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PRODUCTION OF METHYL ESTER FROM PALM STEARIN AND FATTY ACID BY TWO STEP METHOD

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งานวิจัยนี้ศึกษาการผลิตเมทิลเอสเทอร์ด้วยวิธีสองขั้นตอนโดยใช้ไขปาล์มสเตียรินและกรดไขมันเป็นสารตั้งต้นผสมกันในอัตราส่วนร้อยละ 10 15 และ 25 โดยน้ำหนักของกรดไขมันในไขปาล์มสเตียรินทำปฏิกิริยากับเมทานอลในถังปฏิกรณ์แบบกะโดยใช้กรดกำมะถันเป็นตัวเร่งปฏิกิริยาในขั้นตอนแรกและใช้โพแทสเซียมไดรอกไซด์เป็นตัวเร่งปฏิกิริยาในขั้นตอนที่สอง ทำการทดลองที่อุณหภูมิ 60 องศาเซลเซียสภายใต้ความดันบรรยากาศ และศึกษาถึงปัจจัยที่มีผลต่อการเกิดปฏิกิริยา คือ เวลาในการทำปฏิกิริยา อัตราส่วนระหว่างเมทานอลต่อน้ำมัน และปริมาณของตัวเร่งปฏิกิริยา

จากการทดลองพบว่าสภาวะที่เหมาะสมในกระบวนการเอสเทอริฟิเคชันโดยมีกรดเป็นตัวเร่งปฏิกิริยาในขั้นตอนแรก คือ การใช้เมทานอลที่มากเกินพอร้อยละ 300 โดยสัดส่วนโมล มีกรดกำมะถันเป็นตัวเร่งปฏิกิริยาร้อยละ 2 โดยน้ำหนัก ภายในเวลา 70 นาที ทำให้สามารถลดปริมาณของกรดไขมันอิสระให้เหลือน้อยกว่าร้อยละ 2 และตัวเร่งปฏิกิริยาที่เป็นกรดสามารถเร่งให้เกิดปฏิกิริยาได้ทั้งกระบวนการเอสเทอริฟิเคชันของกรดไขมันและกระบวนการทรานส์เอสเทอริฟิเคชันของไตรกลีเซอร์ไรด์ในเวลาเดียวกัน สำหรับขั้นตอนที่สองพบว่าการใช้อัตราส่วนโดยโมลของเมทานอลที่มากเกินพอร้อยละ 100 ปริมาณตัวเร่งปฏิกิริยาโพแทสเซียมไฮดรอกไซด์ร้อยละ 1 โดยน้ำหนัก ที่เวลา 60 นาทีจะทำให้ได้ปริมาณเมทิลเอสเทอร์ไม่ต่ำกว่าร้อยละ 85

ภาควิชา.............วิศวกรรมเคมี...........ลายมือชื่อนิสิต.........ณัฐพร คงสมุทร.........
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KEY WORD : METHYL ESTER / PALM FATTY ACID / PALM STEARIN / ESTERIFICATION / TRANSESTERIFICATION / TWO STEP

NATTAPORN KONGSAMUTR : PRODUCTION OF METHYL ESTER FROM PALM STEARIN AND FATTY ACID BY TWO STEP METHOD. THESIS ADVISOR : JIRDSAK TSCHEIKUNA, Ph.D., 81 pp.

The objective of this study is to investigate the production of methyl ester by two step method. Palm stearin and fatty acids were used as raw materials and were mixed at a ratio of 10%, 15% and 25% of free fatty acids. The experiments were carried out in a batch reactor using sulfuric acid as a catalyst in the first step and potassium hydroxide in the second step. The experiments were conducted at the temperature of 60°C and at atmosphere's pressure. Reaction time, methanol to oil ratio and amount of catalysts were varied in each experiment.

The suitable conditions on acid esterification process were 300% mole of excess methanol from its stoichiometric ratio in the presence of 2% wt H_2SO_4 as a catalyst and at the reaction time of 70 minutes. High free fatty acids level was reduced to less than 2% in the first step. Acid catalyst can simultaneously catalyze both esterification of free fatty acids and transesterification of triglyceride. The suitable conditions on transesterification process were 100% mole of excess methanol from its stoichiometric ratio in the presence of 1% wt KOH as a catalyst in the second step. Final methyl ester was higher than 85% concentration within 60 minutes.

Department:.....Chemical Engineering......Student's signature:...ณัฐพร กงสมุทร...
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CHAPTER I

INTRODUCTION

1.1 Motivation

Nowadays, methyl esters are of greater importance in organic chemistry because they are used in many applications i.e. they are intermediates in the synthesis of many products e.g. plastics, surfactants, solvents, lubricants and other oleo-chemicals. Moreover, methyl esters can be used as an alternative diesel fuel for diesel engines because they are renewable source from vegetable oils, can be produced locally, and are environmentally friendly. Also, they contain less of both sulfur and aromatic compounds, and have a higher cetane number than petroleum diesel. The common methods to produce methyl ester are esterification and transesterification.

Methyl ester from esterification is a reversible reaction wherein the palm fatty acids (PFA) are successively transformed into fatty acid methyl esters and water. Methyl esters are prepared from palm fatty acids with methanol in excess as compared to the stoichiometric proportion. The stoichiometric of this reaction requires one mole of alcohol per one mole of PFA to give one mole of fatty acid alkyl ester and one mole of water.

The most widely accepted method to produce methyl ester is transesterification. The transesterification is chemical reaction between triglyceride and methanol in the presence of catalyst or non catalyst to produce alkyl monoesters of fatty acids wherein the long branched chain of triglyceride molecules are transformed to monoesters and glycerol. The conventional method uses catalysts including acids (e.g. sulfuric acid or hydrochloric acid), alkaline (e.g. sodium hydroxide or potassium hydroxides), or enzymes such as lipase. Acid-catalyzed transesterification typically requires a long time to complete; while alkaline-catalyzed transesterification has a disadvantage in that soap might be produced when alkali reacts with the free fatty acids in the oil. Furthermore, in both cases, extensive washing is required to remove these catalysts from the methyl ester product which results in a large amount of waste water. Enzyme-catalyzed reactions are a more environment-friendly method; however, the high cost of enzymes makes this process unattractive on an industrial scale.

For the high free fatty acids in vegetable oil, the alkaline catalyst cannot be applied directly because of what it does to the competing saponification reaction of palm fatty acids with alkaline. For this reason, the acid-catalyzed process must be used, but it generally requires a long reaction time. Alternatively, a two-step method has been proposed in which acid-catalyzed esterification is initially carried out, followed by esterification with alcohol in an alkali catalyst to complete the reaction.

In this study, the production of fatty acid methyl esters can be achieved in two steps by using the mixture of triglyceride (palm stearin) and palm fatty acids (PFA) instead of using high free fatty acid vegetable oil. Palm stearin and palm fatty acids are by product of palm oil refinery; on the other hand, they are more attractive because of low cost raw materials, compared with purified palm oil.

1.2 Objectives

1. To investigate the effects of operating conditions for the two-step method of palm stearin and fatty acids on the concentration of methyl ester in a batch reactor.

1.3 Working Scope

1. Use palm stearin with 10%, 15% and 25% of palm fatty acids as raw materials
2. Use the temperature of reaction at 60 ºC
3. Determine the suitable reaction time between 0-120 minutes
4. Determine the effects of molar ratio of palm stearin and palm fatty acid with 100%, 200% and 300% mole of excess methanol from its stoichiometric ratio
5. Determine the effects of catalyst (1%, 2% for the first step and 0.5%, 1% for the second step) by a two-step method

1.4 Expected benefits

1. This investigation will provide suitable conditions for the production of fatty acid methyl ester by a two-step method of palm stearin and fatty acids in which the conditions of the reaction will be able to be used in the chemical industry.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Methyl ester

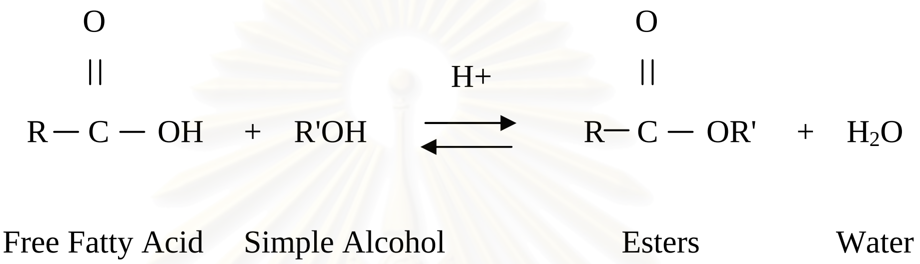
Methyl esters are aliphatic organic esters which are obtained by the chemical reaction between natural fats or oils and methanol in order to change their chemical structures to like those of diesel from petroleum. General properties of methyl esters are low volatility, high flash point, high viscosity and easy to decompose. The chemical structure of methyl esters is CH_3COOR and has R as $(CH_2)_xCH_3$ that depend on fatty acid groups; for example, Methyl palmitate which R represents Palmitic acid, Methyl stearate which R represents Stearic acid, and Methyl laurate which R represents Lauric acid as shown in Table 2.1. The most widely used methyl ester can be produced by esterification, transesterification and two steps method.

Table 2.1 Characteristics of Common fatty acid methyl esters

Fatty acid methyl esters	Molecular weight	Melting point (°C)
Methyl caprylate (methyl octanoate); 8:0	158.24	-
Methyl caprate (methyl decanoate); 10:0	186.30	-
Methyl laurate (methyl dodecanoate); 12:0	214.35	5
Methyl myristate (methyl tetradecannoate); 14:0	242.41	18.5
Methyl palmitate (methyl hexadecanoate); 16:0	270.46	30.5
Methyl stearate (methyl octadecanoate); 18:0	298.51	39.1
Methyl oleate (methyl 9Z-octadecenoate); 18:1	296.49	-20
Methyl linoleate (methyl 9Z,12Z octadecadienoate); 18:2	294.48	-35
Methyl linolenate (methyl 9Z,12Z,15Z octadecatrienoate); 18:3	292.46	-57

2.2 Esterification

The formation of ester occurs through a condensation reaction known as esterification. This requires two reactants: carboxylic acids (fatty acids) and alcohols. Esterification reactions are acid catalyzed and proceed slowly in the absence of strong acids such as sulfuric acid, phosphoric acid, organic sulfonic acids, and hydrochloric acid. The equation for an esterification reaction can be seen in Equation 2.1.



$$\mathrm{R-\overset{\overset{O}{||}}{C}-OH} + \mathrm{R'OH} \xrightleftharpoons{H+} \mathrm{R-\overset{\overset{O}{||}}{C}-OR'} + \mathrm{H_2O}$$

Equation 2.1 Esterification reaction of free fatty acids with alcohol

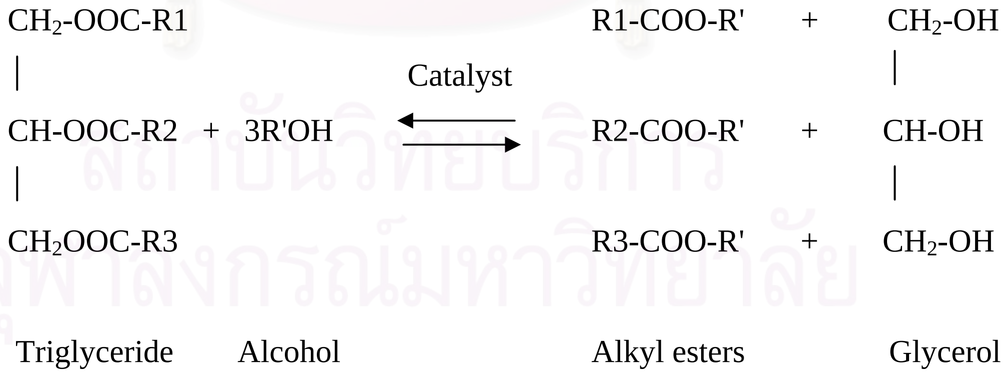
High free fatty acids (high FFA) feedstock will react with the catalyst and will form soaps if they are fed to base catalyzed system. The acceptable maximum amount of free fatty acids in a base catalyzed system is less than two percent, and preferable less than one percent. Some approaches that use high free fatty acid feedstock use this concept to “refine” the free fatty acids out of the feed for disposal or separate treatment in an acid esterification unit. The caustic is added to the feedstock and the resulting soaps are stripped out using a centrifuge. This is called caustic stripping. Some triglycerides are lost with the soaps during caustic stripping. The soap mixture can be acidulated to recover the fatty acids and lost oils in a separate reaction tank. The refined oils are dried and sent to the transesterification unit for further processing. Rather than waste, the free fatty acids are removed in this manner; they can be transformed into methyl ester by using an acid esterification process. As described earlier, acid catalyzed processes can be used for the direct esterification of free fatty acids in a high free fatty acid feedstock.

Direct acid esterification of a high free fatty acids feed requires water removal during the reaction, or the reaction will be quenched prematurely. Also, a high alcohol to free fatty acids ratio requires, usually between 20:1 and 40:1. Directly esterification may also require rather large amounts of the acid catalyst depending on the process used.

The esterification reaction of free fatty acids with methanol produces water as by product that must be removed, but the resulting mixture of esters and triglyceride, can be used directly in a conventional base catalyzed system. The water can be removed by vaporization, settling, or centrifugation as a methanol-water mixture. Counter-current continuous-flow systems will wash out the water with the exiting stream of acidic methanol.

2.3 Transesterification (Alcoholysis)

Transesterification (also called Alcoholysis) means taking a triglyceride molecule or complex fatty acids, neutralizing the free fatty acids, and removing the glycerin then creating alcohol esters. The general equation of this reaction is shown in Equation 2.2. R1, R2, and R3 of the oil molecules are long chain hydrocarbon constituting fatty acids which may be the same or different. A catalyst is usually used to improve the reaction rate and yield. Theoretically, the transesterification reaction is an equilibrium reaction. In this reaction, a larger amount of alcohol is generally used to shift the reaction equilibrium to the right side and produce more methyl esters products.



$$\begin{array}{lcccccc}
CH_2\text{-OOC-R1} & & & & \text{R1-COO-R'} & + & CH_2\text{-OH} \\
| & & & \text{Catalyst} & & & | \\
CH\text{-OOC-R2} & + & 3R'OH & \rightleftarrows & \text{R2-COO-R'} & + & CH\text{-OH} \\
| & & & & & & | \\
CH_2OOC\text{-R3} & & & & \text{R3-COO-R'} & + & CH_2\text{-OH} \\
\text{Triglyceride} & & \text{Alcohol} & & \text{Alkyl esters} & & \text{Glycerol}
\end{array}$$

Equation 2.2 General equation of transesterification reaction (Fukuda, 2001)

Transesterification reaction shown in Equation 2.2 is indeed the overall reaction for three stepwise reactions with intermediate formation of diglyceride and monoglyceride (Equation 2.3.). In the first reaction, triglyceride (TG) reacts with alcohol to produce diglyceride (DG), then in the second reaction, diglyceride (MG) reacts with alcohol to form monoglyceride (MG). Finally, in the third reaction, monoglyceride (MG) reacts with alcohol to give glycerol.

$$\text{Triglyceride} + \text{R'OH} \rightleftharpoons \text{Diglyceride} + \text{R'COOR1}$$

$$\text{Diglyceride} + \text{R'OH} \rightleftharpoons \text{Monoglyceride} + \text{R'COOR2}$$

$$\text{Monoglyceride} + \text{R'OH} \rightleftharpoons \text{Glycerol} + \text{R'COOR3}$$

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

Alcohols used in the transesterification can be primary or secondary monohydric aliphatic alcohol having 1- 8 carbon atoms. Among these alcohols, methanol and ethanol are used most frequently. Ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products, and is renewable and biologically less objectionable in the reaction in the environment. However, methanol is used in practice because of its physical and chemical advantages of having shortest chain, so it easy to react. In general, transesterification reaction can be carried out with a catalyst using alkalis, acids, or enzymes. Non-catalytic transesterification in supercritical alcohols is also carried out.

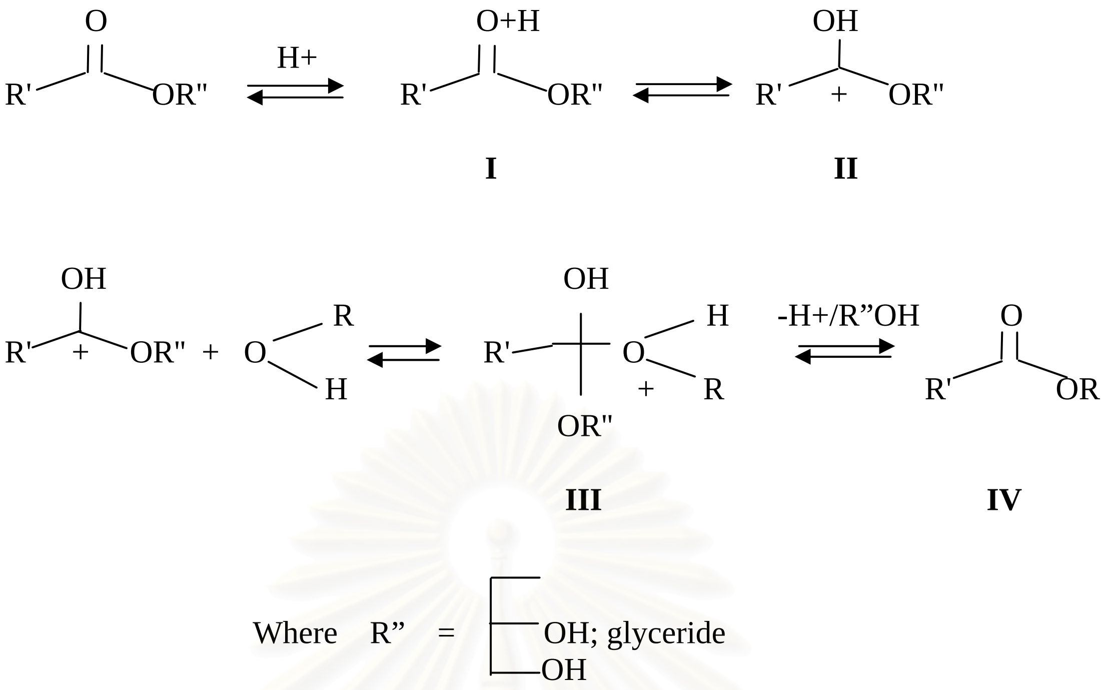
2.3.1. Acid catalyst Process

Most of the methyl ester is currently made from edible oils by using methanol and alkaline catalyst. However, if there are large amounts free fatty acids in the starting oil such as waste oils and fats, this large amount of free fatty acids cannot be effectively converted to methyl ester using alkaline catalyst. Consequently, acid catalyst can be used for transesterification. Thus, acid catalyzed process can reduce methyl ester production cost as low cost feedstock (waste frying oil) with high free fatty acid can be used as a raw material.

Although this process can be used with vegetable oils and fats that have more free fatty acids, it requires long reaction time more than several hours, and high temperature that typically above 100 °C to complete. Methanolysis of soybean oil in the presence of 1 mole % of H_2SO_4 with an alcohol/oil molar ratio of 30:1 at 65 ° C takes 50 h to reach complete conversion of the vegetable oil (>99 %), while the butanolysis (at 117°C) and ethanolysis (at 78°C) that use the same quantities of catalyst and alcohol take 3 and 18 h, respectively (Freedman et al., 1986). The acid catalyst has to be removed from product. In addition, the presence of water in the oil has negative effect on the yield methyl ester. With the acid catalyzed process, water has more negative effect on methyl esters formation than the alkali catalyzed process. Because the presence of polar compounds during acid catalyzed transesterification significantly reduces the reaction rates. Considering the strong affinity acid has for water, it is likely that the acid will interact more strongly with water molecules than alcohol molecules. Thus, if water is present in the reactant or during the reaction, the acid catalyst will bind to the water, and lead to a reversible type of catalyst deactivation.

The alcohol vegetable oil molar ratio is one of the main factors that influence transesterification. An excessive amount of alcohol favors the formation of the products. On the other hand, it makes the recovery of the glycerol difficult, so that ideal alcohol/oil ratio has to be established empirically, considering each individual process.

The mechanism of the acid catalyzed transesterification of vegetable oils is shown in Figure 2.1 for a monoglyceride. However, it can be extended to diglyceride and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation II, which after a nucleophilic attack of the alcohol produces the tetrahedral intermediate III. Elimination of glycerol forms the new ester IV, and regenerates the catalyst H+.



R’ = Carbon chain of fatty acid

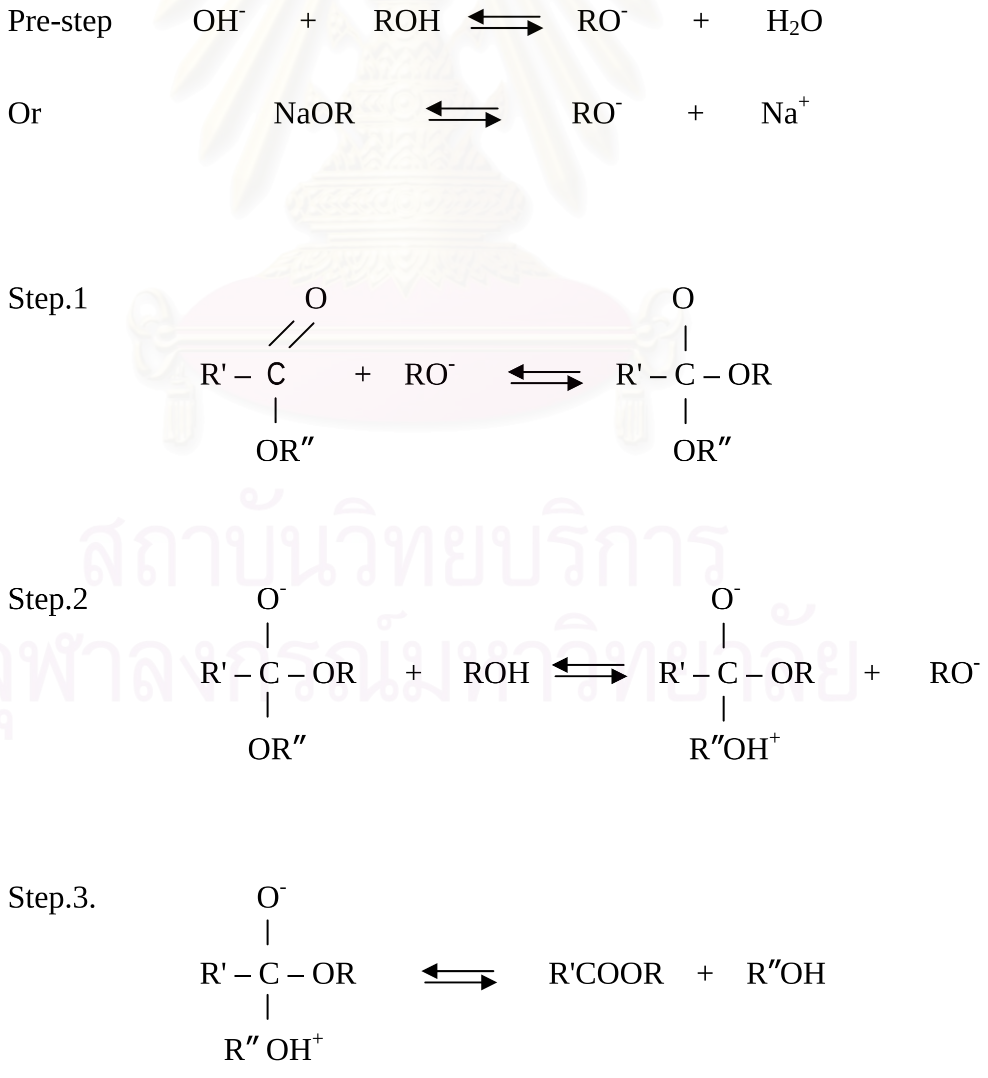
R = Alkyl group of alcohol

Figure 2.1 Mechanism of acid-catalyzed transesterification (Meher, 2006)

2.3.2 Alkaline catalyst process

All commercial methyl ester production in today employs an alkaline-catalyzed transesterification process. The alkalines that are generally used include NaOH, KOH, carbonates and corresponding sodium, and potassium alkoxides such as sodium methoxide, ethoxide, propoxide, and butoxide. Sodium hydroxide is the most common alkaline catalyst that is used, due to economical reasons and availability. (Alkaline catalyst is used, due to economical reasons and availability). Alkaline catalyst reactions are used more often commercially than acid catalyst, as the reaction is faster. This process is accomplished by mixing methanol (alcohol) with potassium hydroxide or sodium hydroxide to make potassium methoxide and sodium methoxide. Then the sodium methoxide is added to vegetable oil in a reactor at molar ratio of oil and alcohol 6:1. The mixture was stirred and heat at 60-63°C. After complete reaction mixture is allowed to cool to room temperature, and the ester and glycerol in were separated. Glycerol is left on the bottom and methyl esters, or biodiesel, is left on top. The ratio of 6:1 was found to be the best condition because if methanol/oil molar ratio less than 6:1, the reaction resulted in incomplete reaction, and if that above 6:1 methanol/oil molar ratio, the separation of glycerol was difficult, since the excess methanol hindered the decantation by gravity so the apparent yield of esters decreased because part of the glycerol remained in the methyl ester phase (Freedman et al., 1984).

The mechanisms of alkaline catalyzed transesterification are depicted in Figure 2.2. The first step is an attraction on the carbonyl carbon atom of the triglyceride molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid esters and a diglyceride (Fangrui Ma et al., 1999).



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

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

Step.1 $$R'-\overset{O}{\overset{\|}{\underset{OR''}{\underset{|}{C}}}} + RO^- \rightleftharpoons R'-\overset{O}{\overset{|}{\underset{OR''}{\underset{|}{C}}}}-OR$$

Step.2 $$R'-\overset{O^-}{\overset{|}{\underset{OR''}{\underset{|}{C}}}}-OR + ROH \rightleftharpoons R'-\overset{O^-}{\overset{|}{\underset{R''OH^+}{\underset{|}{C}}}}-OR + RO^-$$

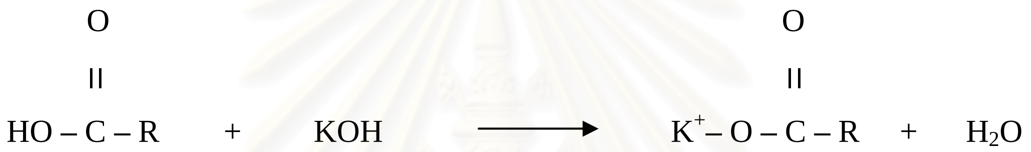
Step.3. $$R'-\overset{O^-}{\overset{|}{\underset{R''OH^+}{\underset{|}{C}}}}-OR \rightleftharpoons R'COOR + R''OH$$

Where R'' = CH_2 -
|
CH - OCOR'
|
CH_2- OCOR'

R' = Carbon chain of fatty acid

R = Alkyl group of alcohol

Figure 2.2 Mechanism of alkaline catalyzed transesterification (Meher, 2004)



$$HO-\overset{\overset{\displaystyle O}{\|}}{C}-R \quad + \quad KOH \longrightarrow K^{+}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R \quad + \quad H_2O$$

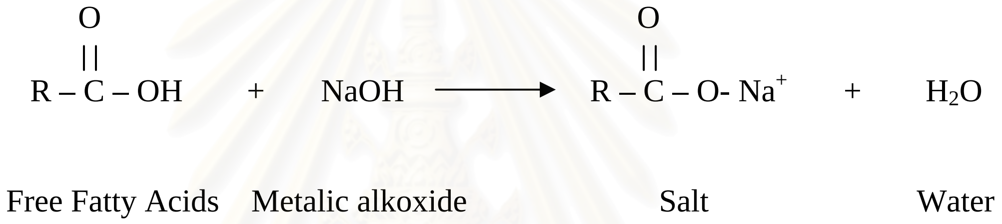
Fatty Acids Potassium Hydroxide Potassium soap Water

Equation 2.4 Reaction of fatty acids reacts with base catalyst.

When the triglyceride contains high free fatty acid (about 5%), alkali-catalyst is ineffective because reaction want more alkali-catalyst for neutralization and the excess catalyze can react with free fatty acid to form soap (Equation 2.4). The soap increases the viscosity, formation of gel, or emulsion and interferes with separation of ester and glycerol (Freedman et al., 1984). Although the alkali catalyzed process has short reaction time and high conversion, the process has several problems such as difficult recovery of glycerol due to the soap production from free fatty acid and the catalyst. In addition, the alkaline catalyst has to be removed from the product by washing with water, thus alkaline waste water in generated. Thus, for oil with high content of free fatty acids, an acid catalyst, such as sulfuric acid, can be used to esterification the free fatty acids to methyl esters.

2.3.3 Saponification

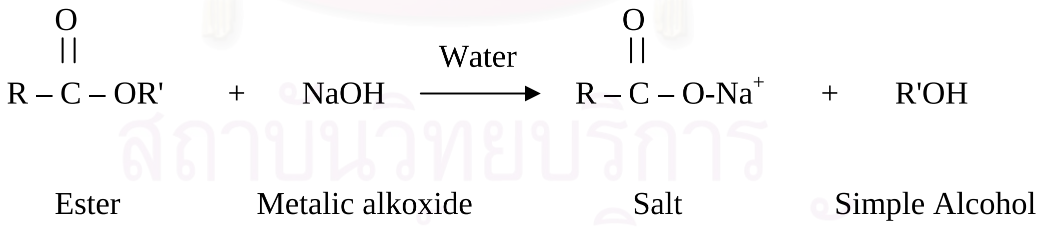
The production of soap sometime is called alkaline hydrolysis, converts triacyglycerols to glycerol and a mixture of salts of long-chain carboxylic acids. As can be seen from Equation 2.5 and Equation 2.6, the reaction can be carried out with an ester (i.e. triglycerides) or with carboxylic acids (i.e. free fatty acids). 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 complete and then adding sodium chloride to precipitate the soap (Solomon, 1996).



$$R-\overset{\overset{O}{||}}{C}-OH \quad + \quad NaOH \longrightarrow R-\overset{\overset{O}{||}}{C}-O^-Na^+ \quad + \quad H_2O$$

Equation 2.5 Saponification from free fatty acids

Or



$$R-\overset{\overset{O}{||}}{C}-OR' \quad + \quad NaOH \xrightarrow{Water} R-\overset{\overset{O}{||}}{C}-O\text{-}Na^+ \quad + \quad R'OH$$

Equation 2.6 Saponification from esters

2.4 Two-step Method

Because of soap occurred in conventional method, two-step method is used to convert high free fatty acid vegetable oils to methyl ester; for example, crude palm oil, rubber seed oil, rice bran oil, tobacco oil, and frying oil. Two steps are combining esterification and transesterification by pretreatment of high free fatty acids vegetable oil with methanol in a present of acid catalyst in the first step. This pretreatment can reduce FFA in triglyceride and prevent production of soap. Second step is obtained by alkaline catalyst esterification of product from the first step. Product of methyl esters by two steps has high conversion as compare with the conventional method.

2.5 Factors affecting methyl ester production

The processes of transesterification and esterification are affected by various factors, depending upon the reaction conditions used. The effects of these factors are described below.

2.5.1 Ratio of alcohol to oil or fatty acid

For transesterification, it is generally known that one of the most important variables affecting the yield of ester is molar ratio of alcohol to triglyceride. The stiochiometric ratio for transesterification requires three moles of alcohol and one mole triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. For maximum conversion, a molar ratio of 6:1 should be used. However, the high molar ratio of alcohol to vegetable oil interferes with separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it drives the equilibrium to back to the left, lowering the yield of esters.

For esterification, the molar ratio of alcohol to fatty acids is also importance. In this case, however, the stiochiometric ratio requires 1 to 1 mole ratio of the two reactants. Furthermore, no glycerol is produced. As a result, it is expected lower alcohol to fatty acids molar ratio would be needed compared with triglyceride transesterification.

2.5.2 Reaction temperature

The rate of reaction is strongly influenced by the reaction temperature. However, given enough time, the reaction will proceed to near completion even at room temperature. Generally, the catalytic reactions are conducted close to the boiling point of alcohol (60 °C to 70 °C), under atmospheric pressure.

2.5.3 Reaction time

The conversion increases with reaction time. For example, Freedman et al. (1984) studied the transesterification of peanut, cotton-seed, sunflower and soybean oil under the condition of methanol to oil molar ratio of 6:1, 0.5 % sodium methoxide catalyst, and at 60°C. An approximate yield of 80% was observed after 1 minute for soybean and sunflower oils. After 1 hour, the conversion was almost the same (93-98%) for all four oils.

2.5.4 Use of organic co-solvent

An improved process was investigated by Krisnangkura and Simamaharnnop (1992) for methanolysis and ethanolysis of fatty acid glycerides such as those found in naturally occurring fats and oils derived from plant and animals. The processes comprise solubilizing oil, or fat in methanol or ethanol by addition of toluene as co-solvent in order to form a one phase reaction mixture in presence of an acid catalyst. The processes were found to proceed quickly, usually in less than 20 min, at ambient temperature, atmospheric pressure, and without agitation. The co-solvent increased the rate of reaction by making the oil soluble in methanol, thus increasing contact of the reactant. The lower alkyl fatty acid monoesters produced by the process, can be used as biofuels and are suitable as diesel replacement or additives.

2.5.5 Purity of reactant

Impurities present in the oil also affect conversion levels. Under the same condition, 67 to 84 % conversion into ester using crude vegetable oils can be obtained, compared with 94 to 97 % when using refined oils. The free fatty acids in the original oils interfere with catalyst, however, under conditions of high temperature and pressure this problem can be overcome (Freedman et al., 1984).

2.5.6 Catalyst type and concentration

Catalysts that are used for transesterification of triglyceride are classified as alkaline, acid, among which alkaline are the most effective transesterification catalyst compared to acid catalyst. Sodium alkoxides are among the most efficient catalyst used, although KOH and NaOH can also be used. The alkaline catalyst concentration in range of 0.5 to 1 % by weight yields 94 to 99%. The acid could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Acid catalyst transesterification was studied with waste vegetable oil. The reaction was conduct at four different catalyst concentration, 0.5, 1.0, 1.5, and 2.25M HCl in presence of 100 % excess alcohol and the results were compared with 2.25 M H_2SO_4. H_2SO_4 was found to have superior catalyst activity in the range of 1.5-2.25 M concentration (Mohamad, 2002).

2.5.7 Presence of water

In methyl esters production, it is well known that the vegetable oils used as a raw material for the transesterification should be water free since water has a negative effect on the reaction. As it consumes the catalyst and reduces catalyst efficiency. It is generally recommended that for typical transesterification of vegetable oil, the water content should be kept below 0.06 % (Ma et al., 1998).

2.6 Production of methyl ester from palm stearin and fatty acid

2.6.1 Palm stearin

Palm stearin is the minor product about 30-35% from separated from process crude palm oil. Palm stearin is the more saturated and more solid fraction of palm oil. Palm stearin is the solid fraction obtained by fractionation of palm oil after crystallization at a controlled temperature. It is not used directly for edible purposes due to its high melting point ranging from 44 to 56°C (Pantzaris, 2000). At room temperature (25°C), palm stearin behaves as a solid and lacks the spreadability needed in products like margarine and shortening. The components of palm stearin are palmitic acids, oleic acids, linoleic acids, stearic acids, and others. The cost of palm stearin is about 6-11 bahts per kilogram and high production is 124,200 tons/year (Suriya Ayachanun, 2006). Methyl ester from palm stearin process is established mainly to add value of byproducts from the refinery. Obtained methyl ester has high cetane, pour point and clound point as compare with the product from palm oleain. The property of palm stearin can be study in Chapter IV.

2.6.2 Fatty acid

Palm fatty acids are separation of liquid mixture into their several components are one of the major process of the chemical industries. Fatty acid in palm oil contains saturated and unsaturated fatty acids which palmitic acids, stearic acids oleic acids and linoleic acids are the main component acids.

Palmitic acid

The scientific name of palmitic acid is “hexadecanoic acid”. It has molecular formulae of $C_{16}H_{32}O_2$ (see Figure 2.3). Other Names include 1-Pentadecanecarboxylic acid; n-hexadecanoic acid; n-hexadecoic acid, cetylic acid. Palmitic acid is a saturated acid, since there are no double bonds between neighboring carbon atoms. The palmitic acid has a molecular weight of 256.5, melting point of palmitic acids is between 61 - 64 °C, the boiling point is at 352 ºC, and the density is approximately 0.84 g cm-3 at room temperature.

Figure 2.3 Structure of palmitic acid (Richardson J.F., 1983)

Stearic Acid

The scientific name of stearic acid is “octadecanoic acid”, having a molecular formulae of $C_{18}H_{36}O_2$ (see Figure 2.4). Other name is 1-heptadeca necarboxylic acid. Stearic acid has a molecular weight of 284.5, melting point of 67-69 °C, boiling point of 355.2 °C, and density of 0.8390 g cm-3.

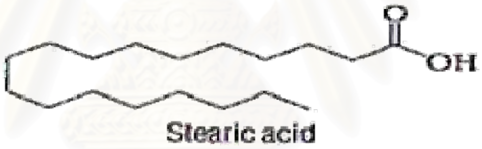


Figure 2.4 Structure of Stearic acid (Richardson J.F., 1983)

Oleic Acid

The scientific name of otearic acid is “9-Octadecenoic acid”. Oleic acid is a fatty acid found in animal and vegetable oils having a molecular formulae of $C_{18}H_{34}O_2$ (see Figure 2.5)., molecular weight of 282.47, and melting point of 13 °C, and boiling point of 360 °C and density of 0.8935 g cm-3. It is called a mono-unsaturated fatty acid because of the single double bond between the carbons.

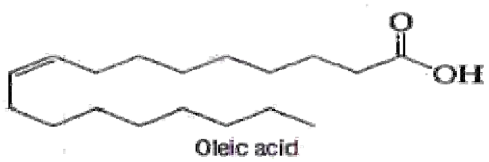


Figure 2.5 Structure of Oleic acid (Richardson J.F., 1983)

Linoleic Acid

The scientific name of linoleic acid is “9, 12-Octadecadienoic acid”. Linoleic acid has a molecular formulae of $C_{17}H_{32}O_2$, molecular weight of 280.46, boiling point 230 °C, melting point -5°C, and density of 0.9025 g cm-3 at room temperature. Other Names include 9-cis, 12-cis-linoleic acid; 9Z, 12Z-linoleic acid.

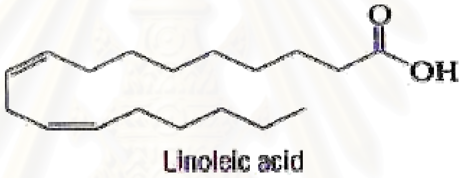


Figure 2.6 Structure of linoleic acid (Richardson J.F.,1983)

Fatty acids, any of the organic carboxylic acids present in fats and oils as esters of glycerol. Molecular weights of fatty acids vary over a wide range. The carbon skeleton of any fatty acid is unbranched. Some fatty acids are saturated, i.e., each carbon atom is connected to its carbon atom neighbors by single bonds; and some fatty acids are unsaturated, i.e., they contain at least one carbon-carbon double bond (see chemical bond).

2.8 Literature reviews

A number of studies on preparation of methyl ester from vegetable oils have been reported using a variety of oils, alcohols, different catalyst, and reaction conditions. For esterification process, Srirala et al., (2004) studied the esterification of palmitic acid with methanol on zirconia supported tungsten oxide solid catalysts by both impregnation and co-precipitation methods. The results of variables affect found that 5 wt% WO_3/ZrO_2 of catalyst in 1 hour can be completed ester to 95% conversion**.** This high activity showed that increase reaction time and catalyst concentration, the esterification activity is increased. Waeasae et al., (2005) studied ester from coconut oil or palm oil was prepared by reactions between fatty acid and alcohol using sulfuric acid as a catalyst. The experiment started from refluxing the oil with 7 M sodium hydroxide at the ratio of 5:6 v/v and the temperature of 75°C for 9 hours to form soap. Fatty acid was then prepared by adding 4 M hydrochloric acid to soap. It was further reacted with methanol, ethanol or isopropanol in the present of sulfuric acid for 8 hours to obtain esters with the percentage yield of more than 80% t-Butyl ester, however, was prepared by a different route. T-Butanol was reacted with fatty acid chloride to give t-butyl ester. Prepared T-Butyl ester has the characteristics of having low ash and low viscosity. It has a boiling point in the range of 160-210°C which is lower than the other esters, and a specific gravity of 0.8593 Kg/L which is comparable to that of methyl ester. It is expected that t-butyl ester prepared from palm oil is able to use for better diesel oil.

An alternative esterification process is the acid-base catalyzed transesterification process. For acid catalyzed process, Canaki et al., (1999) studied how the reagent molar ratio affected reaction rates and product yield in the transmethylation of soybean oil by sulfuric acid. Five different molar ratios, from 3.3:1 to 30:1, were studied. Their results indicated that ester formation increased with increasing molar ratio, reaching its highest value, 98.4%, at the highest molar ratio used, 30:1 used. Beside oil and methanol molar ratio, the effect of temperature was determined in the study by Freedman et al. (1986). However, the benefits from higher alcohol-to–triglycerides molar ratios became limited with increasing ratio, ester formation increase sharply from 77% at 3.3:1 to 87.8 % at 6:1 and ultimately reaching a plateau value of 94.8% at 30:1. Mohamad et al., (2003) studied transesterification of waste palm oil using acid catalyst was under various conditions such as different H_2SO_4 and HCl concentrations. In this study, ethanol at different excess levels was also used. They found that higher catalyst concentrations produced biodiesel with lower specific gravity, in much shorter reaction time than lower concentrations. The H_2SO_4 performed better than HCl, as it results in diesel with lower specific gravity in about 3 hours. Moreover, a 100 % excess alcohol resulted in significant reductions in reaction time and lower specific gravity. 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 ester 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 ester at 70 ºC with oil:methanol:acid molar ratios of 1:245:3.8 and at 80 ºC with oil:methanol:acid molar ratios in range 1:74:1.9-1:245:3.8. As a result of the large excess of methanol, the reaction completed (99 ± 1% conversion) in 4 hours. Although acid catalyzed process has advantages such as reduced the purification costs, the reaction is much slower.

Alternatively, alkaline catalyzed process was invaestigated**.** Freedman et al., (1984) studied the variables that affect yield and purity of alcohol ester product from crude and refined vegetable oils. These are such as molar ratio of methanol and oil, type of catalyst, and temperature. Their results showed that alkaline catalyzed reaction of fully refine oil at 60 ºC or higher, with the molar ratio of 6:1 could be complete and the conversion to esters resulted in 1 hr. At 32ºC, vegetable oil 99% transesterification was obtained in 4 hours with alkaline catalyst. The reason for low reaction rate at low temperature was that the miscibility of methanol and oil were low. Antolin et al., (2002) studied the transformation process of sunflower oil in order to obtain methyl ester by means of transesterification. The following variable affects were studied:catalyst amount, methanol amount, reaction temperature, and washing. The samples were analysed using chromatographic techniques to determine mono, di and triglycerides, methanol and free glyceraol contents. The experiments were carried out with 0.28 w/w of potassium hydroxide related to the quantity of oil that had to be tranesterified. Methanol in excess is necessary; three times of the stoichiometric quantity were used at 70ºC. A yield superior to 96% was reached. The results have been enabled us to confirm that sunflower oil may be used as raw material to obtain biodiesel. Laoprasert (2002) studied the methyl ester synthesis from used cooking oils by transesterification. The investigated variables were temperature, catalyst type, catalyst concentration, methanol concentration, and reaction time. For NaOH as catalyst, the optimum conditions were 25%MeOH, 1.0%NaOH, 30 °C and reaction time of 30 min and the maximum yield was 94.95%. For KOH as catalyst, the optimum conditions were 25%MeOH, 1.0%KOH, 30 °C for reaction time of 30 min and the maximum yield was 91.87%. The %yield of the methyl ester by using NaOH was higher than KOH for all experiments. Tomasevic et al., (2003) studied the transesterification of used sunflower oil (which has an acid value of ~ 4) with methanol, using alkaline catalysts such as KOH and NaOH and different molar ratios of methanol to oil (4.5:1, 6:1, 9:1). The effects of various parameters such as the variation in oil quality, the molar ratio of methanol to oil, the type and the amount of alkaline catalyst, the time and the temperature of reaction on the yield, and the properties of esters were studied. The optimum conditions developed for the production of good-quality biodiesel from used sunflower oil were as follows: molar ratio of methanol to oil, 6:1, with 1% of KOH; reaction temperature, 25ºC; and reaction time, 30 min. It was observed that, under the optimal conditions of methanolysis, the quality of the used frying oil did not have an essential effect on the quanlity of methyl esters production. An increase in the quantity of catalyst and molar ratio of methanol to oil did not change the yield or quality of the esters. Of the two catalysts NaOH and KOH, 1%KOH has given the best yields and viscosities of esters. Udomsab (2005) studied the transesterification of crude palm oil and palm stearin with ethanol was carried out in a batch reactor by using sodium hydroxide as a catalyst. The major variables were investigated: molar ratio of ethanol/oil, amount of catalyst, reaction temperature and reaction time. The optimal condition to transesterify crude palm oil and palm stearin were similar as follows: 12:1 molar ratio of ethanol/oil, 75°C of reaction temperature, 1% weight of sodium hydroxide and 60 minute reaction time. At this condition, the ethyl ester conversion of crude palm oil and palm stearin were 87.79% and 94.42% by weight, respectively. The characteristics of ethyl esters from both crude palm oil and palm stearin were similar to low speed diesel. Leung et al., (2006) studied transesterification by using sodium hydroxide, potassium hydroxide and sodium methoxide as the catalysts, were evaluated using edible Canola oil and used frying oil. With variables that influence the transesterification of triglycerides, such as catalyst concentration, molar ratio of methanol to raw oil, reaction time, reaction temperature, and free fatty acids content of raw oil in the reaction system, were investigated and optimized. From this research the maximum ester content and yield is 93.5% for canola oil and 88% for used frying oil.

In conventional method when used raw materials contain high free fatty acids, one step reaction in alkaline catalyst cannot be used. Ramadhas et al., (2005) proposed a two–step transesterification process developed to convert the high free fatty acid (FFA) oil to its mono-ester in the first step via acid catalyzed esterification to reduce FFA content of the oil to less than 2%. Then, in the second step, alkaline catalyzed transesterification process converts the product of the first step to its mono-esters and glycerol. The major factors affecting the conversion efficiency of the process consist of many factors such as oil to methanol molar ratio, the amount of catalyst, reaction temperature, and reaction duration. Siti et al., (2005) found that most triglyceride in rice bran oil stored at the room temperature was hydrolyzed and fatty acid content was raised up to 76% in six months. A two-step acid-catalyzed methanolysis process was employed for the efficient conversion of rice bran oil into fatty acid methyl ester. The first step was carried out at 60ºC. Depending on the initaial FFA, 55-90% FAME content in the reaction product was obtained. More than 98% FFA and less than 35% of TG were reacted in 2 hours. The organic phase of the first step product was used as the substrate for a second acid-catalyzed methanolysis at 100ºC. By this two-step reaction, more than 98% FAME in the product can be obtained in less than 8 hours. Shashikant et al., (2005) has been developed a technique to produce biodiesel from mahua oil (Madhuca indica) having high free fatty acids (19% FFA). The high FFA level of mahua oil was reduced to less than 1% by a two-step pretreatment process. Each step was carried out with 0.30–0.35 v/v methanol-to-oil ratio in the presence of 1% v/v H_2SO_4 as an acid catalyst in 1-hour reaction at 60°C. After the reaction, the mixture was allowed to settle for an hour and methanol–water mixture that separated at the top was removed. The second step product at the bottom was transesterified using 0.25 v/v methanol and 0.7% w/v KOH as alkaline catalyst to produce biodiesel. Following this process, a yield of 98% biodiesel was obtained from mahua oil. The fuel properties of mahua biodiesel were found to be comparable to those of diesel and conforming to both the American and European standards. Veljković et al., (2006) investigated the production of fatty acid methyl esters (FAME) from crude tobacco seed oil (TSO) having high free fatty acids (FFA). Due to its high FFA, the TSO was processed in two steps: the acid-catalyzed esterification followed by the base-catalyzed methanolysis. The first step reduced the FFA level to less than 2% in 25 min for the molar ratio of 18:1. The second step converted the product of the first step into FAME and glycerol. The maximum yield of FAME was about 91% in about 30 min. The obtained tobacco biodiesel had the fuel properties within the limits prescribed by the latest American and European standards, except a somewhat higher acid value than that prescribed by the latter standard (<0.5). Thus, tobacco seeds, as agricultural wastes, might be a valuable renewable raw material for the biodiesel production. Young et al., (2006) studied a two step catalyzed process to prepare biodiesel from waste cooking oil whose acid value was 75.93 ± 0.036 mgKOH/g. The free fatty acids of WCO were esterified with methanol calalyzed by ferric sulfate in the first step. The results showed that ferric sulfate had high activity to catalyze the esterification in 4 hours, and transesterification of the remained triglyceride was perform at 65ºC in a reaction system containing 1 wt% of potassium hydroxide. The final product was performed 97.02% of biodiesel. This new process has many advantages, compared with the old processes, such as no acidic waste water, high efficiency, low equipment cost, and easy recovery of the catalyst. Hanny et al., (2007) has been developed the technique to produce biodiesel from crude *Jatropha curcas* seed oil (CJCO) having high free fatty acids (15%FFA). The high FFA level of JCJO was reduced to less than 1% by a two-step pretreatment process. The first step was carried out with 0.60 w/w methanol to oil ratio in the presence of 1% w/w H_2SO_4 as an acid catalyst in 1 hour reaction at 50 °C. After the reaction, the mixture was allowed to settle for 2 hours and the methanol–water mixture separated at the top layer was removed. The second step was transesterified using 0.24 w/w methanol to oil and 1.4% w/w NaOH to oil as alkaline catalyst to produce biodiesel at 65 °C. The final yield for methyl esters of fatty acids was achieved 90% yield.

CHAPTER III

EXPERIMENTAL AND ANALYTICAL METHODS

3.1 Materials

3.1.1 Palm Fatty Acids and Palm Stearin

Palm fatty acids and palm stearin were used in this study. Both of them were derived from a process of palm oil refinery in Thailand.

3.1.2 Chemicals

All chemical used in the experiments are shown in Table 3.1. They were used without purification.

Table 3.1 Chemicals used in the research

Name	Source	Purity
Methanol	Fisher Scientific	95% (industrial grade)
Potassium hydroxide	Ajax Chemicals	98% (analytical reagent grade)
Sulfuric acid	J.T. Baker	98% (analytical reagent grade)
Hydrochloric	J.T. Baker	36.5-38%
Toluene	Ajax Chemicals	99.8% (analytical reagent grade)
Ethanol	Fisher Scientific	95% (industrial grade)
Iso-propanol	Fisher Scientific	99.8% (analytical reagent grade)
N-heptane	CARLO ERBA	99.7 (GLC grade)
Myristic acid	Sigma-Aldrich	95%
Palmitic acid	Sigma aldrich	95%
Oleic acid	Sigma-Aldrich	90%
Stearic acid	Sigma-Aldrich	95%
Methyl decanoate	Sigma aldrich	99%
Methyl palmitate	Acros	95%
Methyl stearate	Wako chemicals	99.5%
Methyl linoleate	Wako Chemicals	90%

3.2 Experimental

3.2.1 Analysis of Palm stearin and Palm fatty acids

The palm stearin and palm fatty acids were analyzed based on the density at 60 °C

3.3.1.1 Acid Value (AOCS Cd – 3d – 63)
3.3.1.2 Saponification Value (AOCS Cd – 3b – 76)

3.2.2 Investigation the effect on acid esterification

A batch type reactor was used for the two step method of methyl esters. The mixture of palm stearin and palm fatty acids (10%, 15% and 25% FFA) reacted with methanol by acid esterification. The schematic diagram of the system employed is shown in Figure 3.1. Palm stearin and palm fatty acids were first melted by heating at 50˚C. The calculated weight of palm stearin, palm fatty acids and methanol at the specified molar ratio were charged into the flask (250ml) connected with a condenser as shown in the Figure 3.2. For the reaction, 50 g of palm stearin and free fatty acids in calculated amount of methanol at the molar ratio were charged into the reactor. The reaction mixture was then heated to 60 ˚C. Sulfuric acid was added to the reaction mixture of palm stearin, fatty acids and methanol. The reaction was allowed to take place for a specified reaction time. Note that the addition of the acid caused the temperature to rise to 67 ˚C. After the reaction, the product was allowed to cool down and separated into two phases. The upper phase was some of methyl esters, remaining palm stearin and fatty acid and the bottom phase were water, glycerol and methanol. Bottom phase was first removed from the reaction product using a separation funnel, and the remaining methanol was then removed by evaporation. The product was then neutralized by washing repeatedly with warm water in a separation funnel and the remaining water was then removed by vacuum evaporator.

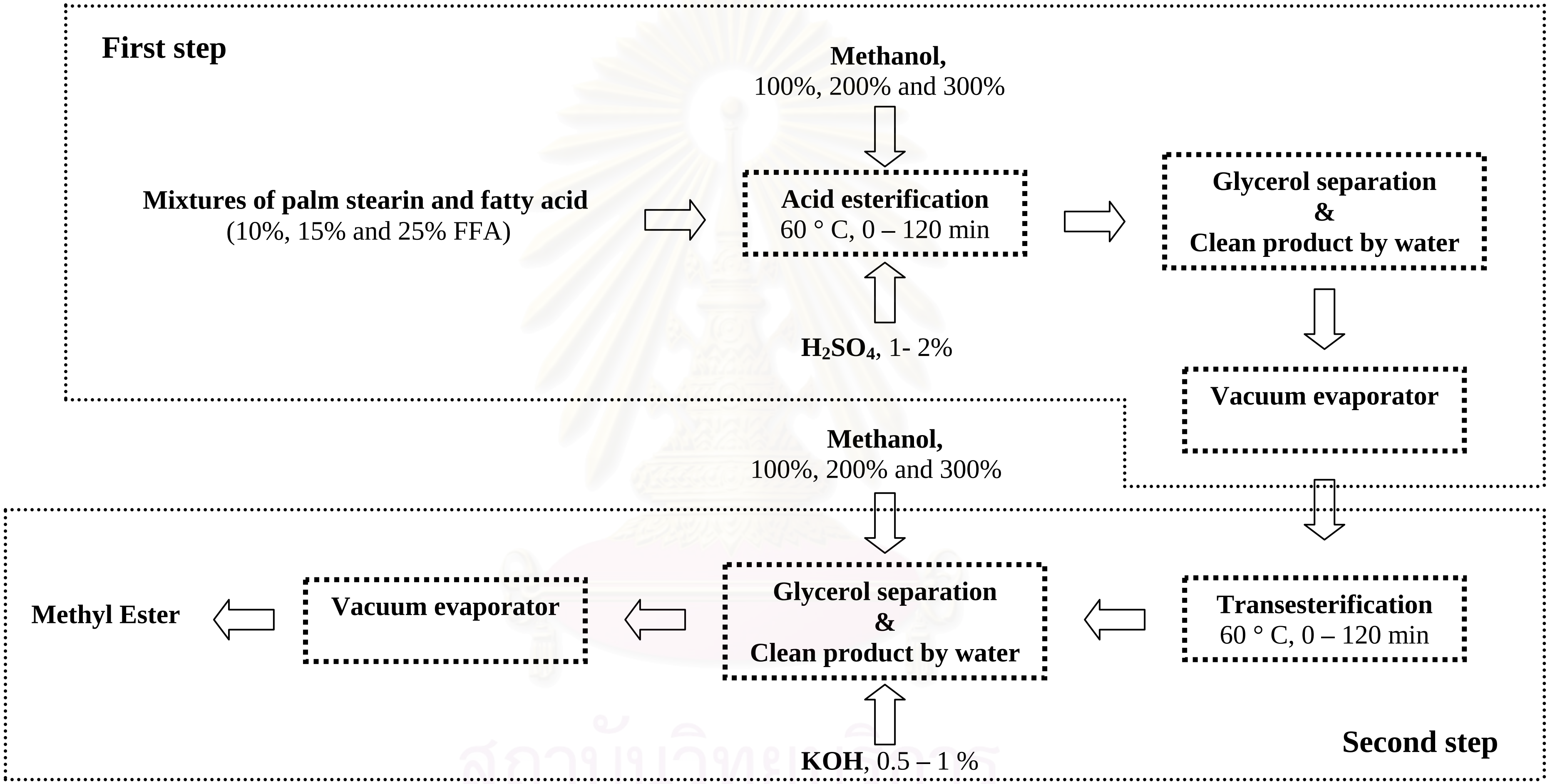


Figure 3.1 Schematic diagram of two-step process

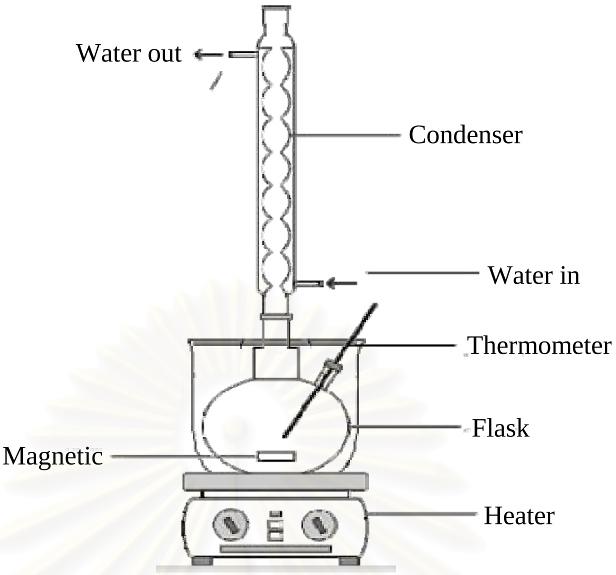


Figure 3.2 Experimental set-up used for two-step method

3.2.3 Investigation the effect on transesterification

In order to investigate the effect on transesterification, best conditions in the first step were selected. The product from the first step was set according to acid esterification process, added alkaline as a catalyst and then washed with distilled water until the water layer was pH 7. The water present is eliminated by heating to above 100°C to boil off water and reduce water content.

3.3 Analysis of methyl ester and fatty acid composition using gas chromatography

After the reaction of two-step, since the methyl esters and fatty acid content was our interest in the study, it was further purified by washing with distilled water, which was recommended for the best purification. The samples of product were analyzed by Perkin elmer 8700 gas chromatography with a flame ionization detection as shown in Figure 3.3. There were separations carried out in a Carbowax 20M fused silica column (30 m × 0.32 mm × 0.25 micron; Ohio Valley. Marietta, Ohio). The operating conditions are shown in Table 3.2. Temperatures of injector and detector were set at 300°C. Helium was used as carrier gas at 9.5 psig with split ratio 1:4. The samples of 0.1 g were dissolved in 1.5 g of methyl decanoate solution and 1 μl of sample was injected into the column.

Figure 3.3 Gas chromatograph for analysis of methyl ester

Table 3.2 Conditions analyzed by Perkin elmer 8700 gas chromatograph

Oven	Iso time.	Ramp rate
1=80°C	1=10.0	1=10
2=230°C	2=10.0	2=1
3=230°C	3=10.0	3= 0

Products were analyzed by gas chromatography (GC). The retention time of each methyl esters and fatty acids are different. Therefore, to find the type of methyl ester and fatty acid by compare retention time with methyl ester and fatty acid standard. The retention time are shown in Table 3.3.

Table 3.3 Retention time of methyl ester and fatty acid in GC chromatogram

Number of peak	**Retention time (min)**	**Peak of sample**
1	3.25	N-heptane
2	15.87	Methyl decanoate
3	22.19	Methyl myristate
4	24.54	Methyl palmitate
5	26.66	Methyl stearate
6	26.92	Methyl oleate
7	27.45	Methyl linoleate
8	34.03	Palmitic acid
9	39.97	Stearic acid
10	41.29	Oleic acid

The concentration of methyl ester 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.

$$\%\text{Methyl ester or fatty acid} = \frac{\text{Weight of methyl ester or fatty acid}}{\text{Weight of sample}} \times 100 \qquad (3.1)$$

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

3.4 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.

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

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

3.4.1 Analytical Error

In this section, from experiment the same sample was analyzed for 3 times by gas chromatography at the same condition. The condition constant at 1% wt H_2SO_4 on the basis of the palm fatty acids, 100% mol of excess methanol from its stoichiometric ratio in 70 minutes at 60°C. Average concentration of methyl ester and standard deviation of this analysis are shown in Table 3.4.

Table 3.4 The average concentration of methyl ester (% wt) and % standard deviation from analysis of esterification of palm fatty acids with methanol

Concentration of methyl ester (wt %)			**Concentration of methyl ester average (%)**	**Standard Deviation from mean (%)**
Analysis 1	**Analysis 2**	**Analysis 3**		
65.32	66.62	63.18	65.04	1.74

The result shows that the percents standard deviation concentration of methyl ester analysis is 1.74%.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter presents the results of methyl ester production from the mixtures of palm stearin and palm fatty acid reacting with methanol by a two-step method. An acid catalyst was used in the first step to reduce high free fatty acids in triglyceride. The effects of different operating conditions such as reaction time, molar ratio of methanol to oil feedstock and amount of catalyst were determined in the batch reactor. In the second step, methyl ester was produced by the transesterification process using potassium hydroxide as an alkaline catalyst. The effects of different operating conditions were determined as in the first step and the results and discussion of experiments will be categorized into the following seven sections:

4.1 Characterization of palm fatty acids and palm stearin
4.2 Determination of suitable reaction time for acid esterification
4.3 The effects of excess methanol on acid esterification
4.4 The effects of acid catalyst amount
4.5 Determination of suitable reaction for transesterification
4.6 The effects of excess methanol on transesterification
4.7 The effects of alkaline catalyst amount

4.1 Characterization of palm fatty acid and palm stearin

Palm fatty acid is light brown solid at room temperature and melts into a brown liquid on heating. A by-product from refining crude palm oil, palm stearin is a white solid fraction at room temperature and melts into a clear yellow liquid on heating, which is obtained by fractionation of the palm oil after crystallization at a controlled temperature. Table 4.1 shows the properties of palm fatty acids and palm stearin used in this study. Palm fatty acids contain relatively high free fatty acids which also results in a high acid value as compared to palm stearin. The molecular weight of palm fatty acids and palm stearin was calculated based on acid and saponification value and was found to be 272.42 and 811.88 g/mole respectively (the method of calculation is shown in Appendix A).

Table 4.1 Properties of Palm Fatty Acids and Palm Stearin

Properties	Palm Fatty Acids	Palm stearin
Density at 60°C, (g/ml)	0.8691	0.8705
Viscosity at 100°C, (cSt)*	6.50	9.01
Acid Value, (mg KOH/g)	188	0.36
Saponification Value, (mg KOH/g)	203.36	207.34
Melting Point °C	47.0	51.0
% Free Fatty Acid	98.21	0.16
Mean molecular Weight, (g/mole)	272.42	811.88

**Both palm fatty acids and palm stearin are in the solid phase at 40°C, so their viscosity can be obtained at 100°C by an adapter method.*

The fatty acid composition of palm fatty acids and palm stearin can be analyzed in terms of fatty acid methyl ester by gas chromatography (GC). In Table 4.2, the results show that the main saturated fats in both palm fatty acids and palm stearin are palmitic acid and stearic acid, while the main unsaturated fats in both palm fatty acids and palm stearin are oleic acid and linoleic acid, subsequently.

Table 4.2 Composition of Palm Fatty Acids and Palm Stearin

Composition		Palm Fatty Acids (% composition)	Palm Stearin (% composition)
Myristic Acid	C 14 : 0	-	1.3
Palmitic Acid	C 16 : 0	42.8	54.0
Stearic Acid	C 18 : 0	4.5	4.7
Oleic Aacid	C 18 : 1	40.5	32.3
Linoleic Acid	C 18 : 2	10.1	7.0
Others	-	2.1	0.7

The methyl ester was carried out in a batch reactor by using palm stearin and palm fatty acids with methanol wherein sulfuric acid and potassium hydroxide were used as catalysts. The samples were analyzed by gas chromatography and the peak area was used for the calculation of methyl ester and fatty acid concentration.
The percentage of methyl ester and free fatty acids is defined as the ratio of the weight methyl ester or free fatty acids and was determined by using gas chromatography as shown in Equation 4.1.

$$\%\text{Methyl esters or fatty acid} = \frac{\text{Weight of methyl ester or fatty acid}}{\text{Weight of sample}} \times 100 \qquad (4.1)$$

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

4.2 Determination of suitable reaction time for acid esterification

The objectives of the study in this section is to determine the suitable reaction time for pretreatment of high free fatty acids in triglyceride and to study effects of reaction time on the concentration of methyl ester. The reaction of acid esterification was carried out in a batch reactor between five oils feedstock (pure palm fatty acid, pure palm stearin, mixtures of palm stearin and 10%, 15% and 25% FFA, respectively) and 100% mole of excess methanol from its stoichiometric ratio using 1% wt H_2SO_4 (based on oil weight) as a catalyst at 60ºC. Samples were taken every 10 minutes from 10-120 minutes throughout the experiment. The concentrations of methyl ester and free fatty acids by the process under these conditions were obtained as a function of time as shown in Table 4.3.

The results presented in Table 4.3 can be plotted on a graph as shown in Figure 4.1-4.5 wherein the esterification process of palm fatty acids (100% FFA) using H_2SO_4 as a catalyst progressed rapidly during the first 30 minutes, then slowed down in the next 40 minutes and was nearly at a steady state at 70-120 minutes.
The concentration of methyl ester (% wt) from this experiment was obtained between 63.48 and 64.65%, whereas 30.87-32.67% of free fatty acids could not be converted to methyl ester in the reaction.

The results indicate that the concentration of methyl ester increased with increasing reaction time to 70 minutes, after which the concentration of methyl ester had no changes in the reaction. Our results are concur with the research of Chonghong et al. (2007), but may not have obtained as high an amount of methyl ester due to the amounts of methanol and the catalysts may have been insufficient, thus obtaining a lesser amount of methyl ester. Chonghong et al (2007) studied the esterification of palm fatty acid distillate (PFAD) in a batch reactor. The reaction was carried out to study the influence of including reaction temperatures of 70-100 °C, molar ratios of methanol to PFAD of 0.4:1-12:1, amounts of catalysts at 0-5.502 % (wt of sulfuric acid/wt of PFAD) and reaction time of 15-240 minutes. After the experiment, they found that a rapid formation of methyl ester was observed within the first 90 minutes, after which the conversion rate slowed down and finally reached a steady state at the molar ratio of methanol to PFAD 5.3:1 with 1.834 %wt of H_2SO_4 in which a conversion of over 90% was obtained.

Table 4.3 The results of concentrations of methyl ester and free fatty acids (%wt) using 1.0% wt H_2SO_4, 100% mole of excess methanol from its stoichiometric ratio at 60 ºC

Time	**%Concentration of Methyl Ester (%wt)**					**% Concentration of Free Fatty Acid (%wt)**				
	0%FFA	**10%FFA**	**15%FFA**	**25%FFA**	**100%FFA**	**0%FFA**	**10%FFA**	**15%FFA**	**25%FFA**	**100%FFA**
0	0	0	0	0	0	0.16	9.82	14.73	24.55	98.21
10	2.05	7.56	10.21	14.06	49.02	0.06	7.84	10.80	14.38	48.41
20	2.38	10.59	11.54	14.44	51.15	0.04	6.49	9.41	12.50	44.97
30	3.64	11.80	14.20	16.88	52.79	0.03	6.07	9.22	12.11	43.85
40	6.58	11.22	14.67	16.24	53.06	0.01	5.24	7.77	10.18	41.87
50	6.69	11.03	15.72	18.48	57.89	0.01	5.04	5.53	11.16	38.15
60	8.74	12.17	15.06	19.62	60.47	0	4.41	6.51	9.81	35.01
70	8.23	12.96	15.02	21.83	64.65	0	3.51	4.82	8.14	31.47
80	8.40	12.71	15.37	21.42	64.34	0	3.48	5.21	9.23	31.59
90	8.15	13.27	16.19	22.39	63.48	0	3.19	4.30	9.60	32.67
100	8.28	12.51	15.26	23.09	64.04	0	3.43	5.89	9.48	30.87
110	8.59	12.37	14.53	22.37	64.50	0	3.20	5.03	8.24	31.43
120	8.33	12.86	16.68	22.25	64.30	0	3.99	5.46	8.89	32.13

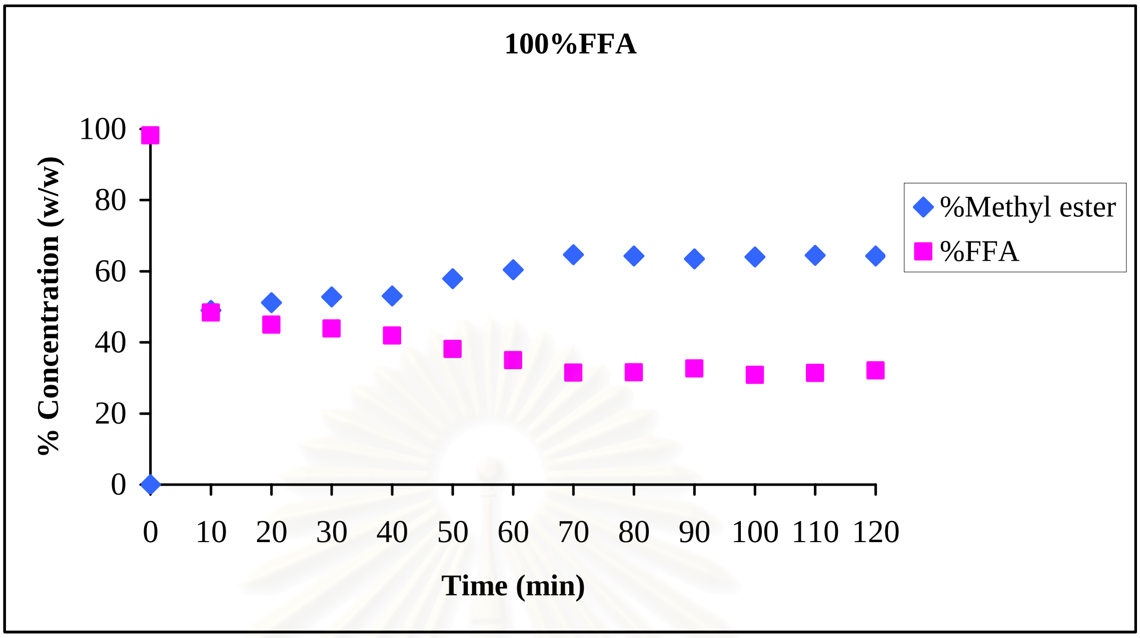


Figure 4.1 Effects of reaction time on acid esterification of 100% FFA (or 0% triglyceride) with methanol 100% mole of excess methanol by using 1% wt H_2SO_4 at 60 ºC

The transesterification reaction of palm stearin (0% FFA) using acid as a catalyst increased steadily in the first 60 minutes as shown in Figure 4.2. After 60-120 minutes, the reaction slowed dramatically and nearly reached the steady state. Under these reaction conditions, the concentration of methyl esters was between 8.15-8.59%, respectively. According to the experiments, it is also possible to use acid as a catalyst for a transesterification reaction of triglyceride, but the concentration of methyl ester from this process was less than that obtained by the esterification process. Siti Zullaikah et al. (2005) stated that acid-catalyzed transesterification of triglyceride affected a slow reaction. Substantial amounts of unreacted triglyceride were detected even after 24 hours (data not shown) when 2% wt H_2SO_4 and nine times of the amount of methanol from its stoichiometric ratio was used. Therefore more catalyst and methanol may be required to achieve a high quantity of methyl ester.

In a study of the acid-catalyzed transesterification of soybean oil, Canakci and Van Gerpen (1999) found that the yield of methyl esters increased with increasing temperature, catalyst and reaction time wherein the transesterification reaction was inhibited by the presence of water in the oil phase and high molar ratios of methanol:oil were found necessary to drive the transesterification reaction to completion.

Although the acid-catalyzed reaction required a longer reaction time and higher temperature than the alkaline-catalyzed reaction, Zhang et al. (2003) found that acid catalysis was more efficient when the amount of free fatty acids in the oil exceeds 1%. An economic analysis study has shown that the acid-catalyzed procedure, being a one-step process, was more economical than the alkaline-catalyzed process, which requires an extra step to convert free fatty acids to methyl esters, thus avoiding soap formation.

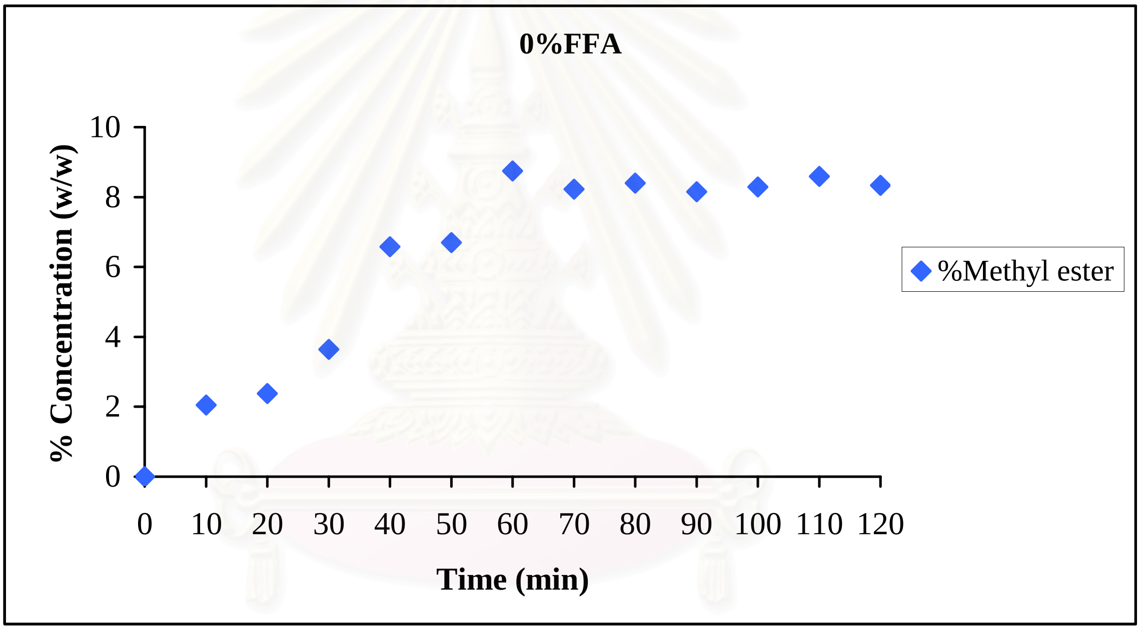


Figure 4.2 Effects of reaction time on acid esterification of 0% FFA (or 100% triglyceride) with methanol 100% mole of excess methanol by using 1% wt H_2SO_4 at 60 °C

In the case of triglycerides with high free fatty acids, the results are shown in Figures 4.3, 4.4 and 4.5. The rate of reaction for three oils feedstock (10%, 15% and 25% FFA) increased the same trend as in the case of 100% FFA. After 70 minutes, there was no significant reduction in free fatty acid content.

Increasing the reaction time affected the rate of reaction and the results in Table 4.3 show that the free fatty acids can be reduced to 3.51%, 4.82 and 8.14% with increasing reaction times of up to 70 minutes for three oils feedstock, subsequently. Thus, the acid catalyst could be used for pretreatment high free fatty acids in triglyceride. It’s also noted that the concentration of methyl ester as shown in Table 4.3 is more than the free fatty acids which had been converted to methyl ester. This is due to the fact that, in addition to the esterification of free fatty acids, triglycerides were also tranesterified, thus causing the production of methyl ester when an acid catalyst was used in the reaction.

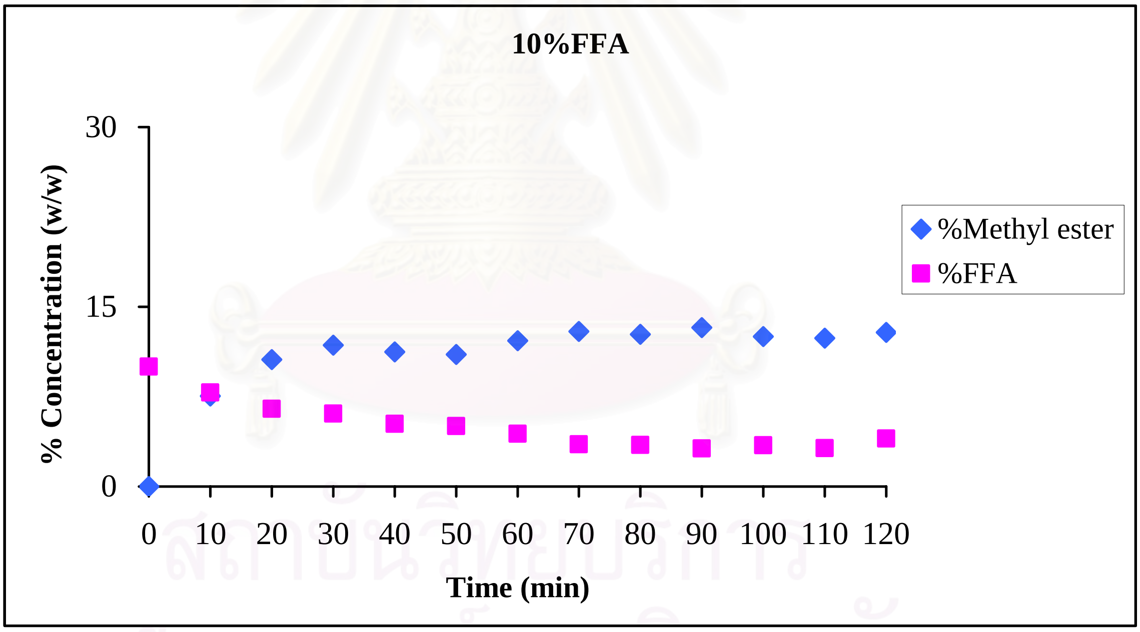


Figure 4.3 Effects of reaction time on the acid esterification of palm stearin and free fatty acids (10%FFA) with methanol 100% mole of excess methanol by using 1% wt H_2SO_4 at 60 ºC

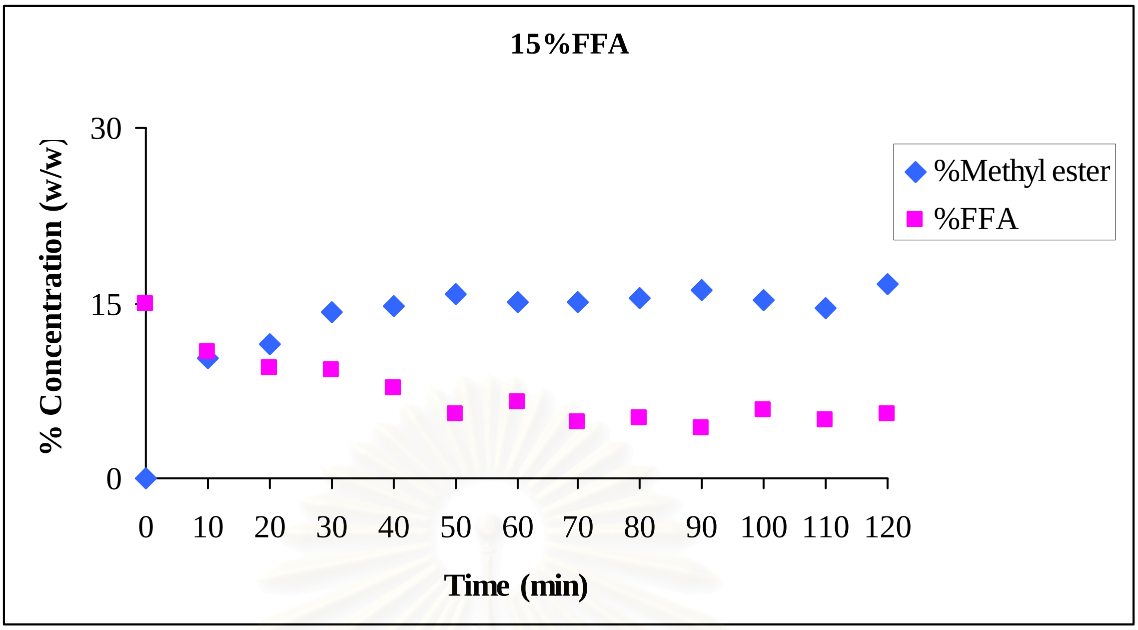


Figure 4.4 Effects of reaction time on the acid esterification of palm stearin and free fatty acids (15% FFA) with methanol 100% mole of excess methanol by using 1% wt H_2SO_4 at 60 ºC

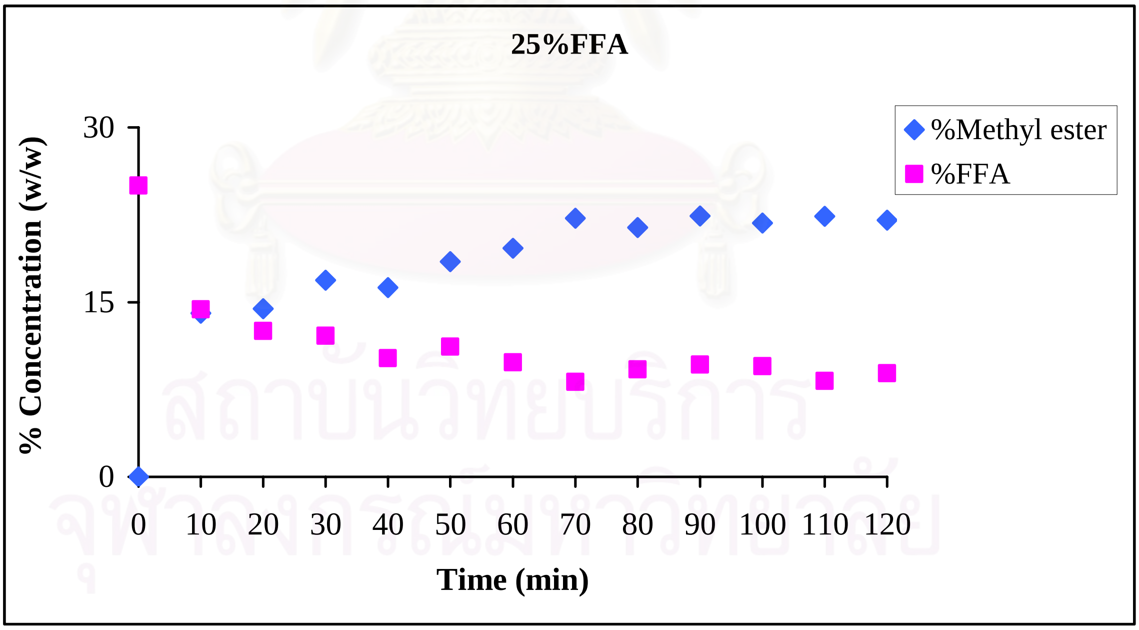


Figure 4.5 Effects of reaction time on the acid esterification of palm stearin and free fatty acids (25%FFA) with methanol 100% mole of excess methanol by using 1% wt H_2SO_4 at 60 ºC

From the remaining free fatty acid, the conversion was calculated as shown in Table 4.4. It was observed that the conversion of free fatty acid of four-oil feedstock (10%, 15%, 25% and 100% FFA) were the same conversion at steady state which is about 0.6. This behavior can predict the conversion of free fatty acid should be close to 0.6 when initial free fatty acid in triglyceride was higher to 50%, 60% and 75% FFA, for example. In the case of 0% FFA, pure triglyceride has low free fatty acids, so the reaction rate was very fast. The amount of methanol and catalyst used in this reaction was very excess, and then the conversion of free fatty acid thus was complete within 60 minutes.

After the experiments, the reaction time of 70 minutes was selected to study in the other factors which affected to the fatty acid reduction in the first step.

Numerous studies have examined the effects of reaction time on acid esterification. The results of reaction time from their experiments, however, are different due to varying conditions such as free fatty acid content, temperature, excess amount of methanol and catalyst concentration. Ghadge and Raheman (2005) and Veljković et al. (2006) reported that complete free fatty acids esterification in some vegetable oils could be obtained at a reaction time of one hour and an acid H_2SO_4 to oil ratio 1% wt at a reaction of temperature 50 °C wherein remaining free fatty acids of no more than 1% can be obtained. For rice bran oil with initial free fatty acid content of 76%, Siti Zullaikah et al. (2005) studied acid-catalyzed esterification at 60 °C using 2 % wt H_2SO_4 and a methanol:oil molar ratio of 5:1, finding that rapid formation of methyl esters were observed during the first 2 hours due to rapid esterified free fatty acids. Analysis of the reaction products showed a free fatty acid content of 2-3% wt which remained the same even after 24 hours of reaction.

Table 4.4 The conversion of free fatty acid which converted to methyl ester

	Conversion of free fatty acid				
Time	**0%FFA**	**10%FFA**	**15%FFA**	**25%FFA**	**100%FFA**
0	0.00	0.00	0.00	0.00	0.00
10	0.63	0.20	0.27	0.41	0.51
20	0.75	0.34	0.36	0.49	0.54
30	0.81	0.37	0.37	0.51	0.55
40	0.94	0.47	0.47	0.59	0.57
50	0.94	0.49	0.53	0.55	0.61
60	1.00	0.55	0.56	0.60	0.64
70	1.00	0.64	0.67	0.67	0.68
80	1.00	0.65	0.65	0.62	0.68
90	1.00	0.68	0.68	0.65	0.67
100	1.00	0.65	0.60	0.64	0.69
110	1.00	0.67	0.66	0.66	0.68
120	1.00	0.60	0.63	0.64	0.67

4.3 The effects of excess methanol on acid esterification

The molar ratio of methanol to oil is one of the important factors that affect the reduction of high free fatty acids in triglyceride. In this study, 100%, 200% and 300% mole of excess methanol from its stoichiometric ratio was used in the reaction by having 1% and 2% wt H_2SO_4 as a catalyst in 70 minutes at 60 °C. The results obtained by these conditions are shown in Tables 4.5 and 4.6.

The changes in concentration of free fatty acids and methyl ester of reaction mixture during the acid esterification are shown in Figure 4.6-4.13. The results indicate that the reduction of free fatty acids was influenced by the quantity of methanol. At 200% and 300% mole of excess methanol, the concentration of free fatty acids could be reduced by better than at 100% mole of excess methanol which the catalyst based on oil weight and total weight was used. The reduction of free fatty acids was raised when the molar ratio of methanol to oil feedstock was increased for both catalyst concentrations of 1% and 2% wt. The concentration of methyl ester also increased with increasing methanol. It was observed that the rate of reaction of catalyst based on total weight was higher than the rate of reaction of catalyst based on oil weight. As the methanol was excess from 100% to 200% and 300% mole from its stoichiometric ratio, the catalyst based on oil weight was diluted and the rate of reaction was slower. However, the calculation for both catalysts shows the same trend which the rate of reaction increased with increasing methanol. Following the experiments of this section, 300% mole of excess methanol was sufficient to reduce free fatty acid levels of three-oil feedstock (10%, 15% and 25% FFA) to less than 2%.

Table 4.5 The results of concentrations of methyl ester and free fatty acid from 0%, 10%, 15%, 25% and 100% FFA using 100%, 200% and 300% mole of excess methanol, 1% and 2% wt H_2SO_4 (based on oil weight), at 60 ºC

%Excess methanol	% wt H_2SO_4 (based on oil weight)	% wt H_2SO_4 (as total weight)	%Concentration of methyl ester (w/w)					%Concentration of free fatty acid (w/w)				
			0% FFA	10% FFA	15% FFA	25% FFA	100% FFA	0% FFA	10% FFA	15% FFA	25% FFA	100% FFA
100%	1%	0.81%	8.23	12.96	15.02	21.58	64.65	0.00	3.51	4.30	8.14	31.47
	2%	1.62%	9.97	15.14	16.96	24.97	70.06	0.00	2.38	2.90	5.19	25.63
200%	1%	0.74%	9.31	14.33	15.17	23.22	66.15	0.00	3.24	3.93	6.23	28.25
	2%	1.48%	11.46	17.64	19.34	28.36	77.64	0.00	1.54	1.65	3.57	17.74
300%	1%	0.68%	10.04	15.53	16.24	25.21	69.03	0.00	3.17	3.59	4.75	25.65
	2%	1.36%	12.18	19.52	20.02	31.37	81.59	0.00	0.65	1.01	1.41	13.45

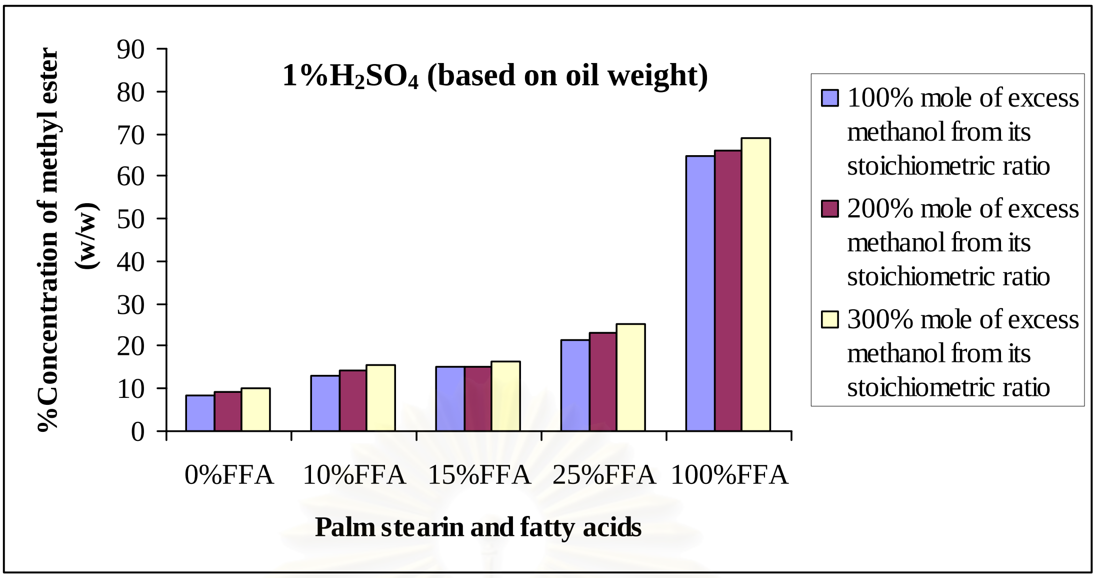


Figure 4.6 The effects of excess methanol on acid esterification by using 1% wt H_2SO_4 based on oil weight as a catalyst (% methyl ester)

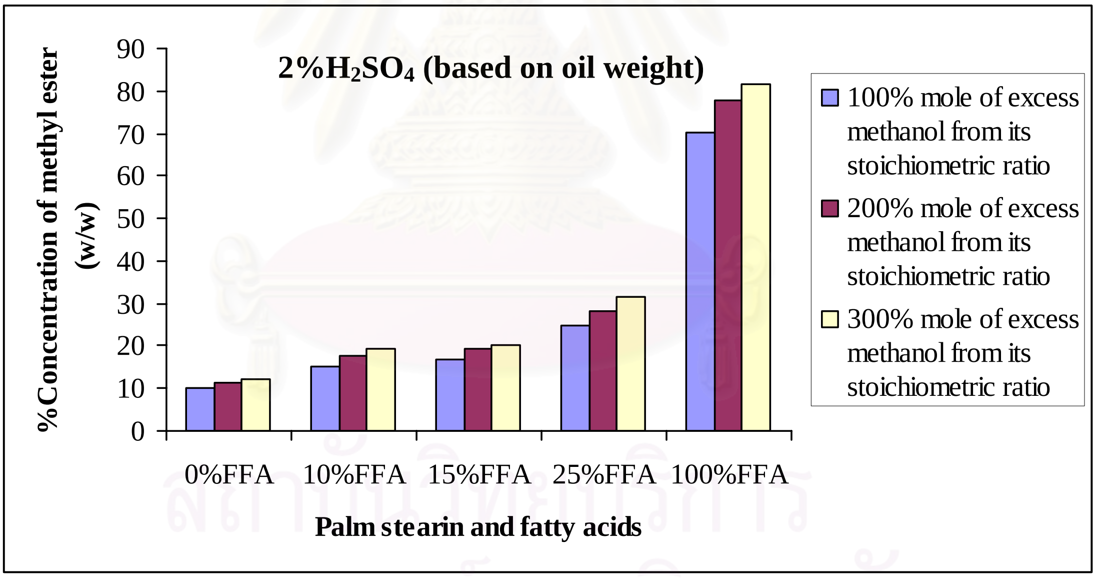


Figure 4.7 The effects of excess methanol on acid esterification by using 2% wt H_2SO_4 based on oil weight as a catalyst at 60 ºC (% methyl ester)

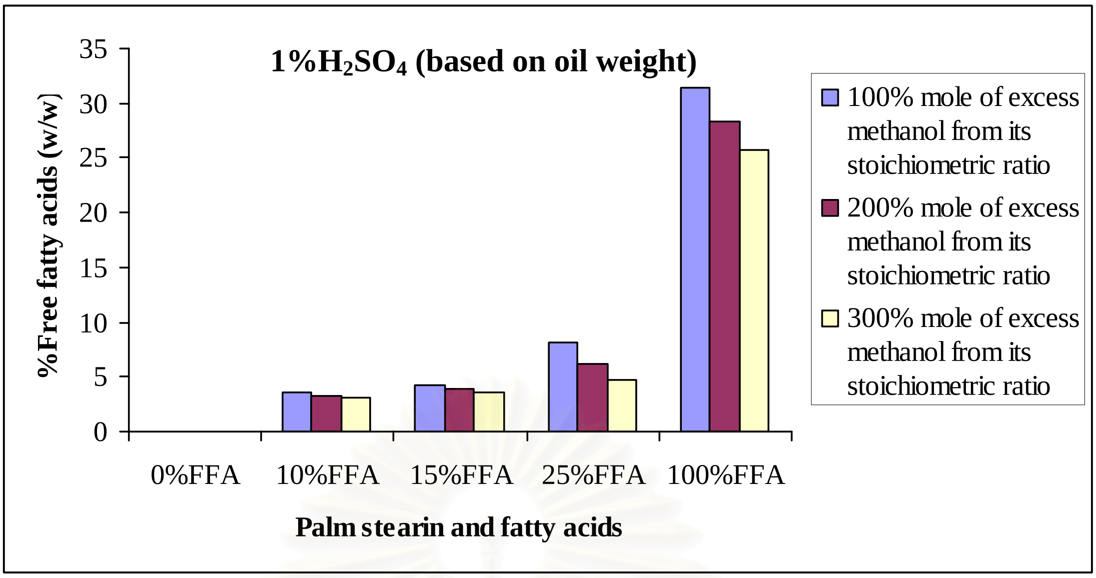


Figure 4.8 The effects of excess methanol on acid esterification by using 1% wt H_2SO_4 based on oil weight as a catalyst (% free fatty acids)

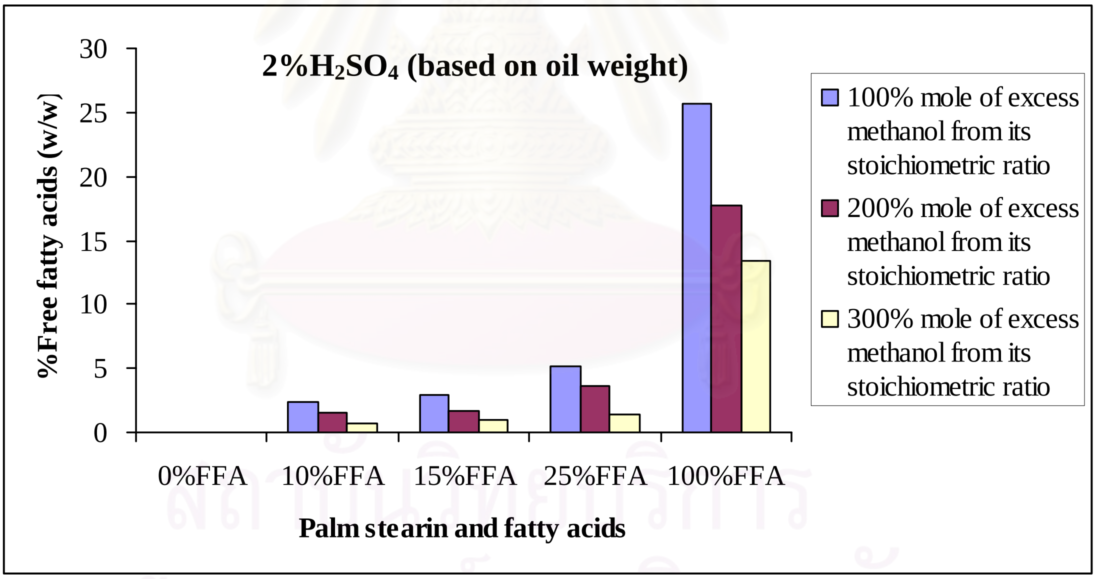


Figure 4.9 The effects of excess methanol on acid esterification by using 2% wt H_2SO_4 based on oil weight as a catalyst (% free fatty acids)

Table 4.6 The results of concentrations of methyl ester and free fatty acid from 0%, 10%, 15%, 25% and 100% FFA using 100%, 200% and 300% mole of excess methanol, 1% and 2% wt H_2SO_4 (based on total weight), at 60 ºC

%Excess methanol	**% wt H_2SO_4 (based on total weight)**	**%Concentration of methyl ester**					**%Concentration of free fatty acid**				
		0% FFA	**10% FFA**	**15% FFA**	**25% FFA**	**100% FFA**	**0% FFA**	**10% FFA**	**15% FFA**	**25% FFA**	**100% FFA**
100%	1%	8.43	13.78	15.20	22.63	66.78	0.00	3.42	4.60	7.34	29.98
	2%	11.00	16.09	18.30	26.56	79.00	0.00	1.76	1.26	3.87	17.31
200%	1%	9.81	15.18	15.92	24.94	70.63	0.00	3.05	3.27	6.48	25.19
	2%	15.63	19.40	22.70	32.38	85.44	0.00	0.84	0.95	1.72	10.50
300%	1%	10.70	16.06	17.96	27.03	75.64	0.00	2.88	3.44	4.57	20.33
	2%	19.78	22.56	24.41	34.45	91.06	0.00	0.57	0.78	0.98	4.64

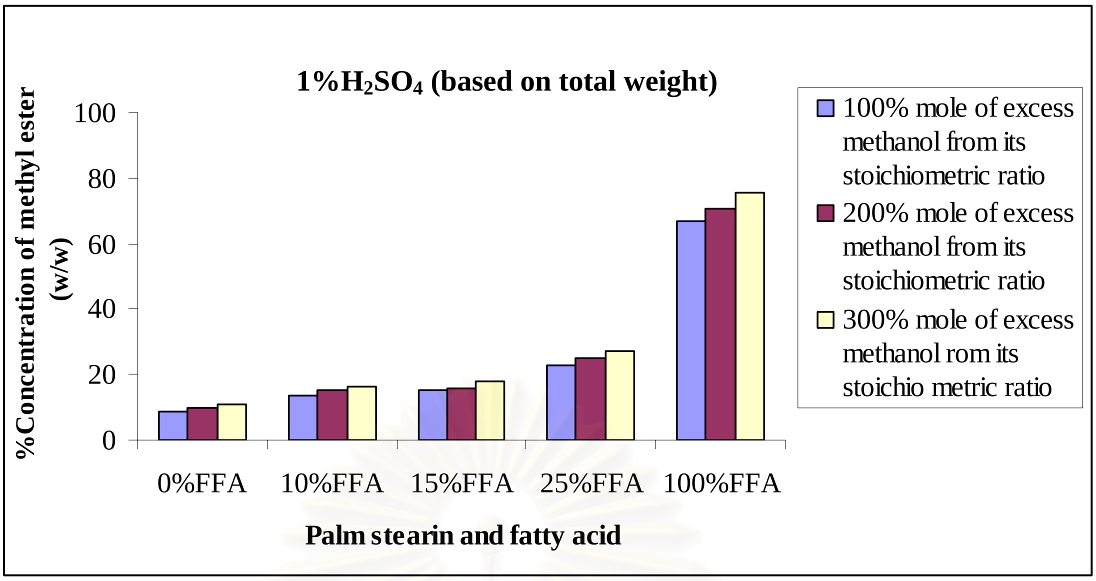


Figure 4.10 The effects of excess methanol on acid esterification by using 1% wt H_2SO_4 based on total weight as a catalyst (% methyl ester)

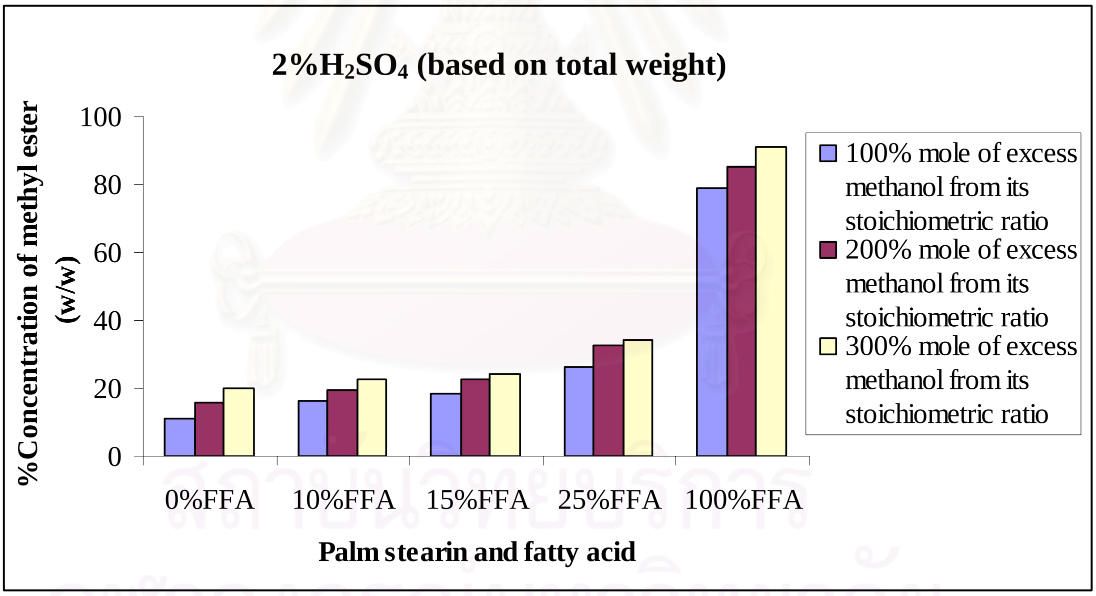


Figure 4.11 The effects of excess methanol on acid esterification by using 2% wt H_2SO_4 based on total weight as a catalyst (% methyl ester)

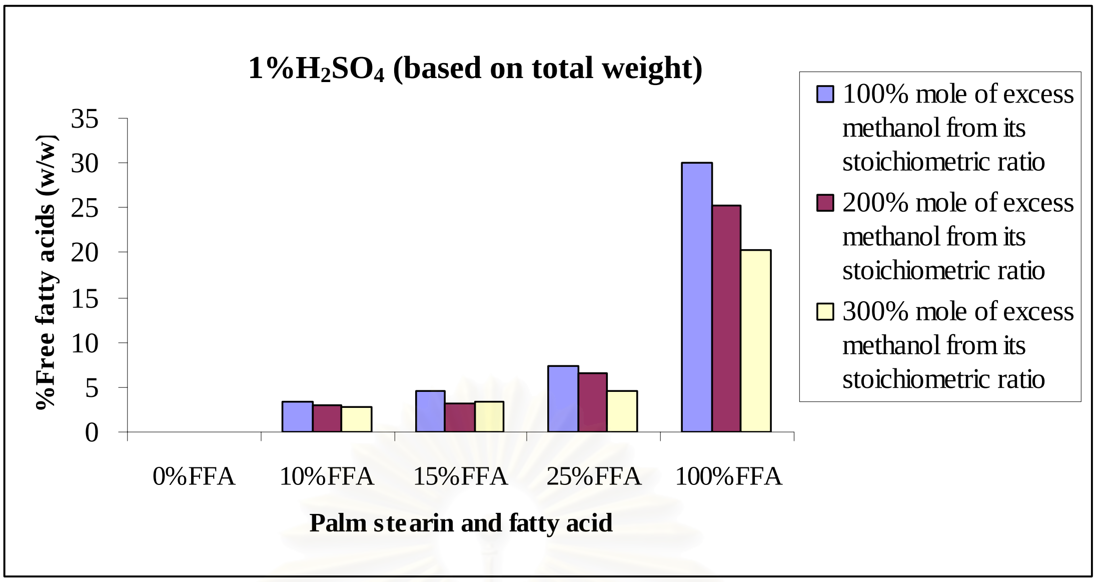


Figure 4.12 The effects of excess methanol on acid esterification by using 1% wt H_2SO_4 based on total weight as a catalyst (% free fatty acids)

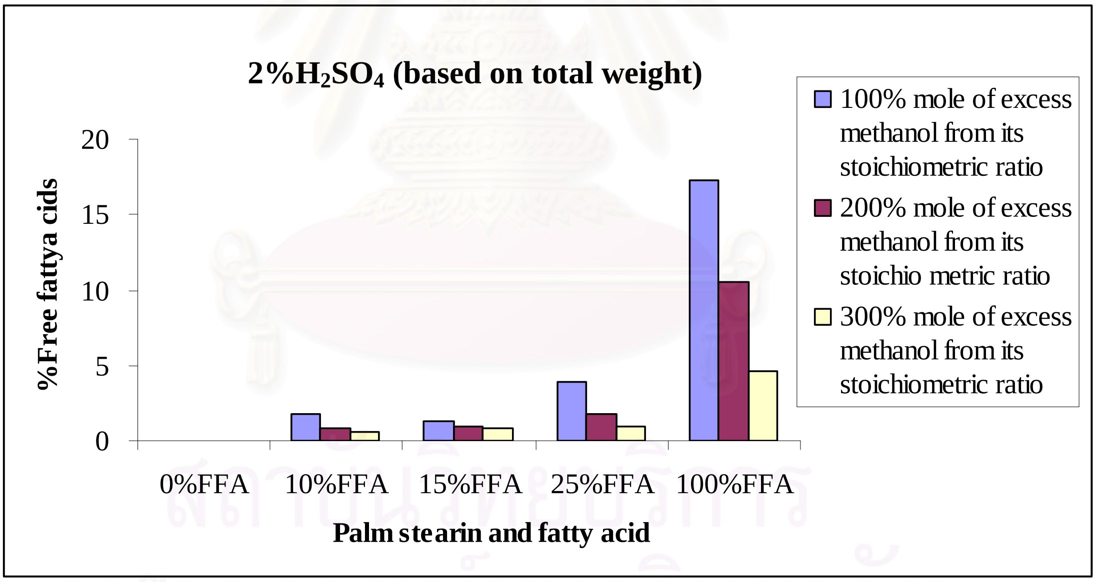


Figure 4.13 The effects of excess methanol on acid esterification by using 2% wt H_2SO_4 based on total weight as a catalyst (% free fatty acids)

The results of the present study are in agreement with the results published by previous workers as the concentration of free fatty acids reduced when the methanol was increased. Ghadge and Raheman (2005) studied methyl ester production from mahua (*Maduca indica*) oil with high free fatty acids, finding that the methanol to oil ratio increased (from 0.15 to 0.3 v/v) while the acid value could be lowered to within the desirable range of less than 5 mg KOH/g by using 1% v/v H_2SO_4 as a catalyst.

Veljković et al. (2006) studied methyl ester production from tobacco (*Nicotiana tabacum* L.) seed oil which has high free fatty acids (above 17%) by using 1% and 2% wt of H_2SO_4 (based on oil weight) as a catalyst. In the first step, they found that the reaction rate was greatly affected by the molar ratio. The acid value of the reaction mixture was reduced from over 30 mg KOH/g to below 1 mg KOH/g at 25 and 50 minutes for molar ratios of 18:1 and 13:1, respectively.

Berchmans and Hirata (2007) studied the pretreatment of crude *Jatropha curcas* L. seed oil (CJCO) in the presence of 1 % wt H_2SO_4 (based on oil weight) as a catalyst, finding that the free fatty acid concentration reduced sharply to 3% at 10% w/w of methanol to oil and decreased gradually to 1% at 60% w/w of excess methanol. If the excess methanol was higher than 60% w/w, there would be no significant effect on the free fatty acid concentration reduction which was due to the effect of water produced during the esterification of free fatty acids.

4.4 The effects of acid catalyst amount

To investigate the influence of catalyst amounts on the free fatty acid concentration of palm stearin with 10%, 15% and 25% FFA, two different sulfuric acid amounts (1% and 2% wt) were used. The results are summarized in Tables 4.7 and 4.8 at 300% mole of excess methanol from its stoichiometric ratio in 70 minutes at 60 °C.

Table 4.7 The results of concentrations of methyl ester and free fatty acids (%wt) using 1% and 2% wt H_2SO_4 base on oil weight

% wt H_2SO_4	%Concentration of methyl ester					%Concentration of free fatty acid				
	0% FFA	10% FFA	15% FFA	25% FFA	100% FFA	0% FFA	10% FFA	15% FFA	25% FFA	100% FFA
1%	10.04	15.53	16.24	25.21	69.03	0.00	3.17	3.59	4.75	25.65
2%	12.18	19.52	20.02	31.37	81.59	0.00	0.65	1.01	1.41	13.45

Table 4.8 The results of concentrations of methyl ester and free fatty acids (%wt) using 1% and 2% wt H_2SO_4 base on total weight

% wt H_2SO_4	%Concentration of methyl ester					%Concentration of free fatty acid				
	0% FFA	10% FFA	15% FFA	25% FFA	100% FFA	0% FFA	10% FFA	15% FFA	25% FFA	100% FFA
1%	10.70	16.06	17.96	27.03	75.64	0.00	2.88	3.44	4.57	20.33
2%	19.78	22.56	24.41	34.45	91.06	0.00	0.57	0.78	0.98	4.64

The influence of catalyst amount on free fatty acid and methyl ester concentrations indicates that the free fatty acid concentration could be reduced as the acid catalyst was increased from 1% to 2% wt. For the mixtures of palm stearin with 10%, 15% and 25% FFA, the final free fatty acid concentrations of about 0.65, 1.01 and 1.41 at the catalyst based on oil weight and 0.57, 0.78 and 0.98 at the catalyst based on total weight remained in the reaction, respectively. Therefore, H_2SO_4 of 2% wt was adequate to complete the reduction of free fatty acids in triglyceride.

These results also agreed with those of Edward et al. (2001) who found that the rate of reaction increased as the amount of acid catalyst increased from 1% to 5% in acid-catalyzed esterification of crude palm oil at the molar ratio of alcohol to oil at 40:1. The methyl ester production also increased from 52% to 83%, respectively.

Zheng et al. (2006) found that the conversion of free fatty acids increased as the acid catalyst amount increased from 1.5% to 2.5% mole when the molar ratio of methanol to oil at 50:1 was used in acid esterification of waste frying oil.

The results are observations that when acid was used as a catalyst, the amount of methyl esters from the initial free fatty acids of 25% FFA nearly changed to methyl ester that was better than methyl ester from initial free fatty acid concentrations of 15% and 10% FFA, respectively. This is because the reaction of esterification is faster than transesterification. The theory of esterification reaction uses one mole of methanol for one mole of free fatty acids, while the theory of transesterification reaction uses one mole of methanol for three moles of free fatty acids, which is the same amount with excess methanol. In addition, the feedstock with higher free fatty acids can be changed to methyl ester better than at lower initial free fatty acids.

Siti Zullaikah et al. (2005) stated that the rate of methyl esters in the product depended upon the initial FFA content, which concurs with the research of Canakci and Van Gerpen (2001) who found that the methyl ester of 40% palmitic mixture in triglyceride could be increase better than the case of 20% palmitic acid mixed in triglyceride when the acid catalyst was increased from 5% to 25% H_2SO_4.

Based on the overall results of experiments in the previous three sections, the optimum conditions for the pretreatment three-oil feedstock is 2% wt H_2SO_4 with 300% mole excess methanol from its stoichiometric ratio at 70 minutes in which the free fatty acid concentration of less than 2% was obtained before the product of acid esterification could be substrates for transesterification reaction.

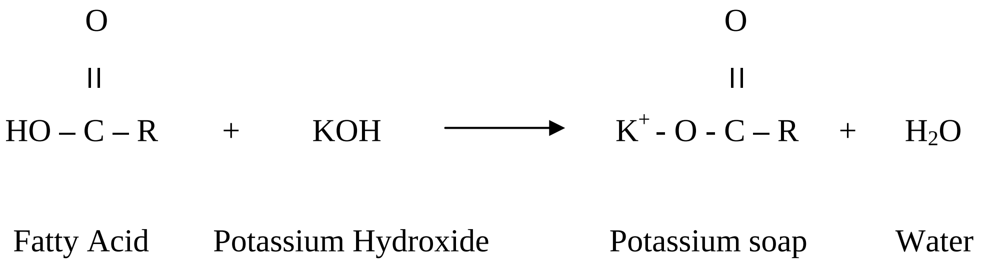
4.5 Determination of suitable reaction time for transesterification

Following the acid pretreatment of acid-catalyzed esterification in the first step, free fatty acids in triglyceride moved into the methanol phase. The cleaned triglyceride was then brought to the second step. The objective of this section was to find a suitable reaction time for the transesterification reaction. The reactions of product from the first step were carried out with 100% mole of excess methanol from its stoichiometric at 60 ºC. Potassium hydroxide at a concentration of 0.5 % (based on oil weight) was used as a catalyst in reaction times between 0-120 minutes.
The results from these experiments are shown in Table 4.9.

Table 4.9 The concentrations of methyl ester at various times using 100% mole of excess methanol from its stoichiometric ratio and 0.5% wt KOH

Time	**%Concentration of methyl ester**		
	10%FFA	**15%FFA**	**25%FFA**
0	0	0	0
10	78.86	77.55	78.17
20	94.01	93.48	82.97
30	92.12	89.91	79.92
40	91.44	89.45	78.06
50	90.19	88.32	78.14
60	88.31	85.52	76.92
70	88.38	85.99	77.20
80	87.82	84.54	76.31
90	87.74	86.17	76.21
100	89.04	86.81	76.07
110	88.53	86.52	75.40
120	88.69	85.91	76.27

Figure 4.14-4.16 shows a plot between the formations of methyl esters and reaction times for the second step of 10%, 15% and 25% FFA. The results show that the reaction was very fast during the first few minute wherein a product of more than 70% methyl ester content was formed within the first 20 minutes. After that, at times of 20-50 minutes, the methyl ester content decreased slightly until it reached a steady state within 60 minutes at 60 °C, and then remained relatively constant despite the increasing reaction time. The results indicated that an extension of the reaction time from 60 minutes to 120 minutes had no significant effect on the concentration of methyl esters. However, as the methyl ester content decreased slightly until it reached a steady state at reaction times of 20-50 minutes, which can be explained by the remaining free fatty acids in the product from the first step that predominantly reacted with the alkaline to form potassium base soap and water, as shown in Equation 4.3.



$$HO-\overset{\overset{\displaystyle O}{\|}}{C}-R \quad + \quad KOH \longrightarrow K^{+}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R \quad + \quad H_2O$$

Equation 4.3 The reaction of fatty acids using an alkaline catalyst

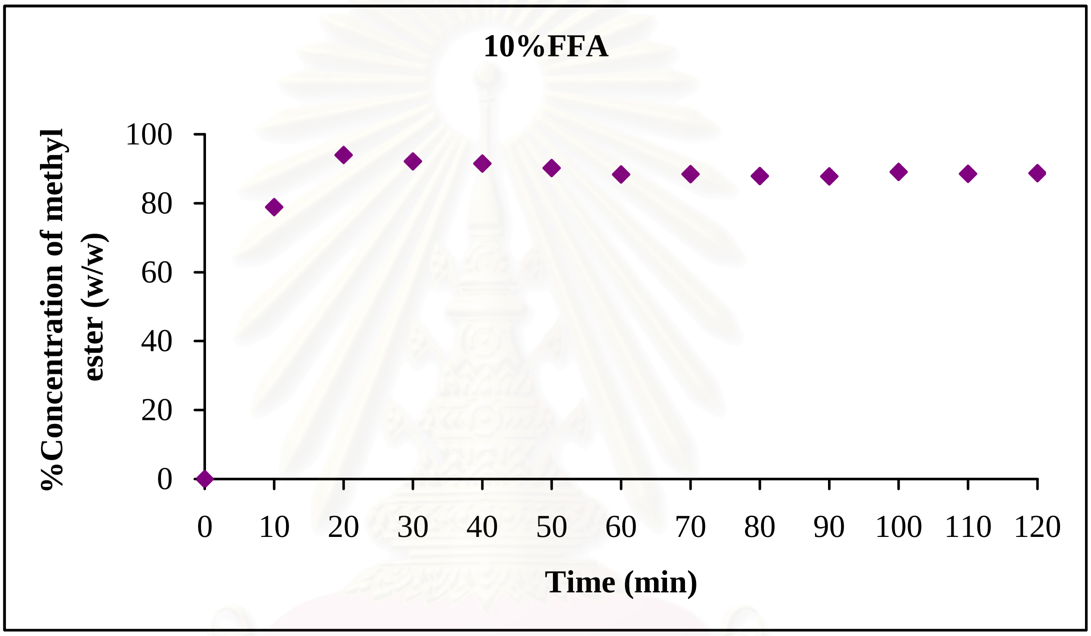


Figure 4.14 The effects of reaction time on the transesterification of palm stearin and free fatty acids (10%FFA) with 100% mole of excess methanol by using 0.5% wt KOH at 60 ºC

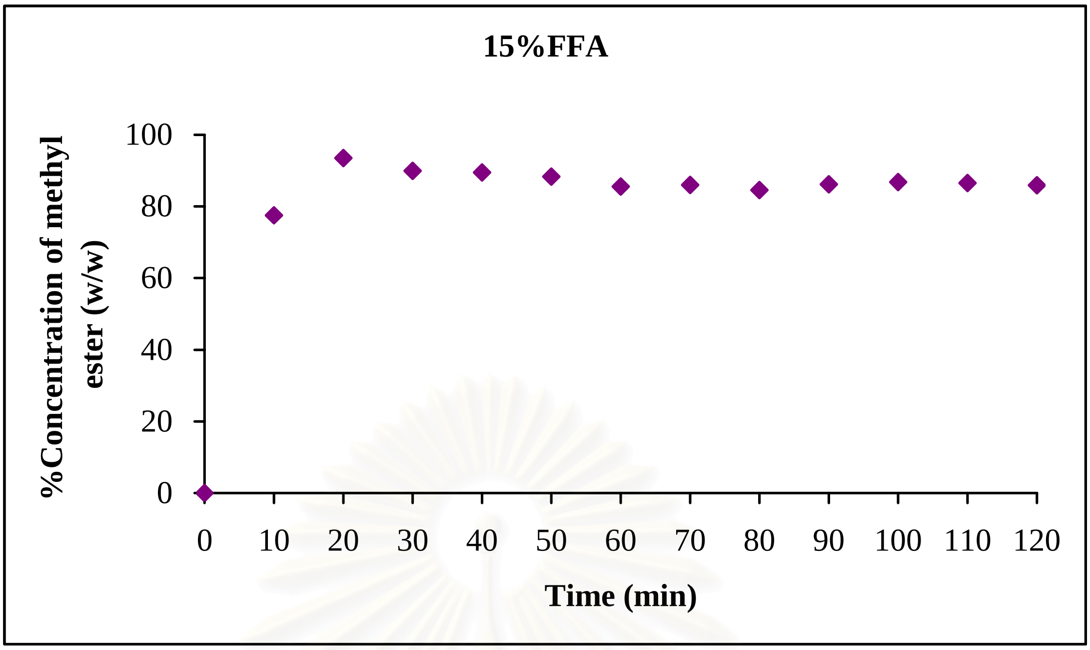


Figure 4.15 The effects of reaction time on the transesterification of palm stearin and free fatty acids (15%FFA) with 100% mole of excess methanol by using 0.5% wt KOH at 60 ºC

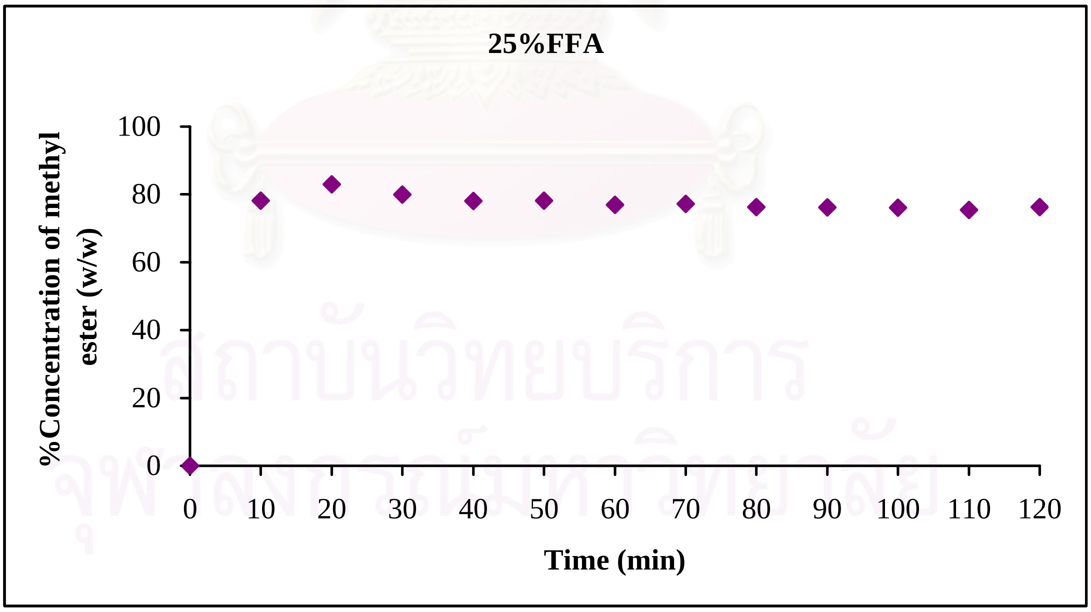


Figure 4.16 The effects of reaction time on the transesterification of palm stearin and free fatty acids (25%FFA) with 100% mole of excess methanol by using 0.5% wt KOH at 60 ºC

The results obtained by the present study are in agreement with the results published by earlier workers. Freedman et al. (1984) found that the conversion rate increased with the reaction time in transesterified peanut, cotton-seed, sunflower and soybean oils under the conditions of methanol to oil at 6:1, 0.5% sodium methoxide catalyst and 60 °C wherein an approximate yield 80% was observed after 1 minute for soybean and sunflower oils. After 60 minutes, the conversions of 93-98% were nearly the same for all four oils.

Ma et al., (1998a) studied the effects of reaction time on the transesterification of beef tallow reacted with methanol wherein the reaction was very slow during the first minute due to the mixing and dispersion of methanol into beef tallow. From one to five minutes, the reaction proceeded very quickly, and the production of beef tallow slowed down and reached the maximum value at about 15 minutes.

Darnoko and Cheryan (2000) studied the production of methyl ester wherein palm oil was transesterified with 1% wt KOH at 60 °C and a molar ratio of 1:6 (oil:methanol) in a continuous stirred tank reactor. The results obtained were a yield of 58.8% of methyl esters at a reactor residence time of 40 minutes which increased to 97.3% at a residence time of 60 minutes.

4.6 The effects of excess methanol on transesterification

The alcohol to triglyceride molar ratio is one of the most important factors that can affect the concentration of esters. In order to study the effects of excess methanol on methyl ester concentration, the experiments were conducted with 100%, 200% and 300% mole of excess methanol from its stoichiometric by using 0.5% KOH, respectively. The reaction time as optimized in the previous section was adopted. The concentration of methyl ester at different mole of excess methanol from its stoichiometric ratio is shown in Tables 4.10 and 4.11.

Table 4.10 The effect of excess methanol at the catalyst 0.5% KOH based on oil weight, 60 ºC

%Excess methanol	**%wt Catalyst (as total weight)**	**%Concentration of methyl ester (w/w)**		
		10%FFA	**15%FFA**	**25%FFA**
100%*	0.40%	88.31	85.52	76.92
200%*	0.37%	84.55	83.49	74.38
300%*	0.34%	81.45	82.21	71.62

** 100 % excess from its stoichiometic ratio (6:1)*, *200 % excess from its stoichiometic ratio (9:1) and 300 % excess from its stoichiometic ratio (12:1)*

Table 4.11 The effect of excess methanol at the catalyst 0.5% KOH based on total weight, 60 ºC

%Excess methanol	**%wt Catalyst (as total weight)**	**%Concentration of methyl ester (w/w)**		
		10%FFA	**15%FFA**	**25%FFA**
100%*	0.5%	89.28	87.10	81.01
200%*	0.5%	86.74	84.84	77.94
300%*	0.5%	83.39	83.29	75.19

** 100 % excess from its stoichiometic ratio (6:1)*, *200 % excess from its stoichiometic ratio (9:1) and 300 % excess from its stoichiometic ratio (12:1)*

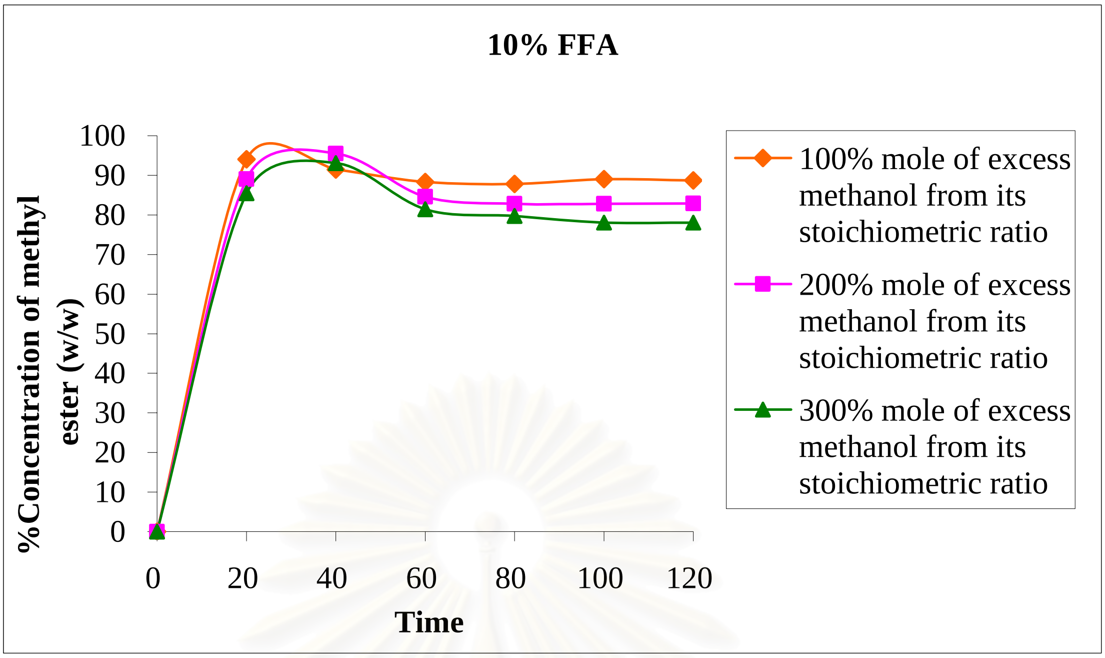


Figure 4.17 The effects of excess methanol on the transesterification of palm stearin and free fatty acids (10%FFA) by using 0.5% wt KOH based on oil weight at 60 ºC

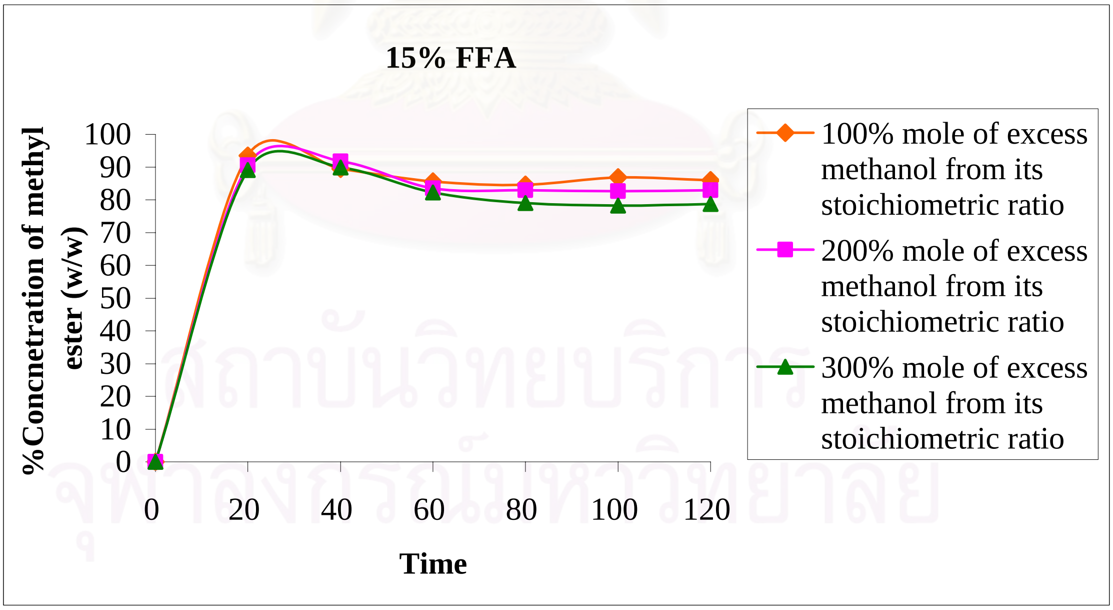


Figure 4.18 The effects of excess methanol on the transesterification of palm stearin and free fatty acids (15%FFA) by using 0.5% wt KOH based on oil weight at 60 ºC

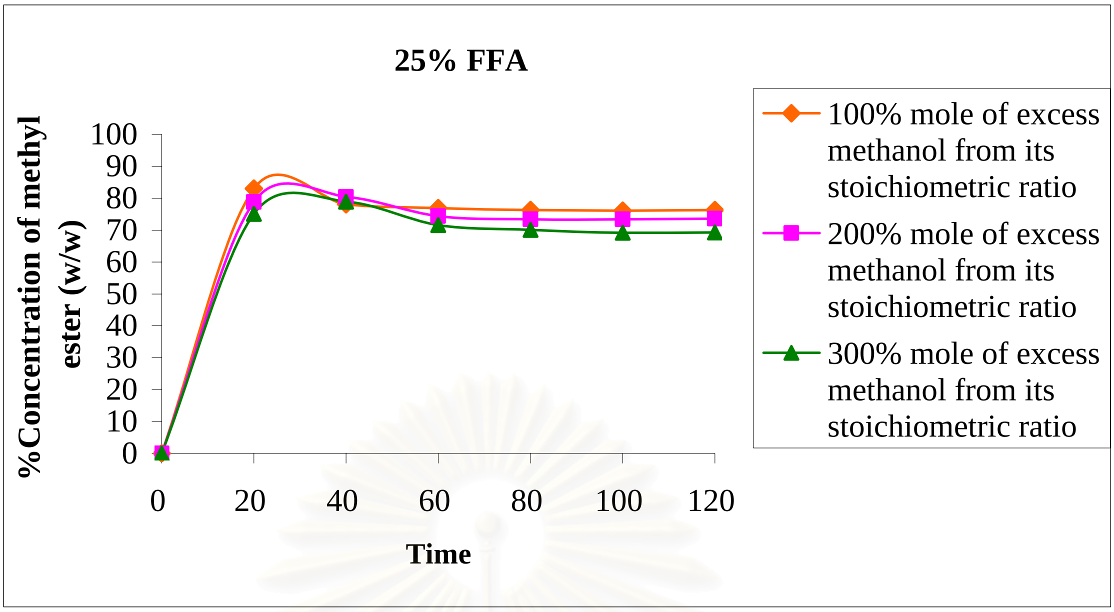


Figure 4.19 The effects of excess methanol on the transesterification of palm stearin and free fatty acids (25%FFA) by using 0.5% wt KOH based on oil weight at 60 ºC

Theoretically, alkaline esterification reaction requires three moles of alcohol for each mole of oil. In practice, however, Ramadhas et al. (2005) said that the molar ratio should be higher than that of stoichiometric ratio in order to drive the reaction towards completion. In the present study, the change of methyl ester was investigated when methanol increased from 100% to 200% and 300% mole of excess methanol from its stoichometric ratio. It is expected therefore that the concentration of methyl ester would increase with increasing methanol. However, the concentration of methyl ester for 200% and 300% mole of excess methanol from its stoichiometric ratio were found to below. The experimental results in Table 4.10 show that increasing methanol to above 100% causes a reduction of methyl ester. In the fact that of increasing methanol, the rate of reaction should be increase but in this study the results show that the rate of reaction decrease. This is due to the catalyst was diluted with increasing methanol. The alkaline catalyst used in this study was calculated based on the weight of oil. Figure 4.17-4.19 shows the rate of reaction when alkaline catalyst based on oil weight was used. As the methanol was excess from 100% to 200% and 300%, the rate of reaction was slower. The amount of catalyst based on oil weight were diluted from 0.40% to 0.37% and 0.34% when calculated based on total weight as shown in Table 4.10. The effect of excess methanol using the amount of catalyst based on total weight was also investigated. The results shown in Table 4.11 indicates that at the concentration of catalyst was constant, the reduction of methyl ester was obtained by increasing methanol as same as the case of using catalyst based on oil weight. This result could be attributed to the high water content in the reactants as the commercial grade methanol (95%) was used. Water would hydrolysis ester to fatty acid react readily with alkaline catalyst under this condition, thus lower concentration of methyl ester.

Following the experiments for both catalysts based on oil weight and based on total weight, the best results of transesterification were obtained for 100% mole of excess methanol from its stoichiometric ratio.

Numerous studies have found that increasing the molar ratio to 6:1 gives the best conversion. Freedman et al. (1984), for example, studied the effects of molar ratios from 1:1 to 6:1 on ester conversion with vegetable oils. Soybean, sunflower, peanut and cotton seed oils behaved similarly and achieved the highest conversions (93-98%) at a 6:1 molar ratio. Nye and Southwell (1983) found that the molar ratio of 6:1 of methanol to oil gave the best conversion in the transesterification of rape seed oil while Umer and Farooq (2007) asserted that when the ratio was increased from 3:1 to 6:1, the ester yield was found to be raised from 57% to 96%. It could be assumed, therefore, that the reaction was incomplete for a molar ratio of less than 6:1.

4.7 The effects of alkaline catalyst amount

The concentration of alkaline catalyst was the last parameter in the present study wherein the effects of KOH concentration on transesterification were investigated with concentrations of 0.5% and 1% wt. The operating conditions during the process were optimized in the previous section (reaction time of 60 minutes and 100% mole of excess methanol from its stoichiometric ratio at the temperature of 60 °C). The results from these experiments are shown in Tables 4.12 and 4.13.

Table 4.12 The results of concentrations of methyl ester (%wt) using 0.5% and 1% wt KOH based on oil weight

% KOH (base on oil weight)	**% KOH (as total weight)**	**% Concentration of methyl ester**		
		10% FFA	**15% FFA**	**25% FFA**
0.5%	0.34%	88.31	85.52	76.92
1%	0.68%	93.71	91.32	85.06

Table 4.13 The results of concentrations of methyl ester (%wt) using 0.5% and 1% wt KOH based on total weight

% KOH (base on total weight)	**% Concentration of methyl ester**		
	10% FFA	**15% FFA**	**25% FFA**
0.5%	89.28	87.10	81.01
1%	95.4	93.57	87.82

As the concentration of potassium hydroxide increased, the concentration of methyl esters also increased. Insufficient amounts of potassium hydroxide resulted in incomplete concentrations of triglyceride into the ester as indicated by its lower esters content (0.5% wt KOH). The results in Tables 4.12 and 4.13 show the optimal methyl esters content and the concentration of the catalyst from three-oil feedstock. It can be seen that when the catalyst concentration was increased from 0.5% to 1% wt, the concentration of methyl esters also increased wherein the maximum methyl ester over 85% was obtained for three-oil feedstock, respectively.

According to the experimental results, the reduction of methyl esters occurred at three-oil feedstock when the initial free fatty acids were increased (10%, 15% and 25% FFA). Siti Zullaikah et al. (2005) stated that the rate of transesterification and the final methyl ester content in the product depended upon the initial free fatty acid content in triglyceride. The soap was formed by the free fatty acids remaining at the first step as studied in previous sections. The free fatty acids of palm stearin with an initial 25% concentration of FFA can form soap better than concentrations of 15% and 10% FFA when alkaline was used as a catalyst in the transesterification process. Therefore, less amounts of methyl esters were obtained.

Therefore, it was shown by the experiments that the optimum alkaline catalyst of 1% wt KOH gave the best methyl ester concentration. In the study of Umer and Farooq (2007), the optimum concentration for KOH catalyst was also 1% KOH.
It can also be observed that the best methyl ester yield (95-96%) was achieved at a catalyst concentration of 1% wt KOH whereas the yields were lower at higher concentrations (1.25% and 1.5% wt KOH). Dorado et al. (2004) and Encinar et al. (2005) confirmed that there were decreases in the content of methyl ester when there were increases in the concentration of the catalyst above 1% wt KOH. Therefore, the formation of soap in the presence of high amounts of catalyst increases the viscosity of the reactants and lowers the methyl ester content. These results were qualitatively similar to those obtained for the transesterification of *Pongamia pinnata* oil by Meher et al. (2006) and used frying oil by Encinar et

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The study of palm stearin and fatty acid by using the two-step method can be concluded as follows:

5.1.1 At the first step, the acid catalyst can simultaneously catalyze both esterification of free fatty acids and transesterification of triglycerides. In this step, the feedstock with high initial free fatty acids can be changed to methyl ester better than low initial free fatty acids.

5.1.2 The optimum conditions for acid esterification are 300% mole of excess methanol from its stoichiometric ratio for 70 minutes by using 2% wt H_2SO_4 as a catalyst at 60 °C. Under these conditions the free fatty acid concentration is reduced to less than 2%.

5.1.3 At the second step, methyl esters which have three-oil (10%, 15% and 25% FFA) as the feedstock are decreased because the soap is formed by the free fatty acids remaining from the first step.

5.1.4 The optimum conditions for transesterification are 100% mole of excess methanol from its stoichiometric ratio for 60 minutes by using 1% KOH as a catalyst at 60 °C wherein maximum methyl ester concentrations of approximately 93.71%, 91.32% and 85.02% were obtained for each oil feedstock, respectively.

5.2 Recommendations

5.2.1 A similar study should be conducted in continuous flow reactor, such as fix flow reactor in order to study the capacity and variable affecting the concentration of product methyl ester comparing with batch reactor.

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APPENDICES

APPENDIX A

EXPERIMENTAL AND DATA ANALYSIS

A-1 Acid Value (Free fatty acids content), AOCS Official Method Cd-3d-63

1. Weigh of sample 10-20 g. in conical flasks 250 ml.
2. Add mix equal volumes of 95% ethanol and iso-propanol molar ratio 1:1 50 ml.
3. Solution is titrated with 0.1 N potassium hydroxide solutions.
4. 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-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 95% ethanol.
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 weigh 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 weigh of the fatty acids (M) may be calculated:

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

Where

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

Note: The saponification value (S.V), which is related to the molecular weigh 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-3 Calculation molecular weight of palm fatty acid

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

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

$$\text{S.V} = \frac{56.1 \times 0.5 \times (22-7.5)}{2}$$

$$= 203.3625$$

For the determination of the mean molecular weigh 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 weigh of the fatty acids (M) may be calculated:

Where

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

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

$$= \frac{56108 - (12.67)\,(\text{S.V. neutral})}{\text{S.V. neutral}}$$

$$\text{S.V. neutral} = \frac{56108 \times \text{S.V}}{56108+12.67(\text{A.V})}$$

$$= \frac{56108 \times 203.3625}{56108+12.67(147.5)}$$

$$= 196.808$$

$$\text{M.W} = \frac{56108 - 12.67(196.808)}{196.808}$$

$$\text{M.W} = 272.42$$

A-4 Calculation molecular weight of palm stearin

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

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

$$\text{S.V} = \frac{56.1 \times 0.5 \times (29.7-7.9)}{2}$$

$$= 207.34$$

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

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

$$= \frac{56108 - (12.67)\ (S.V.\ neutral)}{S.V.\ neutral}$$

$$S.V.\ neutral = \frac{56108 \times S.V}{56108+12.67(A.V)}$$

$$= \frac{56108 \times 207.34}{56108+12.67(0.36)}$$

$$= 207.32$$

$$M.W = \frac{56108 - 12.67(207.32)}{207.32}$$

$$M.W = 257.96$$

Mean Molecular weight of triglyceride

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

$$= (3)\ (257.96) + 38$$

$$= 811.88$$

APPENDIX B

CALCULATION OF CONCENTRATION OF METHYL ESTER

B-1 Response factor of methyl ester and fatty acid

The response factor is defined as

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

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

$$\text{Response factor of methyl myristate} = \frac{6.6526 \times 0.0711}{3.5916 \times 0.0968}$$

$$\text{R.F}_{\text{methyl myristate}} = 1.3601 \sim 1.36$$

$$\text{Response factor of methyl palmitate} = \frac{5.4610 \times 0.0711}{3.4754 \times 0.0959}$$

$$\text{R.F}_{\text{methyl palmitate}} = 1.1652 \sim 1.16$$

$$\text{Response factor of methyl stearate} = \frac{5.7430 \times 0.0710}{3.5511 \times 0.1033}$$

$$\text{R.F}_{\text{methyl stearate}} = 1.1103 \sim 1.11$$

$$\text{Response factor of methyl oleate} = \frac{5.9501 \times 0.0712}{3.8526 \times 0.0909}$$

$$\text{R.F}_{\text{methyl oleate}} = 1.2094 \sim 1.21$$

$$\text{Response factor of methyl linoleate} = \frac{11.1569 \times 0.0720}{5.8254 \times 0.0924}$$

$$\text{R.F}_{\text{methyl linoleate}} = 1.4910 \sim 1.49$$

$$\text{Response factor of palmitic acids} = \frac{7.2170 \times 0.0710}{4.9466 \times 0.0976}$$

$$\text{R.F}_{\text{palmitic acids}} = 1.0694 \sim 1.07$$

$$\text{Response factor of stearic acids} = \frac{5.2598 \times 0.0709}{4.2328 \times 0.1002}$$

$$\text{R.F}_{\text{stearic acid acids}} = 0.8788 \sim 0.88$$

$$\text{Response factor of oleic acids} = \frac{4.5322 \times 0.0709}{3.4369 \times 0.0933}$$

$$\text{R.F}_{\text{oleaic acids}} = 1.0015 \sim 1.00$$

B-2 Analysis of methyl ester and free fatty acid

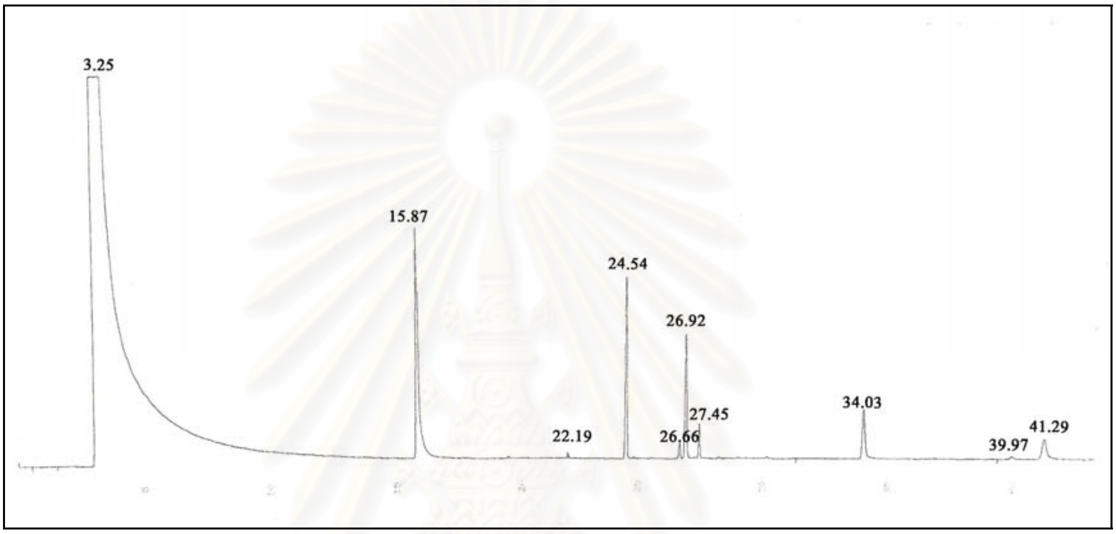
Analysis of methyl ester and free fatty acids in product by used gas chromatography (GC). The retention time of each methyl esters are different. Therefore, for find the type of methyl ester by compare retention time of each methyl ester with methyl ester standard. The retention time are shown in Table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

Table B-1 Retention time of methyl esters and fatty acids in GC chromatogram

Number of peak	Retention time (min)	Peak of sample
1	3.25	N-heptane
2	15.87	Methyl decanoate
3	22.19	Methyl myristate
4	24.54	Methyl palmitate
5	26.66	Methyl stearate
6	26.92	Methyl oleate
7	27.45	Methyl linoleate
8	34.03	Palmitic acid
9	39.97	Stearic acid
10	41.29	Oleic acid

B-3 GC chromatogram of methyl ester and fatty acid from experiment

From experiment of two-step using acid and alkaline catalysts can see main methyl esters and fatty acids.



RT	AREA	BC	AREA%
3.25	128.366		89.0522
15.87	5.9433		4.12307
22.19	0.3300	V	0.22893
24.54	3.0248	V	2.09841
26.66	0.4335	T	0.30073
26.92	2.2485	T	1.55986
27.45	0.8561		0.59391
34.03	1.5438		1.07099
39.97	0.2051	T	0.14229
41.29	1.0693	V	0.74181
43.69	0.1266		0.08783

11 PEAKS > AREA/HT REJECT

Figure B-4 Chromatogram for methyl ester and fatty acid at condition: Palm fatty acids reactant, 100%mol excess of methanol from its stoichometric, 1% wt H_2SO_4, 70 min and 60°C

Example1. From figure B-4, find concentration of methyl ester and fatty acid at 200 % mole of excess methanol from its stoichiometic ratio, temperature of 60 °C, 70 min using acid catalyst. Product of 0.1066 added to 1.5078 g of methyl decanoate solution.

Note that: In methyl decanoate solution 1.5078 g has 0.0720 g of methyl decanoate.

$$\%\text{Methyl esters or free fatty acids} = \frac{\text{g of total methyl esters or fatty acids}}{\text{g of sample}} \times 100$$

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

$$\text{g of methyl myristate} = \frac{0.3300}{5.9433} \times \frac{0.0720}{1.36}$$

$$= 0.0040$$

$$\text{g of methyl palmitate} = \frac{3.0248}{5.9433} \times \frac{0.0720}{1.16}$$

$$= 0.0316$$

$$\text{g of methyl stearate} = \frac{0.4335}{5.9433} \times \frac{0.0720}{1.11}$$

$$= 0.0047$$

$$\text{g of methyl oleate} = \frac{2.2485}{5.9433} \times \frac{0.0720}{1.21}$$

$$= 0.0225$$

$$\text{g of methyl linoleate} = \frac{0.8561}{5.9433} \times \frac{0.0720}{1.49}$$

$$= 0.0069$$

Also; g of total methyl esters $= 0.0040+0.0316+0.0047+0.0225+0.0069$

$= 0.0697$

%Methyl esters $= \frac{0.0697}{0.1066} \times 100$

$=$ **65.3836 % ~ 65.04 %**

g of palmitic acid $= \frac{1.5438}{5.9433} \times \frac{0.0720}{1.07}$

$= 0.0175$

g of stearic acid $= \frac{0.2051}{5.9433} \times \frac{0.0720}{0.88}$

$= 0.0028$

g of oleic acid $= \frac{1.0693}{5.9433} \times \frac{0.0720}{1.00}$

$= 0.01295$

Also; g of total fatty acids $= 0.0175+0.0028+0.01295$

$= 0.03325$

%Free fatty acids $= \frac{0.03325}{0.1066} \times 100$

$=$ **31.1914 % ~ 31.19 %**

APPENDIX C

EXPERIMENTAL DATA ANALYSIS

C-1 Experimental data of acid-catalyzed esterification reaction time

Table C-1.1 The concentration of methyl ester and fatty acid (% wt) from 100% FFA use 1% H_2SO_4, 100% mole of excess methanol from its stoichiometric ratio at 60°C

Time	**100% FFA**							
	Concentration of methyl esters (%wt)				**Concentration of fatty acid (%wt)**			
	Ex1	**Ex2**	**Average**	**S.D**	**Ex1**	**Ex2**	**Average**	**S.D**
0	0.00	0.00	0.00	0.00	98.21	98.21	98.21	0.00
10	48.00	50.04	49.02	1.44	50.29	46.54	48.41	2.65
20	49.46	52.84	51.15	2.38	45.80	44.13	44.97	1.18
30	56.04	49.54	52.79	4.60	41.73	45.97	43.85	3.00
40	49.14	56.98	53.06	5.54	38.38	45.37	41.87	4.95
50	59.40	56.39	57.89	2.13	35.19	41.11	38.15	4.18
60	61.59	59.36	60.47	1.58	35.18	34.83	35.01	0.25
70	65.04	64.26	64.65	0.55	31.19	31.74	31.47	0.39
80	62.66	66.02	64.34	2.37	34.68	28.50	31.59	4.37
90	64.50	62.45	63.48	1.45	34.59	30.75	32.67	2.72
100	61.54	66.53	64.04	3.53	32.50	29.24	30.87	2.30
110	66.66	62.34	64.50	3.05	33.16	29.70	31.43	2.45
120	66.85	61.75	64.30	3.61	34.13	30.14	32.13	2.83

Table C-1.2 The concentration of methyl ester and fatty acid (% wt) from 0% FFA use 1% H_2SO_4, 100% mole of excess methanol from its stoichiometric ratio at 60°C

Time	0% FFA							
	Concentration of methyl ester (%wt)				Concentration of fatty acid (%wt)			
	Ex1	Ex2	Average	S.D	Ex1	Ex2	Average	S.D
0	0.00	0.00	0.00	0.00	0.16	0.16	0.16	0.00
10	0.70	3.39	2.05	1.90	0.05	0.07	0.06	0.01
20	1.11	3.64	2.38	1.79	0.04	0.05	0.04	0.01
30	2.82	4.46	3.64	1.16	0.03	0.03	0.03	0.00
40	6.06	7.10	6.58	0.73	0.01	0.02	0.01	0.00
50	6.03	7.36	6.69	0.94	0.01	0.01	0.01	0.00
60	9.04	8.45	8.74	0.42	0.01	0.00	0.00	0.00
70	8.02	8.43	8.23	0.29	0.00	0.00	0.00	0.00
80	8.15	8.65	8.40	0.36	0.00	0.00	0.00	0.00
90	7.84	8.46	8.15	0.44	0.00	0.00	0.00	0.00
100	8.01	8.56	8.28	0.39	0.00	0.00	0.00	0.00
110	8.36	8.81	8.59	0.32	0.00	0.00	0.00	0.00
120	8.10	8.56	8.33	0.33	0.00	0.00	0.00	0.00

Table C-1.3 The concentration of methyl ester and fatty acid (% wt) from 10% FFA use 1% H_2SO_4, 100% mole of excess methanol from its stoichiometric ratio at 60°C

Time	**10% FFA**							
	Concentration of methyl ester (%wt)				**Concentration of fatty acid (%wt)**			
	Ex1	**Ex2**	**Average**	**S.D**	**Ex1**	**Ex2**	**Average**	**S.D**
0	0.00	0.00	0.00	0.00	9.82	9.82	9.82	0.00
10	7.48	7.64	7.56	0.11	4.61	11.07	7.84	4.57
20	11.68	9.49	10.59	1.55	4.22	8.76	6.49	3.21
30	12.94	10.66	11.80	1.61	7.85	4.30	6.07	2.51
40	12.86	9.59	11.22	2.32	3.69	6.80	5.24	2.20
50	11.35	10.71	11.03	0.46	3.80	6.27	5.04	1.74
60	12.64	11.69	12.17	0.67	4.93	3.88	4.41	0.74
70	13.03	12.88	12.96	0.11	3.76	3.27	3.51	0.34
80	12.35	13.07	12.71	0.50	3.36	3.60	3.48	0.17
90	13.57	12.98	13.27	0.42	3.27	3.11	3.19	0.11
100	12.59	12.42	12.51	0.12	3.79	3.08	3.43	0.50
110	11.52	13.23	12.37	1.21	2.04	4.36	3.20	1.64
120	12.34	13.39	12.86	0.74	4.76	3.23	3.99	1.08

Table C-1.4 The concentration of methyl ester and fatty acid (% wt) from 15% FFA use 1% H_2SO_4, 100% mole of excess methanol from its stoichiometric ratio at 60°C

Time	15% FFA							
	Concentration of methyl ester (%wt)				Concentration of fatty acid (%wt)			
	Ex1	Ex2	Average	S.D	Ex1	Ex2	Average	S.D
0	0.00	0.00	0.00	0.00	14.73	14.73	14.73	0.00
10	9.98	10.43	10.21	0.32	7.22	14.39	10.80	5.07
20	11.69	11.40	11.54	0.20	4.84	13.98	9.41	6.46
30	14.89	13.50	14.20	0.99	9.16	9.29	9.22	0.09
40	13.74	15.60	14.67	1.32	6.73	8.80	7.77	1.46
50	14.53	16.92	15.72	1.70	3.93	7.14	5.53	2.27
60	15.20	14.92	15.06	0.20	6.36	6.65	6.51	0.21
70	14.30	15.74	15.02	1.01	3.27	6.37	4.82	2.20
80	14.71	16.03	15.37	0.94	4.21	6.22	5.21	1.42
90	14.70	17.69	16.19	2.12	3.65	4.95	4.30	0.92
100	15.24	15.29	15.26	0.03	6.07	5.71	5.89	0.26
110	14.91	14.15	14.53	0.53	2.87	7.19	5.03	3.06
120	14.72	18.65	16.68	2.78	7.09	3.83	5.46	2.31

Table C-1.5 The concentration of methyl ester and fatty acid (% wt) from 25% FFA use 1% H_2SO_4, 100% mole of excess methanol from its stoichiometric ratio at 60°C

Time	**25% FFA**							
	Concentration of methyl ester (%wt)				**Concentration of fatty acid (%wt)**			
	Ex1	**Ex2**	**Average**	**S.D**	**Ex1**	**Ex2**	**Average**	**S.D**
0	0.00	0.00	0.00	0.00	24.55	24.55	24.55	0.00
10	16.33	11.79	14.06	3.21	9.30	19.46	14.38	7.18
20	14.21	14.66	14.44	0.32	9.50	15.51	12.50	4.25
30	17.24	16.52	16.88	0.51	7.46	16.77	12.11	6.59
40	15.09	17.38	16.24	1.62	7.16	13.20	10.18	4.27
50	21.91	15.05	18.48	4.85	10.44	11.88	11.16	1.02
60	17.75	21.48	19.62	2.64	11.64	7.99	9.81	2.58
70	22.20	22.22	22.21	0.01	8.17	8.11	8.14	0.04
80	19.28	23.56	21.42	3.03	8.66	9.81	9.23	0.81
90	21.22	23.57	22.39	1.66	9.38	9.91	9.64	0.38
100	21.22	22.38	21.80	0.82	9.73	9.24	9.48	0.35
110	21.26	23.47	22.37	1.56	8.82	7.65	8.24	0.83
120	21.19	22.89	22.04	1.20	9.68	8.10	8.89	1.12

C-2 Experimental data of excess methanol on acid esterification

Table C-2.1 The concentration of methyl ester (% wt) from 0%, 10%, 15%, 25% and 100% FFA use 1% H_2SO_4 (based on oil weight) at the reaction time 70 minutes

% FFA	**%Excess methanol**	**Concentration of methyl ester (%wt)**				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0% FFA	100%	9.04	8.45	-	8.74	0.42
0% FFA	200%	9.79	9.44	8.71	9.31	0.55
0% FFA	300%	9.99	10.12	10.02	10.04	0.07
10% FFA	100%	13.03	12.88	-	12.96	0.34
10% FFA	200%	12.35	16.36	14.28	14.33	2.01
10% FFA	300%	13.73	16.84	16.01	15.53	1.61
15% FFA	100%	14.30	15.74	-	15.02	1.01
15% FFA	200%	15.73	14.52	15.26	15.17	0.61
15% FFA	300%	16.24	16.17	16.32	16.24	0.07
25% FFA	100%	22.20	22.22	-	22.21	0.01
25% FFA	200%	22.30	23.23	24.15	24.15	0.92
25% FFA	300%	23.25	25.83	26.54	25.21	1.73
100% FFA	100%	65.04	64.26	-	64.65	0.55
100% FFA	200%	66.84	65.59	66.03	66.15	0.63
100% FFA	300%	69.50	67.49	70.11	69.03	1.37

Table C-2.2 The concentration of free fatty acid (% wt) from 0%, 10%, 15%, 25% and 100% FFA use 1% H_2SO_4 (based on oil weight) at the reaction time 70 minutes

% FFA	**%Excess methanol**	**Concentration of free fatty acid (%wt)**				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0% FFA	100%	0.01	0.00	-	0.00	0.00
0% FFA	200%	0.00	0.00	0.00	0.00	0.00
0% FFA	300%	0.00	0.00	0.00	0.00	0.00
10% FFA	100%	3.76	3.27	-	3.51	0.34
10% FFA	200%	3.73	2.72	3.28	3.24	0.51
10% FFA	300%	2.60	3.77	3.15	3.17	0.59
15% FFA	100%	3.27	6.37	-	4.82	2.20
15% FFA	200%	2.01	5.92	3.86	3.93	1.96
15% FFA	300%	3.29	3.89	3.58	3.59	0.30
25% FFA	100%	8.17	8.11	-	8.14	0.04
25% FFA	200%	6.71	6.07	5.90	6.23	0.43
25% FFA	300%	5.62	4.27	4.35	4.75	0.76
100% FFA	100%	31.19	31.74	-	31.47	0.39
100% FFA	200%	24.51	31.28	28.96	28.25	3.44
100% FFA	300%	24.41	27.39	25.16	25.65	1.55

Table C-2.3 The concentration of methyl ester (% wt) from 0%, 10%, 15%, 25% and 100% FFA use 2% H_2SO_4 (based on oil weight) at the reaction time 70 minutes

% FFA	%Excess methanol	Concentration of methyl ester (%wt)				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0% FFA	100%	9.37	10.48	10.07	9.97	0.56
0% FFA	200%	10.84	11.07	12.45	11.46	0.87
0% FFA	300%	11.33	12.39	12.83	12.18	0.77
10% FFA	100%	15.17	13.75	16.49	15.14	1.37
10% FFA	200%	19.53	16.49	16.90	17.64	1.65
10% FFA	300%	19.07	19.08	20.42	19.52	0.78
15% FFA	100%	15.61	17.23	18.03	16.96	1.23
15% FFA	200%	16.91	19.64	21.48	19.34	2.30
15% FFA	300%	18.99	19.69	21.37	20.02	1.22
25% FFA	100%	21.44	26.46	27.02	24.97	3.07
25% FFA	200%	25.53	30.43	29.14	28.36	2.54
25% FFA	300%	28.52	34.65	30.94	31.37	3.08
100% FFA	100%	70.49	71.65	68.05	70.06	1.84
100% FFA	200%	77.02	81.29	74.61	77.64	3.38
100% FFA	300%	81.12	80.08	82.77	81.59	1.03

Table C-2.4 The concentration of free fatty acid (% wt) from 0%, 10%, 15%, 25% and 100% FFA use 2% H_2SO_4 (based on oil weight) at the reaction time 70 minutes

% FFA	%Excess methanol	Concentration of free fatty acid (%wt)				
		Ex1	Ex2	Ex3	Average	S.D
0% FFA	100%	0.00	0.00	0.00	0.00	0.00
0% FFA	200%	0.00	0.00	0.00	0.00	0.00
0% FFA	300%	0.00	0.00	0.00	0.00	0.00
10% FFA	100%	2.59	1.69	2.87	2.38	0.62
10% FFA	200%	1.46	1.86	1.31	1.54	0.28
10% FFA	300%	1.21	0.29	0.45	0.65	0.49
15% FFA	100%	3.19	2.86	2.66	2.90	0.27
15% FFA	200%	2.00	1.60	1.37	1.65	0.32
15% FFA	300%	1.22	0.96	0.86	1.01	0.18
25% FFA	100%	5.08	5.55	4.94	5.19	0.32
25% FFA	200%	3.62	3.21	3.87	3.57	0.33
25% FFA	300%	1.33	1.50	1.41	1.41	0.09
100% FFA	100%	26.50	25.29	25.11	25.63	0.75
100% FFA	200%	17.09	20.10	16.04	17.74	2.11
100% FFA	300%	13.29	12.34	14.74	13.45	1.21

Table C-2.5 The concentration of methyl ester (% wt) from 0%, 10%, 15%, 25% and 100% FFA use 1% H_2SO_4 (based on total weight) at the reaction time 70 minutes

% FFA	**%Excess methanol**	**Concentration of methyl ester (%wt)**				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0% FFA	100%	8.94	8.37	7.97	8.43	0.49
0% FFA	200%	9.63	9.04	10.77	9.81	0.88
0% FFA	300%	10.37	11.75	9.97	10.70	0.93
10% FFA	100%	13.85	13.23	14.25	13.78	0.51
10% FFA	200%	14.19	15.70	15.64	15.18	0.86
10% FFA	300%	15.69	15.97	16.51	16.06	0.42
15% FFA	100%	15.77	14.39	15.43	15.20	0.72
15% FFA	200%	16.40	15.49	15.87	15.92	0.46
15% FFA	300%	18.71	18.13	17.05	17.96	0.84
25% FFA	100%	22.37	22.11	23.39	22.63	0.68
25% FFA	200%	24.00	23.96	23.85	23.94	0.08
25% FFA	300%	26.12	27.47	27.51	27.03	0.79
100% FFA	100%	66.48	66.37	67.48	66.78	0.61
100% FFA	200%	70.29	72.31	69.29	70.63	1.54
100% FFA	300%	75.89	74.60	76.44	75.64	0.95

Table C-2.6 The concentration of free fatty acid (% wt) from 0%, 10%, 15%, 25% and 100% FFA use 1% H_2SO_4 (based on total weight) at the reaction time 70 minutes

% FFA	**%Excess methanol**	**Concentration of free fatty acid (%wt)**				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0% FFA	100%	0.00	0.00	0.00	0.00	0.00
0% FFA	200%	0.00	0.00	0.00	0.00	0.00
0% FFA	300%	0.00	0.00	0.00	0.00	0.00
10% FFA	100%	3.33	3.63	3.29	3.42	0.18
10% FFA	200%	3.01	2.97	3.19	3.05	0.12
10% FFA	300%	2.86	2.73	3.04	2.88	0.16
15% FFA	100%	4.60	4.36	4.85	4.60	0.24
15% FFA	200%	3.32	3.14	3.33	3.27	0.10
15% FFA	300%	3.15	3.26	3.92	3.44	0.42
25% FFA	100%	7.61	7.07	7.34	7.34	0.27
25% FFA	200%	6.54	6.62	6.29	6.48	0.17
25% FFA	300%	4.87	4.28	4.58	4.57	0.30
100% FFA	100%	30.02	29.79	30.13	29.98	0.17
100% FFA	200%	24.58	24.59	26.38	25.19	1.04
100% FFA	300%	19.28	20.39	21.31	20.33	1.01

Table C-2.7 The concentration of methyl ester (% wt) from 0%, 10%, 15%, 25% and 100% FFA use 2% H_2SO_4 (based on total weight) at the reaction time 70 minutes

% FFA	**%Excess methanol**	**Concentration of methyl ester (%wt)**				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0% FFA	100%	11.04	11.48	10.47	11.00	0.51
0% FFA	200%	15.48	15.39	16.02	15.63	0.34
0% FFA	300%	19.22	19.84	20.27	19.78	0.53
10% FFA	100%	17.17	14.25	16.86	16.09	1.61
10% FFA	200%	19.49	19.48	19.23	19.40	0.15
10% FFA	300%	22.11	22.72	22.85	22.56	0.39
15% FFA	100%	18.58	17.37	18.94	18.30	0.82
15% FFA	200%	22.98	22.48	22.64	22.70	0.26
15% FFA	300%	24.35	24.76	24.10	24.41	0.33
25% FFA	100%	27.33	26.09	26.27	26.56	0.67
25% FFA	200%	32.36	32.37	32.40	32.38	0.02
25% FFA	300%	34.84	34.03	34.48	34.45	0.40
100% FFA	100%	79.38	78.59	79.02	79.00	0.40
100% FFA	200%	86.67	83.27	86.39	85.44	1.89
100% FFA	300%	90.27	89.30	93.60	91.06	2.26

Table C-2.8 The concentration of free fatty acid (% wt) from 0%, 10%, 15%, 25% and 100% FFA use 2% H_2SO_4 (based on total weight) at the reaction time 70 minutes

		Concentration of free fatty acid (%wt)				
% FFA	**%Excess methanol**	**Ex1**	**Ex2**	**Ex3**	**Average**	**S.D**
0% FFA	100%	0.00	0.00	0.00	0.00	0.00
0% FFA	200%	0.00	0.00	0.00	0.00	0.00
0% FFA	300%	0.00	0.00	0.00	0.00	0.00
10% FFA	100%	1.93	1.48	1.86	1.76	0.25
10% FFA	200%	0.85	0.83	0.84	0.84	0.01
10% FFA	300%	0.51	0.59	0.60	0.57	0.05
15% FFA	100%	1.04	1.27	1.47	1.26	0.22
15% FFA	200%	0.96	0.95	0.93	0.95	0.01
15% FFA	300%	0.91	0.64	0.79	0.78	0.14
25% FFA	100%	3.95	4.01	3.65	3.87	0.19
25% FFA	200%	1.74	1.49	1.93	1.72	0.22
25% FFA	300%	0.98	0.83	1.12	0.98	0.15
100% FFA	100%	17.39	16.03	18.49	17.31	1.23
100% FFA	200%	10.38	9.39	11.74	10.50	1.18
100% FFA	300%	5.49	4.03	4.40	4.64	0.76

C-3 Experimental data of acid catalyzed concentration

Table C-3.1 The concentration of methyl ester (% wt) from 0%, 10%, 15%, 25% and 100% FFA use 300% excess methanol from its stoichiometric ratio at the reaction time 70 minutes (catalyst based on oil weight)

% FFA	**% H_2SO_4 (based on oil weight)**	**Concentration of methyl ester (%wt)**				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0% FFA	1%	9.99	10.12	10.02	10.04	0.07
0% FFA	2%	11.33	12.39	12.83	12.18	0.77
10% FFA	1%	13.73	16.84	16.01	15.53	1.61
10% FFA	2%	19.07	13.03	20.42	19.52	0.78
15% FFA	1%	16.24	16.17	16.32	16.24	0.07
15% FFA	2%	18.99	19.69	21.37	20.02	1.22
25% FFA	1%	23.25	23.83	25.83	25.21	1.73
25% FFA	2%	28.52	34.65	30.94	31.37	3.08
100% FFA	1%	69.50	67.49	70.11	69.03	1.37
100% FFA	2%	81.12	80.08	82.77	81.59	1.03

Table C-3.2 The concentration of free fatty acid (% wt) from 0%, 10%, 15%, 25% and 100% FFA use 300% excess methanol from its stoichiometric ratio at the reaction time 70 minutes (catalyst based on oil weight)

% FFA	**% H_2SO_4 (based on oil weight)**	**Concentration of free fatty acid (%wt)**				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0% FFA	1%	0.00	0.00	0.00	0.00	0.00
0% FFA	2%	0.00	0.00	0.00	0.00	0.00
10% FFA	1%	2.60	3.77	3.15	3.17	0.59
10% FFA	2%	1.21	0.29	0.45	0.65	0.49
15% FFA	1%	3.29	3.89	3.58	3.59	0.30
15% FFA	2%	1.22	0.96	0.86	1.01	0.18
25% FFA	1%	5.62	4.27	4.35	4.75	0.76
25% FFA	2%	1.33	1.50	1.41	1.41	0.09
100% FFA	1%	24.41	27.39	25.16	25.65	1.55
100% FFA	2%	13.29	12.34	14.74	13.45	1.21

Table C-3.3 The concentration of methyl ester (% wt) from 0%, 10%, 15%, 25% and 100% FFA use 300% excess methanol from its stoichiometric ratio at the reaction time 70 minutes (catalyst based on total weight)

% FFA	**% H_2SO_4 (based on total weight)**	**Concentration of methyl ester (%wt)**				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0% FFA	1%	10.37	11.75	9.97	10.70	0.93
0% FFA	2%	19.22	19.84	20.27	19.78	0.53
10% FFA	1%	15.69	15.97	16.51	16.06	0.42
10% FFA	2%	22.11	22.72	22.85	22.56	0.39
15% FFA	1%	18.71	18.13	17.05	17.96	0.84
15% FFA	2%	24.35	24.76	24.10	24.41	0.33
25% FFA	1%	26.12	27.47	27.51	27.03	0.79
25% FFA	2%	34.84	34.03	34.48	34.45	0.40
100% FFA	1%	75.89	74.60	76.44	75.64	0.95
100% FFA	2%	90.27	89.30	93.60	91.06	2.26

Table C-3.4 The concentration of free fatty acid (% wt) from 0%, 10%, 15%, 25% and 100% FFA use 300% excess methanol from its stoichiometric ratio at the reaction time 70 minutes (catalyst based on total weight)

% FFA	**% H_2SO_4 (based on total weight)**	**Concentration of free fatty acid (%wt)**				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0% FFA	1%	0.00	0.00	0.00	0.00	0.00
0% FFA	2%	0.00	0.00	0.00	0.00	0.00
10% FFA	1%	2.86	2.73	3.04	2.88	0.16
10% FFA	2%	0.51	0.59	0.60	0.57	0.05
15% FFA	1%	3.15	3.26	3.92	3.44	0.42
15% FFA	2%	0.91	0.64	0.79	0.78	0.14
25% FFA	1%	4.87	4.28	4.58	4.57	0.30
25% FFA	2%	0.98	0.83	1.12	0.98	0.15
100% FFA	1%	19.28	20.39	21.31	20.33	1.01
100% FFA	2%	5.49	4.03	4.40	4.64	0.76

C-4 Experimental data of transesterification reaction time

Table C-4.1 The concentration of methyl ester (% wt) from 10% FFA use 1% KOH, 100% mole of excess methanol from its stoichiometric ratio at 60°C

Time	**10% FFA**			
	Concentration of methyl ester (%wt)			
	Ex1	**Ex2**	**Average**	**S.D**
0	0.00	0.00	0.00	0.00
10	75.38	82.33	78.86	4.91
20	91.32	96.70	94.01	3.80
30	91.01	93.22	92.12	1.56
40	90.05	92.84	91.44	1.97
50	91.67	88.71	90.19	2.09
60	87.42	89.19	88.30	1.26
70	87.58	89.18	88.38	1.13
80	87.14	88.50	87.82	0.96
90	87.22	88.25	87.74	0.72
100	91.05	87.02	89.04	2.85
110	88.68	88.38	88.53	0.21
120	90.06	87.32	88.69	1.94

Table C-4.2 The concentration of methyl ester (% wt) from 15% FFA use 1% KOH, 100% mole of excess methanol from its stoichiometric ratio at 60°C

Time	**15% FFA**			
	Concentration of methyl ester (%wt)			
	Ex1	**Ex2**	**Average**	**S.D**
0	0.00	0.00	0.00	0.00
10	80.56	74.54	77.55	4.26
20	91.47	95.49	93.48	2.84
30	90.41	89.40	89.91	0.71
40	90.07	88.84	89.45	0.87
50	88.79	87.85	88.32	0.67
60	86.91	84.13	85.52	1.96
70	88.61	83.36	85.99	3.71
80	85.04	84.04	84.54	0.70
90	85.41	86.93	86.17	1.08
100	86.51	87.12	86.81	0.43
110	83.81	89.22	86.52	3.83
120	84.05	87.78	85.91	2.64

Table C-4.3 The concentration of methyl ester (% wt) from 25% FFA use 1% KOH, 100% mole of excess methanol from its stoichiometric ratio at 60°C

Time	**25% FFA**			
	Concentration of methyl ester (%wt)			
	Ex1	**Ex2**	**Average**	**S.D**
0	0.00	0.00	0.00	0.00
10	81.85	74.50	78.17	5.20
20	80.63	85.30	82.97	3.30
30	78.00	81.84	79.92	2.71
40	74.35	81.76	78.06	5.24
50	77.57	78.71	78.14	0.81
60	76.65	77.19	76.92	0.39
70	77.54	76.86	77.20	0.48
80	75.51	77.12	76.31	1.13
90	76.06	76.37	76.21	0.21
100	75.53	76.61	76.07	0.76
110	73.16	77.64	75.40	3.17
120	74.33	78.20	76.27	2.74

C-5 Experimental data of excess methanol on transesterification

Table C-5.1 The concentration of methyl ester (% wt) from 10%, 15% and 25% FFA use 0.5% KOH (based on oil weight) at the reaction time 60 minutes

% FFA	**%Excess methanol**	**Concentration of methyl ester (%wt)**				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
10% FFA	100%	87.42	89.19	-	88.31	1.26
10% FFA	200%	86.61	82.50	84.54	84.55	2.91
10% FFA	300%	79.75	82.56	82.04	81.45	1.99
15% FFA	100%	86.91	84.13	-	85.52	1.96
15% FFA	200%	86.14	81.02	83.30	83.49	3.62
15% FFA	300%	81.49	83.33	81.82	82.21	1.30
25% FFA	100%	76.65	77.19	-	76.92	0.39
25% FFA	200%	74.90	74.51	73.73	74.38	0.28
25% FFA	300%	75.36	67.24	72.26	71.62	5.74

Table C-5.2 The concentration of methyl ester (% wt) from 10%, 15% and 25% FFA use 0.5% KOH (based on total weight) at the reaction time 60 minutes

% FFA	**%Excess methanol**	**Concentration of methyl ester (%wt)**				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
10% FFA	100%	89.48	89.65	88.72	89.28	0.50
10% FFA	200%	86.20	86.59	87.43	86.74	0.63
10% FFA	300%	83.98	83.32	82.86	83.39	0.57
15% FFA	100%	86.80	87.39	87.12	87.10	0.29
15% FFA	200%	84.85	84.92	84.74	84.84	0.10
15% FFA	300%	83.26	84.14	82.48	83.29	0.83
25% FFA	100%	80.02	81.47	81.53	81.01	0.86
25% FFA	200%	78.61	78.36	76.85	77.94	0.95
25% FFA	300%	76.37	75.18	74.02	75.19	1.17

Table C-5.3 The concentration of methyl ester from 10% FFA use 0.5% KOH (based on oil weight), 100% mole of excess methanol from its stoichiometric ratio at 60°C

Time	**10% FFA**				
	Concentration of methyl ester (%wt)				
	Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0	0.00	0.00	-	0.00	0.00
20	91.32	96.70	-	94.01	3.80
40	90.05	92.84	-	91.44	1.97
60	87.42	89.19	-	88.31	1.26
80	87.14	88.50	-	87.82	0.96
100	91.05	87.02	-	89.04	2.85
120	90.06	87.32	-	88.69	1.94

Table C-5.4 The concentration of methyl ester from 10% FFA use 0.5% KOH (based on oil weight), 200% mole of excess methanol from its stoichiometric ratio at 60°C

Time	**10% FFA**				
	Concentration of methyl ester (%wt)				
	Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0	0.00	0.00	0.00	0.00	0.00
20	88.37	88.38	90.37	89.04	1.15
40	95.75	94.27	96.37	95.46	1.08
60	86.61	82.50	84.54	84.55	2.06
80	82.62	81.39	84.29	82.77	1.46
100	82.18	83.83	82.36	82.79	0.91
120	82.36	82.85	83.38	82.86	0.51

Table C-5.5 The concentration of methyl ester from 10% FFA use 0.5% KOH (based on oil weight), 300% mole of excess methanol from its stoichiometric ratio at 60°C

Time	**10% FFA**				
	Concentration of methyl ester (%wt)				
	Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0	0.00	0.00	0.00	0.00	0.00
20	85.31	84.28	86.83	85.47	1.28
40	93.45	93.97	91.74	93.05	1.17
60	79.75	82.56	82.04	81.45	1.99
80	78.39	80.88	79.94	79.74	1.25
100	76.40	77.34	80.39	78.04	2.09
120	76.73	78.39	79.11	78.08	1.22

Table C-5.6 The concentration of methyl ester from 15% FFA use 0.5% KOH (based on oil weight), 100% mole of excess methanol from its stoichiometric ratio at 60°C

Time	**15% FFA**				
	Concentration of methyl ester (%wt)				
	Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0	0.00	0.00	-	0.00	0.00
20	91.47	95.49	-	93.48	2.84
40	90.07	88.84	-	89.45	0.87
60	86.91	84.13	-	85.52	1.96
80	85.04	84.04	-	84.54	0.70
100	86.51	87.12	-	86.81	0.43
120	84.05	87.78	-	85.91	2.64

Table C-5.7 The concentration of methyl ester from 15% FFA use 0.5% KOH (based on oil weight), 200% mole of excess methanol from its stoichiometric ratio at 60°C

Time	15% FFA				
	Concentration of methyl ester (%wt)				
	Ex1	Ex2	Ex3	Average	S.D
0	0.00	0.00	0.00	0.00	0.00
20	91.78	87.33	92.38	90.50	2.76
40	90.27	93.00	91.87	91.71	1.37
60	86.14	81.02	83.30	83.49	3.62
80	85.38	83.09	80.28	82.92	2.56
100	83.63	81.75	82.66	82.68	0.94
120	83.28	82.59	82.93	82.94	0.35

Table C-5.8 The concentration of methyl ester from 15% FFA use 0.5% KOH (based on oil weight), 300% mole of excess methanol from its stoichiometric ratio at 60°C

Time	15% FFA				
	Concentration of methyl ester (%wt)				
	Ex1	Ex2	Ex3	Average	S.D
0	0.00	0.00	0.00	0.00	0.00
20	89.94	87.37	89.93	89.08	1.48
40	88.70	89.53	91.27	89.83	1.31
60	81.49	83.33	81.82	82.21	1.30
80	78.29	79.78	79.03	79.03	0.74
100	77.04	79.11	78.50	78.22	1.06
120	78.28	79.75	78.10	78.71	0.90

Table C-5.9 The concentration of methyl ester from 25% FFA use 0.5% KOH (based on oil weight), 100% mole of excess methanol from its stoichiometric ratio at 60°C

Time	**25% FFA**				
	Concentration of methyl ester (%wt)				
	Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0	0.00	0.00	-	0.00	0.00
20	80.63	85.3	-	82.97	3.30
40	74.35	81.76	-	78.06	5.24
60	76.65	77.19	-	76.92	0.39
80	75.51	77.12	-	76.31	1.13
100	75.53	76.61	-	76.07	0.76
120	74.33	78.20	-	76.27	2.74

Table C-5.10 The concentration of methyl ester from 25% FFA use 0.5% KOH (based on oil weight), 200% mole of excess methanol from its stoichiometric ratio at 60°C

Time	**25% FFA**				
	Concentration of methyl ester (%wt)				
	Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0	0.00	0.00	0.00	0.00	0.00
20	76.04	79.76	80.39	78.73	2.35
40	80.40	79.83	81.04	80.42	0.61
60	74.90	74.51	73.73	74.38	0..28
80	73.17	73.27	73.67	73.37	0.26
100	74.23	73.85	72.12	73.40	1.13
120	73.50	73.29	74.03	73.61	0.38

Table C-5.11 The concentration of methyl ester from 25% FFA use 0.5% KOH (based on oil weight), 300% mole of excess methanol from its stoichiometric ratio at 60°C

Time	**25% FFA**				
	Concentration of methyl ester (%wt)				
	Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
0	0.00	0.00	0.00	0.00	0.00
20	73.85	76.25	75.20	75.10	1.20
40	77.28	79.33	79.92	78.84	1.38
60	75.36	67.20	72.26	71.62	5.74
80	73.48	66.27	70.53	70.10	3.62
100	72.62	66.54	68.44	69.20	3.11
120	70.38	68.83	68.69	69.30	0.94

C-6 Experimental data of alkaline-catalyzed concentration

Table C-6.1 The concentration of methyl ester (% wt) from 10%, 15% and 25% FFA use 100% excess methanol from its stoichiometric ratio at the reaction time 60 minutes (catalyst based on oil weight)

% FFA	**% KOH (based on oil weight)**	**Concentration of methyl ester (%wt)**				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
10% FFA	0.5%	87.42	89.19	-	88.31	1.26
10% FFA	1%	94.23	92.28	94.63	93.71	1.38
15% FFA	0.5%	86.91	84.13	-	85.52	1.96
15% FFA	1%	90.28	92.54	91.13	91.32	1.60
25% FFA	0.5%	76.65	77.19	-	76.92	0.39
25% FFA	1%	85.92	84.02	85.25	85.06	1.34

Table C-6.2 The concentration of methyl ester (% wt) from 10%, 15% and 25% FFA use 100% excess methanol from its stoichiometric ratio at the reaction time 60 minutes (catalyst based on total weight)

% FFA	**% KOH (based on oil weight)**	**Concentration of methyl ester (%wt)**				
		Ex1	**Ex2**	**Ex3**	**Average**	**S.D**
10% FFA	0.5%	89.48	89.65	88.72	89.28	0.50
10% FFA	1%	93.87	95.48	96.84	95.40	1.48
15% FFA	0.5%	86.80	87.39	87.12	87.10	0.29
15% FFA	1%	93.38	93.83	93.48	93.57	0.24
25% FFA	0.5%	80.02	81.47	81.53	81.01	0.86
25% FFA	1%	89.39	87.38	86.68	87.82	1.40

VITA

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