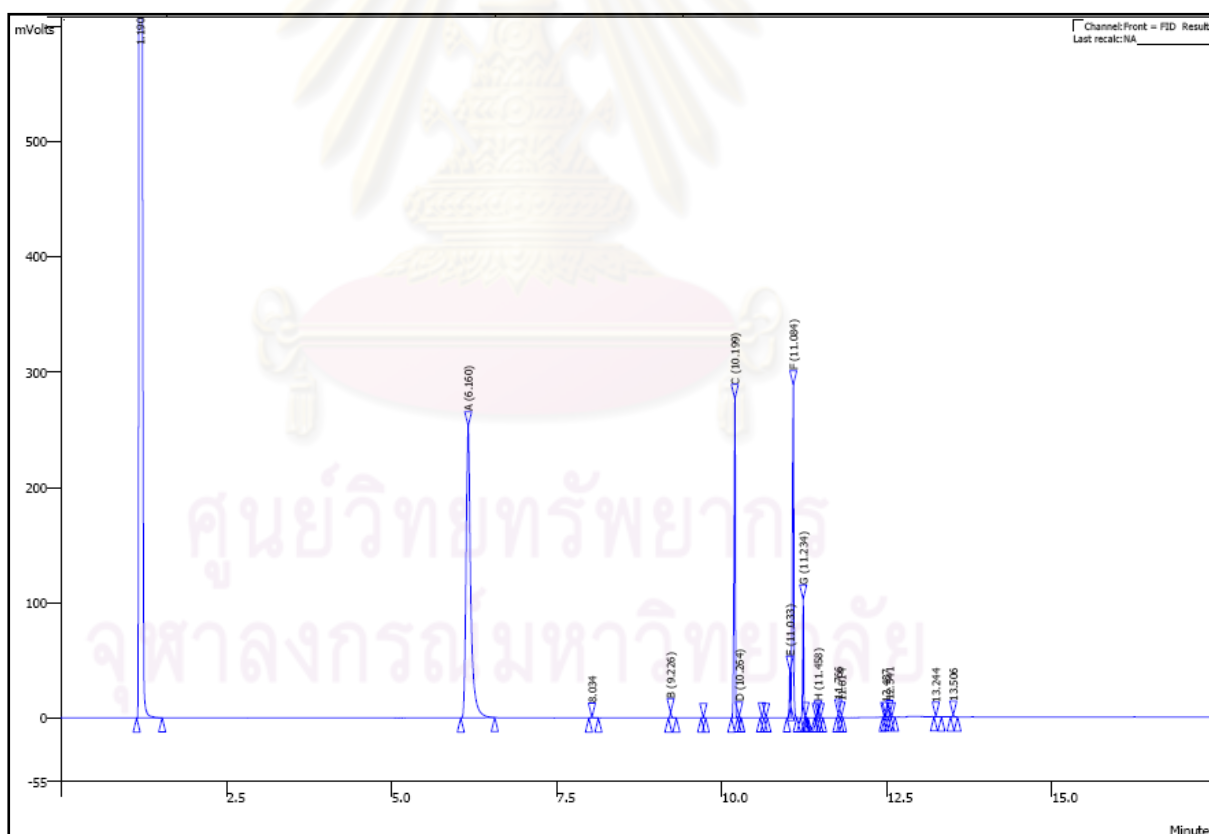
B-1 GC chromatogram of methyl esters and fatty acid from experiment

Figure B-1 Chromatogram for methyl esters and fatty acid at condition: Palm oils reactant, molar ratio of methanol to oil of 6:1, 1% wt NaOCH₃, tetrahydrofuran as cosolvent, 2 min at temperature of 65 °C and at ambient pressure.

Table B-2 Area of methyl esters sample in Gas Chromatogram

Retention Time	Peak of Sample	Area	%Area
6.160	Methyl Decanoate	1350153	50.89
9.226	Methyl Myristate	13209	0.49
10.199	Methyl Palmitate	503089	18.96
10.264	Methyl Palmitoleate	2473	0.09
11.033	Methyl Stearate	51841	1.95
11.084	Methyl Oleate	583908	22
11.234	Methyl Linoleate	145500	5.41
11.458	Methyl Linolenate	2798	0.1

Example 1. From figure B-1, find concentration of methyl esters molar ratio of methanol to oil of 6:1, 1 wt NaOCH₃, tetrahydrofuran was used as a cosolvent, 2 min at temperature of 65 °C and ambient pressure. Product of 0.05 added to 0.75 g of methyl decanoate solution in n-heptane.

Note that: In methyl decanoate solution 0.75g has 0.039 g of methyl decanoate.

$$\text{g of methyl esters} = \frac{\text{Area of methyl esters}}{\text{Area of internal standard}} \times \frac{\text{g of internal standard in solution}}{\text{R.F. of methyl esters}}$$

$$\text{g of methyl myristate} = \frac{13209}{1350153} \times \frac{0.039}{1.11}$$

$$= 3.3 \times 10^{-4}$$

$$\text{g of methyl palmitate} = \frac{503089}{1350153} \times \frac{0.05}{1.15}$$

$$= 1.23 \times 10^{-2}$$

$$\text{g of methyl palmitoleate} = \frac{2473}{1350153} \times \frac{0.05}{1.14}$$

$$= 6.11 \times 10^{-5}$$

$$\begin{aligned} \text{g of methyl stearate} &= \frac{51841}{1350153} \times \frac{0.05}{1.21} \\ &= 1.2 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} \text{g of methyl oleate} &= \frac{583908}{1350153} \times \frac{0.05}{1.15} \\ &= 1.4 \times 10^{-2} \end{aligned}$$

$$\begin{aligned} \text{g of methyl linoleate} &= \frac{145500}{1350153} \times \frac{0.05}{1.09} \\ &= 3.77 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} \text{g of methyl linolenate} &= \frac{2798}{1350153} \times \frac{0.05}{1.05} \\ &= 7.5 \times 10^{-5} \end{aligned}$$

Also; g of total methyl esters = 3.21×10^{-2}

$$\% \text{Methyl esters} = \frac{3.21 \times 10^{-2}}{0.05} \times 100$$

$$= \mathbf{64\%}$$

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APPENDIX C

EXPERIMENTAL DATA ANALYSIS

C-3 Experimental data of basic catalyzed transesterification reaction time

Table C-3.1 The effect of basic catalyzed transesterification reaction at ambient pressure and temperature of 35°C

Time (min)	Methyl esters (% wt)				
	Ex1	Ex2	Ex3	Average	S.D
0	0.00	0.00	0.00	0.00	0.00
2	18	19.2	18.2	18.46	0.64
4	35	35.89	34.98	35.29	0.51
6	49.12	48	47.98	48.36	0.65
8	58.12	58.78	57.98	58.29	0.42
10	63.5	65.12	64.34	64.32	0.81
20	73.1	74.08	73.33	73.50	0.51
30	76	76.55	75.89	76.14	0.36
40	78.11	78.45	78.96	78.5	0.42
50	79	79.8	78.43	79.07	0.68
60	79.95	80.12	80.56	80.21	0.31

Table C-3.2 The effect of basic catalyzed transesterification reaction at ambient pressure and temperature of 65°C

Time (min)	Methyl esters (% wt)				
	Ex1	Ex2	Ex3	Average	S.D
0	0.00	0.00	0.00	0.00	0.00
2	45.78	45.23	45.58	45.53	0.23
4	61.74	62.1	62.4	62.08	0.33
6	65.5	66.2	66	65.9	0.36
8	70.23	70.12	70.58	70.31	0.19
10	72.07	72.12	72.58	72.26	0.23
20	77.98	78.08	78.67	78.24	0.37
30	82.74	82.02	82.67	82.47	0.39
40	85.45	86.11	86.34	85.96	0.37
50	86.98	87.05	87.24	87.09	0.13
60	87.14	87.26	87.21	87.2	0.05

C-4 Experimental data of amount of crude glycerol, crude methyl esters, cosolvents and methanol

Table C-4.1 Amount of crude glycerol, crude methyl esters and methanol

Time (min)	35°C						65°C					
	Glycerol fraction			Methyl esters fraction			Glycerol fraction			Methyl esters fraction		
	CG*	CGA*	Methanol	CM*	CMA*	Methanol	CG*	CGA*	Methanol	CM*	CMA*	Methanol
	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
10	6.5	4.1	2.4	114.5	101.5	14.9	10.2	7.2	3	110.8	101.5	11.2
20	8.9	5.9	3	112.3	101.5	12.6	12.4	9	3.4	108.6	101.5	8.9
30	11.2	7.6	3.6	109	102	9.2	15.8	11.2	4.6	105.2	101.6	5.4
40	13.8	9.2	4.6	107.4	101.6	7.6	17.4	12	5.4	103.7	101.6	3.9
50	14.6	9.8	4.8	106.6	101.7	6.8	18	12.2	5.8	103.1	101.5	3.3
60	15.1	10.3	4.8	106	101.7	6.2	19	12.5	6	102.4	101.6	2.6

“CG* = Crude glycerol, CGA* = Crude glycerol after remove methanol, CM* = Crude methyl esters, CMA* = Crude methyl esters after remove methanol”

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Table C-4.2 Amount of crude glycerol, crude methyl esters and methanol using tetrahydrofuran as cosolvents

Time (min)	35°C						65°C					
	Glycerol fraction			Methyl esters fraction			Glycerol fraction			Methyl esters fraction		
	CG*	CGA*	Methanol	CM*	CMA*	Methanol	CG*	CGA*	Methanol	CM*	CMA*	Methanol
	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
10	8.9	7.2	1.2	153.1	107	14	10.5	8.2	1.4	151.5	109	10.9
20	10	8.1	1.4	152	109	11.4	13.3	10.6	2.2	148.7	109	7.8
30	13	9.7	1.8	149	109	10.4	14.7	11.8	2.6	147.3	109	6.7
40	14.1	10.6	2.2	147.9	109	9.4	16.2	12.3	3	145.8	110	6
50	15	10.8	2.5	147	109	8.6	18.1	12.9	3.4	143.9	110	5.2
60	15.5	11.1	2.6	146.5	109	8.2	18.5	13.1	3.4	143.5	110	5.2

“CG* = Crude glycerol, CGA* = Crude glycerol after remove methanol, CM* = Crude methyl esters, CMA* = Crude methyl esters after remove methanol”

Table C-4.3 Amount of crude glycerol, crude methyl esters and methanol using diethyl ether as cosolvent

Time (min)	35°C						65°C					
	Glycerol fraction			Methyl esters fraction			Glycerol fraction			Methyl esters fraction		
	CG*	CGA*	Methanol	CM*	CMA*	Methanol	CG*	CGA*	Methanol	CM*	CMA*	Methanol
	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
10	8.2	6.9	1.3	158.8	107.3	13.9	9.9	7.9	1.7	157.1	109.9	10.6
20	9.7	7.8	1.7	157.3	109.5	11.1	13	10.3	2.3	154	111.4	7.7
30	11.7	9.5	1.8	155.3	109.9	10.4	15	11.6	2.8	152	111.5	6.5
40	12.8	10.4	2.0	154.2	110.3	9.6	15.5	12.1	3.1	151.5	111	5.9
50	13.3	10.6	2.2	153.7	110.6	8.9	15.6	12.6	3.3	151.4	111	5.3
60	13.8	10.8	2.4	153.2	110.6	8.4	16.1	12.9	3.3	150.9	111.4	5.1

“CG* = Crude glycerol, CGA* = Crude glycerol after remove methanol, CM* = Crude methyl esters, CMA* = Crude methyl esters after remove methanol”

Table C-4.4 Amount of crude glycerol, crude methyl esters and methanol using hexane as cosolvent

Time (min)	35°C						65°C					
	Glycerol fraction			Methyl esters fraction			Glycerol fraction			Methyl esters fraction		
	CG*	CGA*	Methanol	CM*	CMA*	Methanol	CG*	CGA*	Methanol	CM*	CMA*	Methanol
	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
10	8.2	7.0	0.7	219.8	107.1	14.9	10.1	7.9	1.5	217.9	106.3	12.3
20	9.9	7.9	1.5	218.1	108.4	11.3	14.4	10.4	2.3	213.6	107.2	10
30	13.5	9.5	2.5	214.5	108.3	9.7	15.7	11.3	3	212.3	106.3	7.1
40	14.6	10.4	2.9	213.4	107.3	8.6	18.1	12.1	4.4	209.9	105.4	5.2
50	15.9	10.5	3.7	212.1	106.3	7.2	20.2	12.4	5.6	207.8	104.4	3.9
60	16.9	10.8	4.3	211.1	106.2	6.1	22.9	12.6	6.5	205.1	103.3	2.4

“CG* = Crude glycerol, CGA* = Crude glycerol after remove methanol, CM* = Crude methyl esters, CMA* = Crude methyl esters after remove methanol”

Table C-4.5 Amount of crude glycerol, crude methyl esters and methanol using cyclo hexane as cosolvent

Time (min)	35°C						65°C					
	Glycerol fraction			Methyl esters fraction			Glycerol fraction			Methyl esters fraction		
	CG*	CGA*	Methanol	CM*	CMA*	Methanol	CG*	CGA*	Methanol	CM*	CMA*	Methanol
	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
10	7.8	6.8	0.6	284.2	109.4	13	9.5	7.4	0.9	282.5	108.3	13
20	9.8	7.8	1.1	282.2	109.1	11.7	13.9	9.8	1.6	278.1	108.5	10.5
30	13.3	9.3	1.8	278.7	108.5	10.4	15.4	10.8	2.2	276.6	109	7.6
40	14.8	10.1	2.3	277.2	108.4	9.2	15.4	11.8	2.5	276.6	108	6.4
50	16	10.3	2.9	276	107.3	8	16.6	12.1	3.1	275.4	106.4	5.9
60	16.7	10.4	3.2	275.3	107.4	7.2	18.4	12.3	3.6	273.6	106.7	5.2

“CG* = Crude glycerol, CGA* = Crude glycerol after remove methanol, CM* = Crude methyl esters, CMA* = Crude methyl esters after remove methanol”

C-5 Experimental data of residue catalyst in each phase of reaction products of basic transesterification

Table C-5.1 Amount of residue catalyst in glycerol phase of reaction products of basic transesterification at ambient pressure and temperature of 35°C

Time (min)	Amount of residue catalyst in glycerol phase (g)				
	No-cosolvent	Tetrahydrofuran	Diethyl ether	Hexane	Cyclo hexane
10	0.29	0.1	0.1	0.06	0.05
20	0.34	0.12	0.11	0.14	0.12
30	0.48	0.18	0.12	0.2	0.18
40	0.52	0.21	0.14	0.28	0.23
50	0.55	0.23	0.15	0.36	0.33
60	0.57	0.25	0.18	0.43	0.35

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Table C-5.2 Amount of residue catalyst in methyl esters phase of reaction products of basic transesterification at ambient pressure and temperature of 35°C

Time (min)	Amount of residue catalyst in methyl esters phase (g)				
	No-cosolvent	Tetrahydrofuran	Diethyl ether	Hexane	Cyclo hexane
10	0.66	0.85	0.86	0.9	0.9
20	0.61	0.83	0.85	0.83	0.84
30	0.47	0.76	0.83	0.76	0.78
40	0.43	0.75	0.82	0.68	0.73
50	0.41	0.72	0.81	0.6	0.63
60	0.39	0.7	0.77	0.54	0.61

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Table C-5.3 Amount of residue catalyst in glycerol phase of reaction products of basic transesterification at ambient pressure and temperature of 65°C

Time (min)	Amount of residue catalyst in glycerol phase (g)				
	No-cosolvent	Tetrahydrofuran	Diethyl ether	Hexane	Cyclo hexane
10	0.44	0.14	0.12	0.12	0.1
20	0.54	0.2	0.17	0.2	0.18
30	0.65	0.25	0.19	0.3	0.29
40	0.69	0.32	0.25	0.41	0.42
50	0.71	0.35	0.3	0.49	0.52
60	0.73	0.36	0.33	0.58	0.56

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Table C-5.4 Amount of residue catalyst in methyl esters phase of reaction products of basic transesterification at ambient pressure and temperature of 65°C

Time (min)	Amount of residue catalyst in methyl esters phase (g)				
	No-cosolvent	Tetrahydrofuran	Diethyl ether	Hexane	Cyclo hexane
10	0.51	0.83	0.84	0.84	0.86
20	0.42	0.76	0.79	0.76	0.78
30	0.31	0.71	0.77	0.66	0.67
40	0.27	0.64	0.71	0.55	0.54
50	0.25	0.61	0.66	0.45	0.44
60	0.23	0.6	0.63	0.39	0.4

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C-6 Experimental data of basic catalyst transesterification reaction time using cosolvents

Table C-6.1 The effect of transesterification reaction time using basic catalyst and tetrahydrofuran as cosolvent reaction at ambient pressure and temperature of 65°C

Time (min)	Methyl esters (% wt)				
	Ex1	Ex2	Ex3	Average	S.D
0	0.00	0.00	0.00	0.00	0.00
2	68.12	69	68.56	68.56	0.35
4	63.34	63	63.89	73.41	0.36
6	76.12	77	76.89	76.71	0.11
8	81.98	82.12	81.87	81.99	0.12
10	85.3	85.2	84.4	84.96	0.4
20	89.56	89.13	88.35	89.01	0.6
30	91.12	91.2	91.3	91.2	0.09
40	94.9	94.1	94.67	94.22	0.5
50	94.5	94.1	94.5	94.36	0.23
60	94.5	94.23	94.98	94.57	0.37

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Table C-6.2 The effect of transesterification reaction time using cosolvents reaction at ambient pressure and temperature of 65°C

Time (min)	Methyl esters (%wt)				
	Diethyl ether	Hexane	Cyclo hexane	Butanol	T-butanol
0	0.00	0.00	0.00	0.00	0.00
2	63.56	54.12	52.12	72.45	70.12
4	67.41	66.34	63.34	77.76	75.34
6	71	70.45	69.44	81.45	78.67
8	73.99	73.56	72.33	85.56	83.45
10	77.96	77.23	75.32	87.44	86.67
20	82.01	81.34	80.22	93.55	91.67
30	85.2	85.45	83.28	95.56	94.45
40	90.22	88.12	86.34	98.64	97.43
50	91.36	90.34	88.33	98.34	97.54
60	91.55	90.56	88.65	98.88	97.67

Table C-6.3 The effect of transesterification reaction time using cosolvents reaction at ambient pressure and temperature of 35°C

Time (min)	Methyl esters (% wt)					
	Tetrahydrofuran	Diethyl ether	Hexane	Cyclo hexane	Butanol	T-butanol
0	0.00	0.00	0.00	0.00	0.00	0.00
2	61.34	57.34	48.56	43.43	67.45	65.55
4	66.43	62.45	61.23	58.24	72.5	70.32
6	73.12	68.67	66.22	63.43	76.34	73.75
8	75.34	71.32	68.45	65.34	80.44	78.56
10	78.56	74.67	72.32	68.76	82.87	81.45
20	83.78	79.54	77.2	75.67	88.98	86.12
30	87.57	83.44	80.51	78.34	90.7	89.54
40	89.97	85.87	82.33	80.65	93.56	93.23
50	91.75	87.32	84.45	81.56	93.59	93.22
60	91.5	87.3	84.67	81.6	93.6	93.3

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