จลพลศาสตร์ของปฏิกิริยาเอสเทอร์ริฟิเคชันแบบไม่ใช้ตัวเร่งปฏิกิริยาของกรดไขมันจากน้ำมันปาล์ม

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KINETICS OF NON-CATALYTIC ESTERIFICATION OF FATTY ACIDS IN PALM OIL

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A Thesis Submitted in Partial Fulfillment of the Requirements
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สิทธิชัย สมทราย : จลพลศาสตร์ของปฏิกิริยาเอสเทอร์ริฟิเคชันแบบไม่ใช้ตัวเร่งปฏิกิริยาของกรดไขมันจากน้ำมันปาล์ม. (KINETICS OF NON-CATALYTIC ESTERIFICATION OF FATTY ACIDS IN PALM OIL) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: อ. ดร.เจิดศักดิ์ ไชยคุนา, 67 หน้า.

งานวิจัยนี้เป็นการศึกษาจลนพลศาสตร์ของปฏิกิริยาเอสเทอร์ริฟิเคชันของกรดไขมันปาล์มแบบไม่ใช้ตัวเร่งปฏิกิริยา การทดลองทำในถังปฏิกรณ์แบบกะ ที่อุณหภูมิ 60 100 150 200 250 และ 300 องศาเซลเซียส ที่ความดัน 500 และ 1000 ปอนด์ต่อตารางนิ้ว และที่อัตราส่วนโดยโมลระหว่างเมทานอลต่อกรดไขมันปาล์มเท่ากับ 1:1 5:1 และ 10:1 แต่ละการทดลองใช้เวลาในการทำปฏิกิริยา 300 นาที และเก็บตัวอย่างทุก 30 นาที

ผลการทดลองแสดงว่าปฏิกิริยาเอสเทอร์ริฟิเคชันของกรดไขมันปาล์มแบบไม่ใช้ตัวเร่งปฏิกิริยาสามารถทำปฏิกิริยากับเมทานอล ที่อุณหภูมิสูงกว่า 200 องศาเซลเซียสและความดันสูงกว่า 500 ปอนด์ต่อตารางนิ้ว ส่งผลให้ปริมาณกรดไขมันที่อยู่ในกรดไขมันปาล์มลดลง ปฏิกิริยาเกิดขึ้นอย่างรวดเร็วภายในเวลา 90 นาที และปฏิกิริยาเข้าสู่สมดุลหลังจาก 120 นาที อัตราการเกิดปฏิกิริยาเอสเทอร์ริฟิเคชันแบบไม่ใช้ตัวเร่งปฏิกิริยาไม่ได้ขึ้นกับความดัน พลังงานกระตุ้นของปฏิกิริยาเอสเทอร์ริฟิเคชันของกรดไขมันปาล์มแบบไม่ใช้ตัวเร่งปฏิกิริยามีค่าประมาณ 31.5 กิโลจูลต่อโมล

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Kinetic of non-catalytic esterification reaction of palm fatty acids distillate with methanol was investigated in this study. The experiments were conducted in batch reactor, at temperature of 60, 100, 150, 200, 250, and 300°C, pressure of 500 and 1000 psig and methanol to palm fatty acids distillate molar ratio of 1:1, 5:1, and 10:1. Each experiment was conducted for 300 minutes and a sample was taken every 30 minute.

The results show that a non-catalytic esterification reaction of palm fatty acids distillate can react with methanol at temperature higher than 200°C and pressure higher than 500 psig resulting in the reduction of fatty acids content in palm fatty acids distillate. The rate of non-catalytic esterification reaction does not depend on pressure. The reaction proceeded quickly during the first 90 minutes and a reaction equilibrium was reached at approximately 120 minutes. The activation energy of non-catalytic esterification reaction of palm fatty acids distillate was approximately 31.5 kJ/mol.

Department : Chemical Engineering. Student's Signature : สิทธิชัย สมทราย
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CHAPTER I

INTRODUCTION

The major part of all energy consumed worldwide comes from fossil sources (petroleum, coal and natural gas). These sources are limited and exhausted in the near future, agriculture problem, the business of the country problem and environment problem. These cause global warming. A potential diesel fuel substitute is biodiesel. It is mainly produced from vegetable oil constituent and animal fats. Biodiesel is a renewable and environmental friendly, especially carbon dioxide saving. When, it comes to used replace diesel fuel, it will help environment problem. In Thailand, several vegetable oil can be used as a feedstock. Vegetable oil used directly with vehicles, some engine performance problems, such as injector coking and more carbon deposits. Thus must decrease the viscosity of vegetable oil before used, such as, warm oil, mixing petroleum or the other solvent. Moreover, vegetable oil can be polymerization reaction at high temperature. The remedy is modifying chemical structure of vegetable oil by transesterification and esterification which, get the products is an alkyl ester, which has properties closest to that of petroleum diesel.

Tranesterification and esterification reaction can be occurring at atmospheres and room temperature until the boiling point of the alcohol that uses, but these need to catalyst. Acid catalyst, give to high yield but, long reaction time. Alkaline catalyst, fast reaction time when compare acid catalyst. Alkaline catalyst is low selectivity can be sponification or soap to be the end of reaction. Products are purifying by wash to separate catalyst and alcohol. The procedure to have many the steps, such as, long time reaction, a lot of waste ,as acid, base and fatty form procedure greatly.

Non catalytic reaction is a choice to decrease catalytic reaction problem, such as, side reaction, yield, reaction time complicated process. Non catalytic is easy procedure, by vegetable oil or fatty acid and alcohol to react at high temperature and high pressure without catalyst, it get to high conversion of alky ester, because of, react while both of tranesterification of triglyceride and esterification of fatty acid.

Their research also several that tranesterification of fatty acids in vegetable oil can also proceed at supercritical conditions. Developing under the same basic, this work will investigate esterification reaction of palm fatty acids distillate with methanol under high temperature condition at various methanol to palm fatty acids distillate ratios.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Palm oil and palm fatty acids distillate

The palm is the plant gives oil 0.6-0.8 ton / farm / year and low cost when compare with other oil. Palm oil is from 2 part palms, be from outside shell, and from a seed in the palm. Which, palm oil to consist of fatty acid 85 – 90 percentages make inappropriate with consuming, and then apply in all industry, such as, soap, cosmetic, detergent, resin and etc. Oil from the shell of the palm or curd palm composes the fatty acids (palmetic acid and stearic acid) 50 percentages, free fatty acid (oleic acid) 40 percentages, vitamin A and vitamin E. thus, curd palm have the character is liquid mixes with solid. After the extraction get 2 products, palm olein and palm stearin. Palm olein use for consume. Palm stearin use in the margarine industry and soap. Moreover, there is fatty palm acids distillate is the by-product from the distillation process. Consider conversion and the property of palm oil tend to use fuel and raw materials in all industry, because of, there are requirement is food more than other oil.

Palm fatty acids distillate is separation of liquid mixture into their several components is one of the major processes of the chemical industries. Fatty acids in palm oil has saturated and unsaturated fatty acids which palmitic acids and oleic acids are the main component acids. 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., contain at least one carbon-carbon double bond (see chemical bond).

2.2 biodiesel

Biodiesel is liquid fuel that produces from vegetable oil and fat, by Tranesterification reaction or esterification reaction with alcohol have alkyl ester is product, there is combustion property is like the diesel from the petroleum. The name calling is under a kind of the alcohol that uses in reacting, such as; methyl ester get from using methanol is a substance in reacting and ethyl ester get from using ethanol is a substance in reacting. The raw material that use in the production for example, palm oil, coconut oil, sunflower oil, rapeseed oil, soybean oil, groundnut oil, castor oil, sesame oil, and used oil. Among these alcohol, 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 environment. However, methanol is used in practice because of its physical and chemical advantages of having shortest chain, so it easy to react.

2.3 Methyl ester

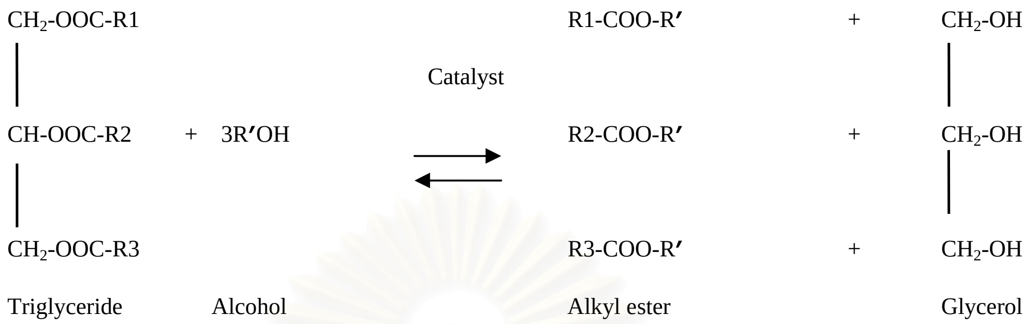
Methyl ester is aliphatic organic ester which is obtained by the chemical reaction between natural fat or oil and methanol in order to change their chemical structures. General properties of methyl ester are low volatility, high flash point and high viscosity. The chemical structure of methyl ester is CH_3COOR and R as $(CH_2)_xCH_3$ that depend on fatty acid group; for example, Methyl palmitate which R represent Palmitic acid, Methyl oleate which R represent Oleic acid and Methyl linoleate which R represent linoleic acid as show in Table 2.1. The most widely used methyl ester can be produced by esterification and transesterification reaction.

Table 2.1 Characteristics of Common fatty acids methyl esters

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

2.4 Transesterification reaction

Transesterification or alcoholysis is the raction of alcohol and vegetable oil or animal fat to produce alkyl ester of fatty acid. This process has been widely used to reduce the high viscosity of triglycerides. The general equation of this reaction is shown in Equation 2.1. R1, R2 and R3 of the oil molecules are long chain hydrocarbon constituting fatty acid which may be the same or different. A catalyst is used to improve the reaction rate and yield. Theoretically, the tranesterification reaction is an equilibrium reaction. In the reaction, it is reversible reaction, thus in reacting, excess of alcohol is used to shift the reaction equilibrium to the right side and produce more methyl ester products.



Equation 2.1 General equation of transesterification reaction

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

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

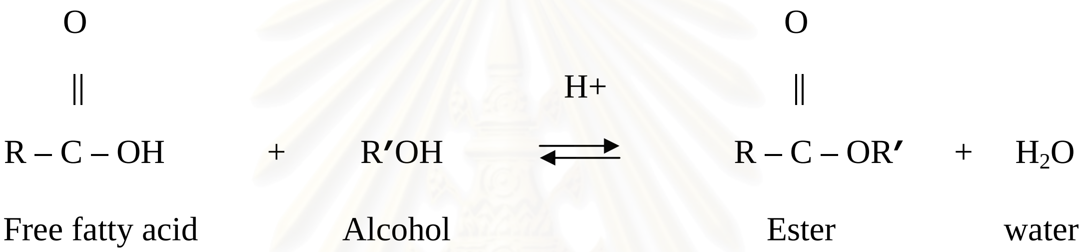
$$\text{Diglyceride} + \text{R'OH} \rightleftarrows \text{Monoglyceride} + \text{R'COOR2}$$

$$\text{Monoglyceride} + \text{R'OH} \rightleftarrows \text{Glcerol} + \text{R'COOR3}$$

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

2.5 Esterification reaction

The formation of ester occurs though a condensation reaction knows as esterification. This requires two reactants: free fatty acid and alcohol. Esterification reaction is acid catalyst and proceeds slowly in the absence of strong acid such as sulfuric acid, phosphoric acid, organic sulfuric acid, and hydrochloric acid. The equation for an estrification reaction can be seen in Equation 2.3.



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

Free fatty acid Alcohol Ester water

Equation 2.3 Esterification reaction of free fatty acid with alcohol

High free fatty acids (high FFA) feed stock will react with the catalyst and will form soaps if they are fed to base catalyst system. The acceptable maximum amount of free fatty acid in 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 fatty acid out of the feed for disposal or separate treatment in an acid esterification unit. The caustic is added to the feedstock and resulting soaps are stripped out using a centrifuge. This is call caustic stripping. Some triglycerides are lost with the soaps during caustic stripping. The soaps mixture can be acidulated to recover the fatty acid 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 acid is removing in this manner; they can be transformed into methyl ester by using an acid esterification of free fatty acids in high free fatty acid feedstock.

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

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

2.6 Biodiesel or methyl ester production process

2.6.1 Basic catalyzed process

Basic catalyzed process dominates current commercial production. These reactions are relatively fast but are sensitive to water content and free fatty acids. The typical alcohol used is methanol with a 6:1 molar ratio. Typical basic concentrations are 0.3 to 1.5 % based on the weight of oil. When sodium methoxide was used, the concentration can be 0.5 % or less. Essentially all of the current commercial operations use basic catalyzed reaction. Most use NaOH as the catalyst. There are some operations that use KOH, in spite of high cost, because the potassium can be precipitated as K_3PO_4, a fertilizer, when the products are neutralized using phosphoric acid. This can make meeting water effluent standards a bit more difficult because of limits on phosphate emissions. The typical alcohol: triglyceride mole ratio for batch reactions and sequential batch reaction is 6:1. There have been reports that continuous flow systems operate better with a ratio 8:1. Sodium methoxide, usually as a 25% solution in methanol, is a more powerful catalyst on a weight basis than the maxture of NaOH and methanol.

2.6.2 Acid catalyzed process

Despite its insensitivity to free fatty acid in the feedstock, acid-catalyzed traesterification has been largely ignored mainly because of its relatively slower reaction rate. Freedman, M et al. (1984) invatigated the tranesterification of soybean oil with methanol using 1wt% concentrated sulfuric acid based on weight of oil. They found that at 65^{o}C and a molar ratio 30:1 of methanol to oil, it took 69 hours to obtain more than 90% oil conversion to methyl ester. Canakci, K and Van Gerpen, J (1999) studied the effects of the molar ratio of alcohol to soybean oil, the reaction temperature, the amount of catalyst, and the reaction time on the ester conversion by acid-catalyzed traesterification reaction. Each effect is studied independently of the other effects. They found that increased ester conversion could be obtain at increased molar ratio of alcohol to oil, increased reaction temperature, increased concentrations of sulfuric acid, and long reaction times. However, possible interaction of these variables was not investigated and optimal condition for the acid-catalyzed reaction was not recommended. In this process the tranesterification reaction of oil with an excess of methanol in the presence of sulfuric acid catalyst at 60^{o}C, a minimum molar ratio of methanol to oil is 6:1 and acid catalyst concentrations 0.5-1% (base on oil) were used.

2.6.3 Enzyme-catalyzed processes

The common aspects of these studies consist in optimizing the reaction conditions (solvent, temperature, pH, type of microorganism which generates the enzyme, etc.) in order to establish suitable characteristics for an industrial application. However, the reaction yields as well as the reaction times are still unfavorable compared to the base-catalyzed reaction systems.

2.6.4 Non-catalyzed process

When a fluid or gas is subjected to temperatures and pressures in excess of its critical point, there are a number of unusual properties exhibited. Firstly, there no longer is a distinct liquid and vapor phase, but a single, fluid phase present. Secondly, solvents containing a hydroxyl (OH) group, such as water or primary alcohols, take on the properties of super-acids. For this reason, transesterification in supercritical alcohol can be achieved without use of catalyst for production of biodiesel. With this process, used oil with high amount of free fatty acids can be used as no alkali is used. The only reactions products are the ester or biodiesel (the upper phase) and lower phase is glycerol. No soap is produced, thus the separation process is simple. In addition, alcohol used in biodiesel production such as methyl or ethyl alcohol are polar solvents and have hydrogen bonding between OH oxygen and OH hydrogen to which normally form clusters of these molecules, separating them from other non-polar compounds such as glyceride. However, because the degree of hydrogen bonding decreases with increasing temperature, the polarity of the alcohol would decrease in supercritical state, thus supercritical alcohol has a hydrophobic nature with the lower dielectric constant. As a result, non-polar triglycerides can dissolve in the supercritical alcohol to form a single phase of vegetable oil/methanol mixture (Kusdiana, D and Saka. S (2001)). The alcohol molecule attacks the carbonyl atom of the triglyceride because of the high pressure. In the supercritical state, depending on pressure and temperature, hydrogen bonding would be significantly decreased, which would allow methanol to be a free monomer. Transesterification is completed via a methoxide transfer, whereby the fatty acid methyl ester and diglyceride are formed.

Saka, S et al. (2001) studied the transesterification reaction of rapeseed oil in supercritical methanol conduct experiment in the bath-type reaction vessel preheated at 350^{o}C and 400^{o}C at a pressure of 45-65 MPa, and with a molar ratio of 42:1 of methanol to rapeseed oil without using any catalyst. They found that, the reaction complete in about 4 minutes and as a higher molar ratio of methanol to rapeseed oil, the methyl esterified compounds were increased with a decrease in the intermediate compounds. This was due perhaps to the increased contact area between methanol and triglycerides.

2.7 Kinetic of reaction and Arrhenius energy of activation

Chemical kinetics, also known as reaction kinetics, is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

2.7.1 Rate of reaction

Chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero order reactions (for which reaction rates are independent of concentration), first order reactions, and second order reactions, and can be derived for others. In consecutive reactions the rate-determining step often determines the kinetics. In consecutive first order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the Arrhenius equation. The main factors that influence the reaction rate include: the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction.

The rate law or rate equation for a chemical reaction is an equation which links the reaction rate with concentrations or pressures of reactants and constant parameters. To determine the rate equation for a particular system one combines the reaction rate with a mass balance for the system. For a generic reaction

$A + B \rightarrow C$ the simple rate equation (as opposed to the much more common complicated rate equations) is of the form:

$$r = k(T)[A]^m[B]^n \qquad (1)$$

In this equation (1), $[X]$ expresses the concentration of a given X, usually in mol/liter (molarity). The k (T) is the reaction rate coefficient or rate constant, although it is not really a constant, as it includes everything that affects reaction rate outside concentration such as temperature but also including ionic strength, surface area of the adsorbent or light irradiation. The exponents n and m are the reaction orders and depend on the reaction mechanism. The stoichiometric coefficients and the reaction orders are very often equal, but only in one step reactions, molecularity (number of molecules or atoms actually colliding), stoichiometry and reaction order must be the same. The rate equation is a differential equation, and it can be integrated in order to obtain an integrated rate equation that links concentrations of reactants or products with time. If the concentration of one of the reactants remains constant (because it is a catalyst or it is in great excess with respect to the other reactants) its concentration can be included in the rate constant, obtaining a pseudo constant: if B is the reactant whose concentration is constant then $r = k[A][B] = k'[A]$. The second order rate equation has been reduced to a pseudo first order rate equation. This makes the treatment to obtain an integrated rate equation much easier.

2.7.2 Arrhenius energy of activation

For many reaction the rate expression can be written as a product of temperature dependent term and a composition dependent term, or

$r_i = f_1(\text{temperature}) \cdot f_2(\text{composition})$

$= k \cdot f_2(\text{composition})$

For such reactions the temperature dependent term, the reaction rate constant has been found in practically all cases to be well represent by Arrhenius' law indicates that

$$k = k_0 e^{-E_a/RT} \qquad (2)$$

Rearrange the Arrhenius equation

$$lnk = lnk_0 - \frac{E_a}{RT} \qquad (3)$$

Where k_o is called the frequency or pre-exponential factor (L/ (mol-s)), E_a is called the activation energy of the reaction (KJ), R is called Gas constant (kJ/ (mol-K)) and T is absolute temperature (K). This expression fits experiment well over wide temperature ranges and is strongly suggested from various standpoints as being a very good approximation to the true temperature dependency. From equation, a plot of ln k vs. 1/T give a straight line, with a slope equal to E_a. Reactions with high activation energies are very temperature sensitive; reactions with low activation energies are relatively temperature insensitive.

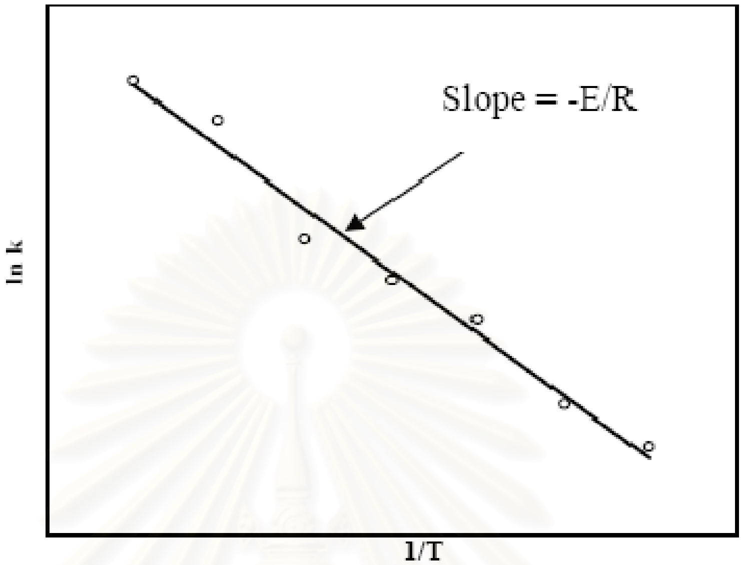


Figure 2.1 Plot of Arrhenius equation

2.8 Literature review

A number of studies on preparation of biodiesel from vegetable oils have been reported using a variety of oils, alcohol, different catalyst, and reaction conditions. Freedman, B et al. (1986) studied the variables that affect yield and purity of alcohol ester product from crude and refined vegetable oil. These are such as molar ratio of methanol and oil, type of catalyst, and temperature. Their results showed that alkaline catalyzed reaction of fully refined oil at 60^{o}C or higher, with the molar ratio of 6:1 could be complete and the conversion to esters resulted in 1 hr. At 32^{o}C, vegetable oil 99% transesterification was obtained in 4 hr with alkali catalyst. The reason for low reaction rate at low temperature was that the miscibility of methanol and oil was low. This could be improved by addition of a solvent.

Alternatively, non-catalytic transesterification was investigated. Studies in these areas had been related to using rapeseed and soybean oils as starting materials. Saka, S and Kusdiana, D (2001) studied the transesterification reaction of rapeseed oil in supercritical methanol in the bath-type reaction vessel. At 350^{o}C and a molar ratio of methanol to rapeseed oil of 42:1, a non-catalytic transesterification gave a 95% conversion after 240 s. And unlike alkali or acid catalyzed reactions, the presence of free fatty acid or water does not affect transesterfication in supercritical methanol. The finding demonstrated that, by a supercritical methanol approach, crude vegetable oil as well as its wastes oil could be readily used for biodiesel fuel production in a simple preparation. However, this reaction requires high temperature and pressure to reach the supercritical state.

Yuchiro, W et al (2003) studied the effect of transesterification of triglycerides and esterification of fatty acids in rapeseed oil. They conduct experiment at temperature of 300^{o}C, and methanol, ethanol, 1-propanol, 1-butanol or 1-octanol was used as the reactant the molar ratio of alcohol to oil of 42:1. The results showed that, transesterification of triglycerides (rapeseed oil) were slower in reaction rates than alkyl esterification of fatty acids for any of the alcohols employed.

Mahesh, N et al (2007) studied synthesis transesterification of triglycerides of higher fatty acid to methyl and ethyl esters from castor oil and linseed oil using methanol and ethanol was investigated at subcritical and supercritical conditions of methanol and ethanol from 200 to 350°C at 200 bars. The effect of molar ratio of alcohol to oil, temperature, and time was investigated in supercritical methanol and ethanol. They found that, the conversion increases with molar ratio of alcohol to oil up to 40:1, the kinetics of the reaction was first order. The activation energies for transesterification of castor oil are 35 and 55 and of linseed oil are 46.5 and 70 kJ/ mol with methanol and ethanol, respectively.

A number of studies have been conducted on the kinetics of transesterification without catalyst. Diasakou, M et al. (1998) investigated the kinetics of the non-catalytic thermal transesterification of soybean oil with methanol. The experiments have been carried out at temperature of 220 and 235°C with various molar ratios of methanol to oil. They suggested the evolution of concentration of each component in ester phase followed the first order kinetic model derived from the proposed consecutive reaction mechanism. Furthermore, triglyceride and diglyceride conversion rate were much higher than the conversion rate of monoglyceride to glycerol.

Mohanprasad et al. (2003) determined the kinetics of non-catalytic transesterification of soybean oil and three different alcohols: methanol, ethanol, and isopropanol (molar ratio of methanol to oil of 6:1), for the reaction temperature between 120 and 180 °C in a glass capillary tube. They suggested that this two phase reaction could be controlled either by diffusion or kinetics. In their work, because of the observed relatively slow reaction rate, the reactions were most likely controlled by kinetics, and thus the solubility of methanol in oil, rather than by diffusion. The reaction rate was also found to increase as the reaction proceeded because the ester product helped increase the solubility of methanol in the reaction mixture. Moreover, they found that the reactions followed the first order kinetics and the reactivity was found to be higher in methanol, and then followed by ethanol, and isopropanol.

Kusdiana, D. and Saka, S (2000) studied kinetic in free catalyst transesterification of rapeseed oil was made in subcritical and supercritical methanol under different reaction conditions of temperatures and reaction times. The experiment were made in a bath-type reaction vessel ranging from 200°C in subcritical temperature to 500°C at supercritical state with different molar ratios of methanol to rapeseed oil to determine rate constants by employing a simple method. They found that the conversion rate of rapeseed oil to its methyl esters was increase dramatically in the supercritical state, and reaction temperature of

350^{o}C was considered as the best condition, with the molar ratio of methanol to rapeseed oil of 42:1.

Berrios, M et al. (2007) was studied kinetics of the esterification reaction of free fatty acids in sunflower oil with methanol in the presence of sulphuric acid at concentrations of 5 and 10wt% relative to free acids as catalyst and molar ratio of methanol to oleic acid of 10:1 to 80:1. They found that a molar ratio of methanol to oleic acid of 60:1, a catalyst (sulphuric acid) concentration of 5wt% and a temperature of 60°C provided a final acid value for the oil lower than 1 mg KOH/g oil within 120 min. The experimental results were found to fit a first-order kinetic law for the forward reaction and a second-order one for the reverse reaction. The influence of temperature on the kinetic constants was determined by fitting the results to the Arrhenius equation. The energy of activation for the forward reaction decreased with increasing catalyst concentration from 50,745 to 44,559 J/mol.

CHAPTER III

EXPERIMENTAL AND ANALYTICAL METHOD

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

3.1 Material

3.1.1 Palm fatty acids distillate

Palm fatty acids distillate was obtained from local palm oil in Thailand

3.1.2 Chemical

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

Table 3.1 All chemicals used in the research

Name	Source	Purity
Methanol	Fisher Scientific	99% (industrial grad)
N-heptane	Qrec	99% (grad AR)
Methyl Decanoate	Sigma-Aldrich	99%
Sulfuric acid	J.T. baker	98%(analytical reagent grad)
Toluene	Ajax chemicals	99.8%(analytical reagent grad)
Ethanol	Fisher Scientific	98% (industrial grad)
Iso-propanol	Fisher Scientific	99.8%(analytical reagent grad)
Mix Fatty Acids Methyl Ester	Restek	Mix

3.2 Equipment

The experiments were conducted in a 2 litre batch reactor. All components of the reactor are made of stainless steel to protect a system from corrosion. A schematic diagram of the system is shown in Figure 3.1.

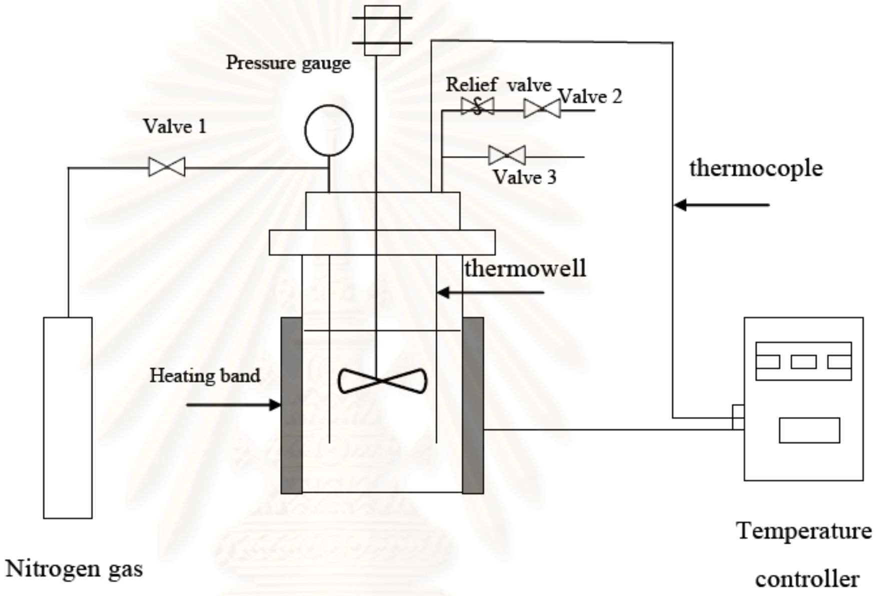


Figure 3.1 schematic diagram of high temperature reactor

3.3 Methodology

3.3.1 Characterization of Palm Fatty Acids

Free fatty acids content (AOCS Ca 5A-40), Acid value (AOCS Cd-3D-63) and Saponification value (AOCS Cd-3b-76).

3.3.2 Non-catalytic esterification reaction

1. Heat palm fatty acids 500 g at 100 °C to eradicate moisture.
2. The molar ratio of methanol to palm fatty acids distillate 1:1 to 10:1. And pour methanol and palm fatty acid thoroughly in the reactor.

3. Heat sample until reach the desired temperature (100 to 300 ^{o}C), pressure was controlled at 500 psig using nitrogen gas and stirrer.
4. Leave the reaction continue for 300 minute mixed when temperature and pressure is constant.
5. And take sample every 30 minute; about 5 g
6. A bottom phase fatty acid methyl ester – layer was separated and purified by evaporation and was analyzed for fatty acids content.

3.4 Analytical method

3.4.1 Free fatty acids content (AOCS Ca 5A-40)

The first step of the process is to reduce FFA content in palm oil by esterification with methanol. Free fatty acids content can check by titration follow standard AOCS Ca 5A-20

3.4.2 Methyl esters analysis

The analysis of standards and the products formed were carried out on Variance 8700 gas chromatography (GC) at Hazardous Laboratory, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. A non-polar capillary column (Carbowax M20) with an internal diameter of 0.32 mm, length of 30 m and film thickness of 0.25 m and flame ionization detector (FID) was used. Helium was used as a carrier gas with pressure 10 psig. The injector and detector were set at 300 °C, respectively. The column temperature was programmed with an initial temperature 80 °C for 5 min, heating at 20 °C /min to 230 °C, then holding on 5 min to a final temperature of 230 °C. Methyl decanoate was chosen as an internal standard and heptane was solvent. Therefore, the type of methyl ester was compared retention time of each methyl esters with methyl esters standard in Figure 3.2 and Table 3.2.

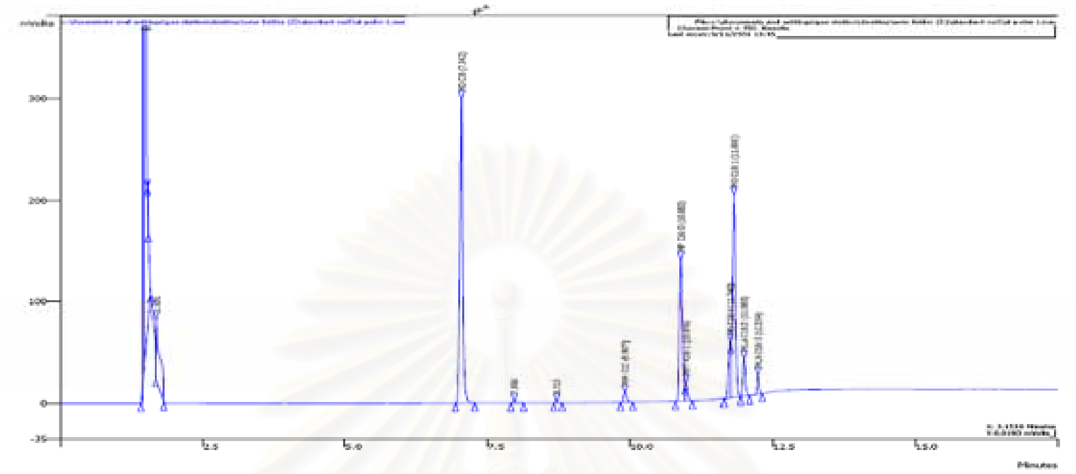


Figure 3.2 GC chromatogram of methyl esters

Table 3.2 Retention time of methyl ester in GC chromatogram

Retention time (min)	Peak of sample
1.48	Heptane
6.94	Methyl Decanoate
9.83	Methyl Myristate
10.85	Methyl Palmitate
10.98	Methyl Palmitoleate
11.68	Methyl Stearate
11.74	Methyl Oleate
11.89	Methyl Linoleate
12.12	Methyl Linolenate

CHAPTER IV

RESULTS AND DISCUSSIONS

Experimental results and discussions of non-catalytic esterification reaction are presented in this chapter. Feed stock used in this study is a palm fatty acids distillate. The effect of temperature, pressure, molar ratio of methanol to palm fatty acids distillate and kinetic of non-catalytic esterification reaction were determined. Results and discussions are presented in eight parts:

4.1 Characterization of palm fatty acids distillate

4.2 Esterification reaction of palm fatty acids distillate without catalyst.

4.3 Esterification reaction of palm fatty acids distillate used catalyst.

4.4 Effect of temperature.

4.5 Effect of pressure.

4.6 Effect of molar ratio of methanol to palm fatty acids distillate.

4.7 Kinetic of esterification reaction without catalyst

4.8 Percent yield of methyl esters by non-catalytic esterification reaction

4.1 Characterization of palm fatty acid

Palm fatty acids distillate used in this studied was obtained from local palm oil refinery in Thailand. Palm fatty acids distillate is solid phase at room temperature. It contains free fatty acids 90.05% which also results in a high acid value. The molecular weight of palm fatty acids distillate was calculated based on acid and saponification value. It found that molecular weight of palm fatty acids distillate are 273.31 g/mol. Palm fatty acids distillate in this studied was analyzed by standards method AOCS Official Method Ca 5a-40, standards method AOCS Official Method Cd 3d-63 and AOCS Official Method Cd 3b-76. The results are shown in Table 4.1.

Table 4.1 Properties of Palm fatty acids distillate

Properties	Palm Fatty Acids Distillate
Free Fatty Acids, (%)	90.05
Acid Value, (mg KOH/g)	176
Saponification Value,(mgKOH/g)	204
Melting Point , (°C)	43
Molecular Weight, (g/mole)	273.31

The fatty acids composition of palm fatty acid distillate can be analyzed in terms of fatty acid methyl ester by gas chromatography (GC). The results in Table 4.2 shows the fatty acids composition of palm fatty acids distillate.

Table 4.2 Composition of Palm fatty acids distillate

Composition		Palm Fatty Acids Distillate (%Composition)
Myristic acid	C14:0	1.1
Palmitic acid	C16:0	46.6
Palmitoleic acid	C16:1	0.2
Stearic acid	C18:0	4.2
Oleic acid	C18:1	39.0
Linoleic acid	C18:2	8.7
Linolenic acid	C18:3	0.2

4.2 Esterification reaction of palm fatty acids distillate without catalyst

The experiments were conducted at temperature of 60^{o}C a molar ratio of methanol to palm fatty acids distillate of 1:1, 5:1, and 10:1, and ambient pressure. The experimental results are in Figure 4.1. It is observed that non-catalytic esterification reaction of palm fatty acids distillate does not occur at low temperature of 60^{o}C. Berrios, M et al (2007) studied esterification reaction of free fatty acids in sunflower oil. The experiment has been carried out in a temperature of 60^{o}C. They found that the reaction does not occur at low temperature and esterification reaction does not take place in catalyst absence. The results conclude that esterification reaction of free fatty acid cannot proceed without acid catalyst at low temperature.

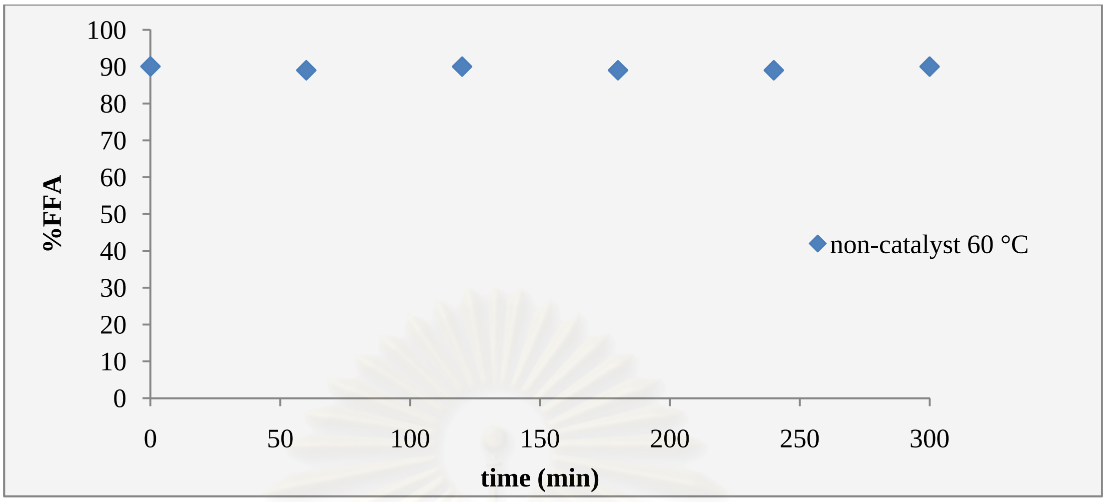


Figure 4.1 Esterification reaction of palm fatty acids distillate

4.3 Esterification reaction of palm fatty acids distillate used catalyst

The experiments were conducted at a sulfuric acid concentration of 1wt%, a temperature of 60^{o}C, a molar ratio of methanol to palm fatty acids distillate of 5:1 and ambient pressure. Figure 4.2 shows experiment results of free fatty acid content using acids catalyst. It shows that when acid catalyst was used, esterification reaction proceeded very well resulting in reduction of fatty acid content in raw material. Berrios, M et al (2007) studied esterification reaction of free fatty acids in sunflower oil. The experiment has been carried out in a temperature of 60^{o}C, sulfuric acid concentration of 5 and 10wt% molar ratio of methanol to oil 10:1 to 80:1. They found that the reaction can occur at low temperature. Chanin et al (2007) studied kinetic of reduction free fatty acid in palm oil. They conducted experiment at temperature at 30 to 60°C, sulfuric acid concentration of 0.05 wt% and molar ratio of methanol to oil 1:1. They found that free fatty acid content in palm oil can reduce from 7% to less than 1%. Thus it can be conclude that at low temperature esterification reaction can occur when acid catalyst (sulfuric acid) was added to the system.

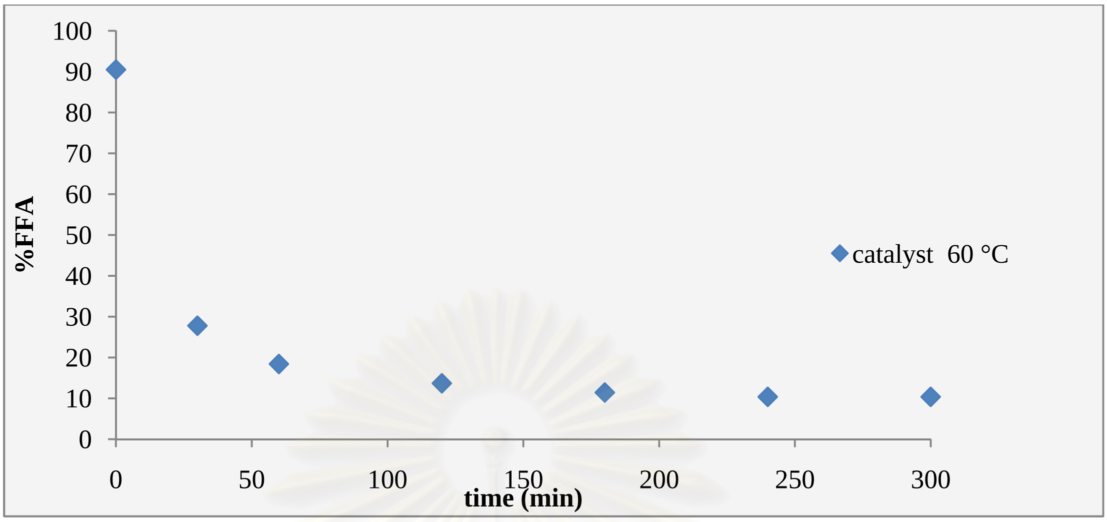


Figure 4.2 Esterification reaction of palm fatty acids distillate

4.4 Effect of temperature

The experiments were conducted at a temperature of 60 and 100^{o}C and a methanol to palm fatty acids distillate molar ratio of 1:1. Figure 4.3 shows analysis results of fatty acids content at various times and low temperature. It shows that non-catalytic esterification reaction between palm free fatty acids distillate and methanol cannot occur at low temperature. At temperature of 100°C palm free fatty acids distillate can react with methanol slightly. When conducted temperature of 150, 200, 250 and 300°C the results fond that the reaction proceeds at faster rate when reaction temperature increases. The results are shown in Figure 4.4. No significant increase in rate of reaction is observed at temperature higher than 250^{o}C. Kusdina, D and Saka, S (2001) also observed that conversion rate of rapeseed oil to methyl ester increased with reaction temperature. Kunchana, B (2006) conducted experiment on continuous production of biodiesel by the tranesterification reaction in supercritical methanol. They found that the best condition to produce methyl ester from coconut oil and palm kernel oil at a reaction temperature of 350^{o}C.

The results conclude that esterification reaction can occur at high temperature without catalyst. The optimum temperature is 250ºC.

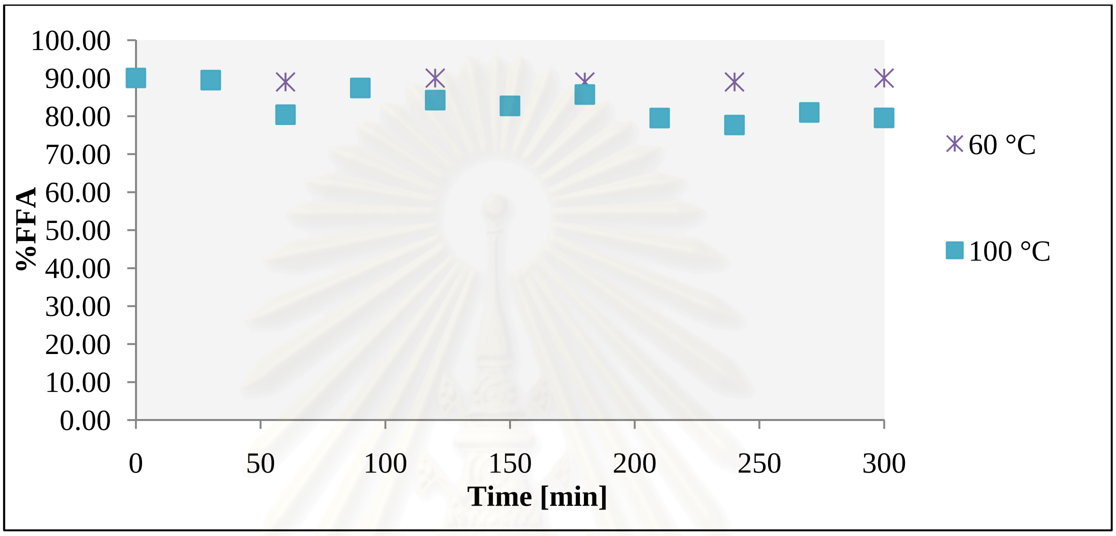


Figure 4.3 Effect of temperature on esterification reaction without catalyst at low temperature

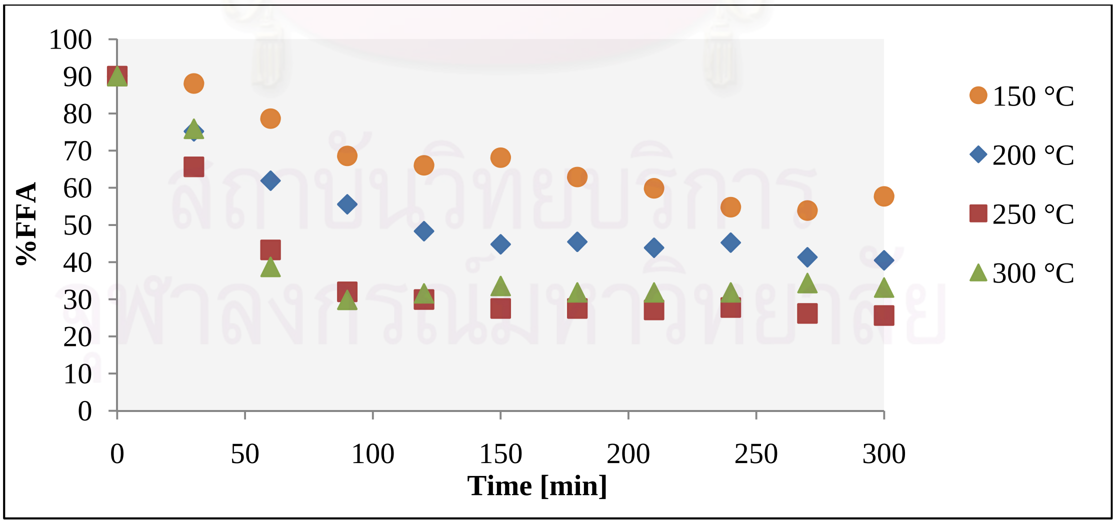


Figure 4.4 Effect of temperature on esterification reaction without catalyst at high temperature

4.5 Effect of pressure

The experiments were conducted at constant temperature of 200, 250 and 300°C, molar ratio of methanol to palm fatty acids distillate of 1:1 and pressure of 500 and 1000 psig. Figures 4.5 to 4.7 shows analysis results of fatty acid content at various times and pressure. It shows that non-catalytic esterification reaction between palm free fatty acid distillate and methanol can be reacting with methanol at high pressure and high temperature. The trend in the results for pressure of 500 psig is similar to those at a pressure of 1000 psig. However, similar results were observed by L. Wang et al (2007). They used the crude oil of rapeseed with supercritical methanol at high temperature and high pressure. They found that high yield of methyl ester, for pressure changing from 5.7 MPa to 24 MPa, the differences in methyl ester yield were not notable. The result conclude that increasing pressure do not effect to esterification reaction.

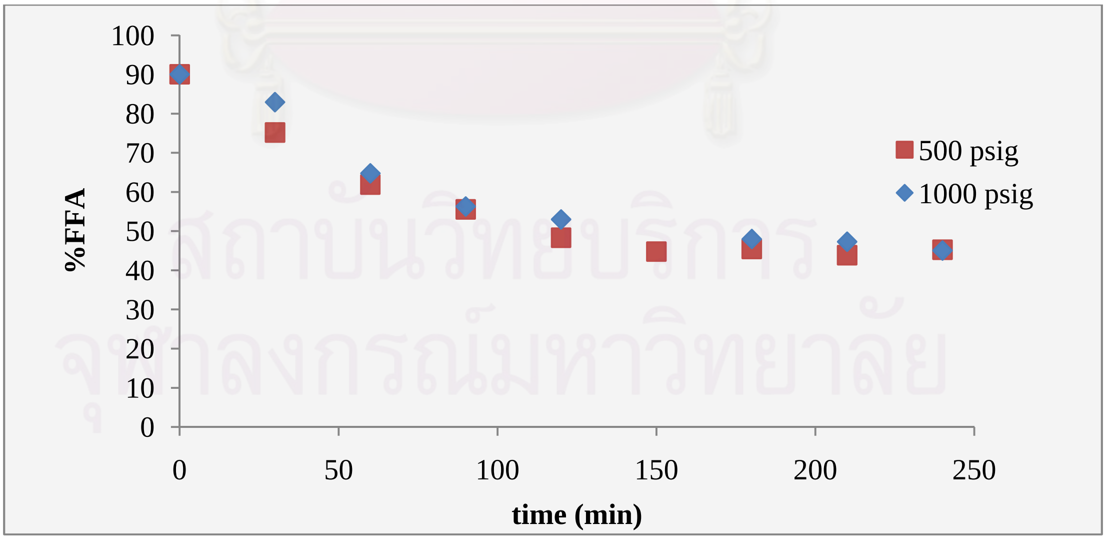


Figure 4.5 Effect of pressure on esterification reaction without catalyst at a temperature of 200°C and molar ratio of methanol to palm fatty acids of 1:1

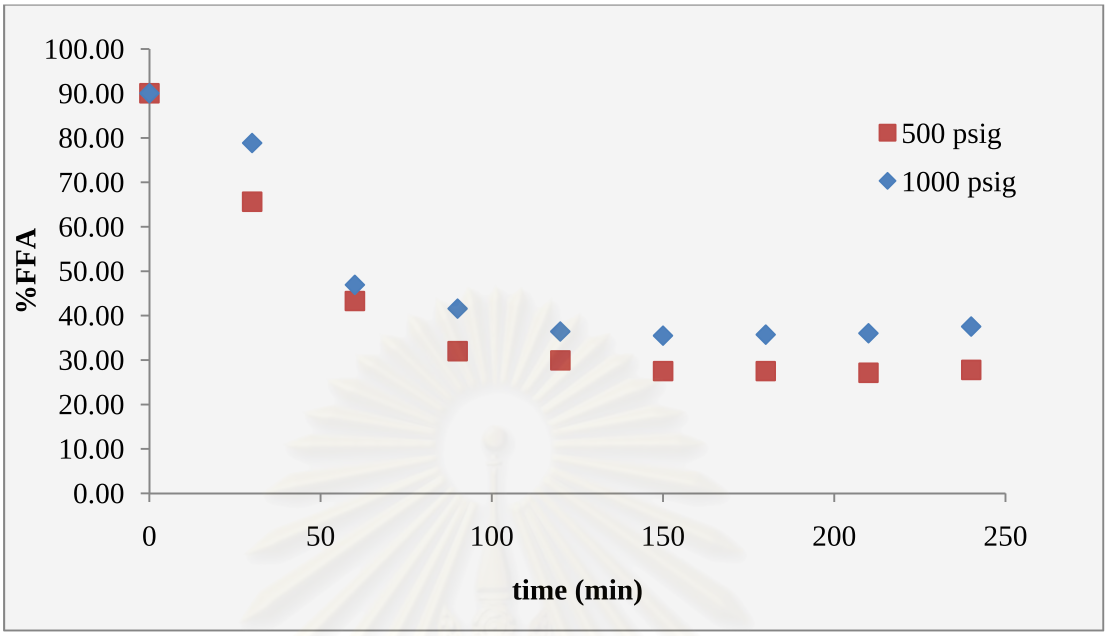


Figure 4.6 Effect of pressure on esterification reaction without catalyst at a temperature of 250°C and molar ratio of methanol to palm fatty acids of 1:1

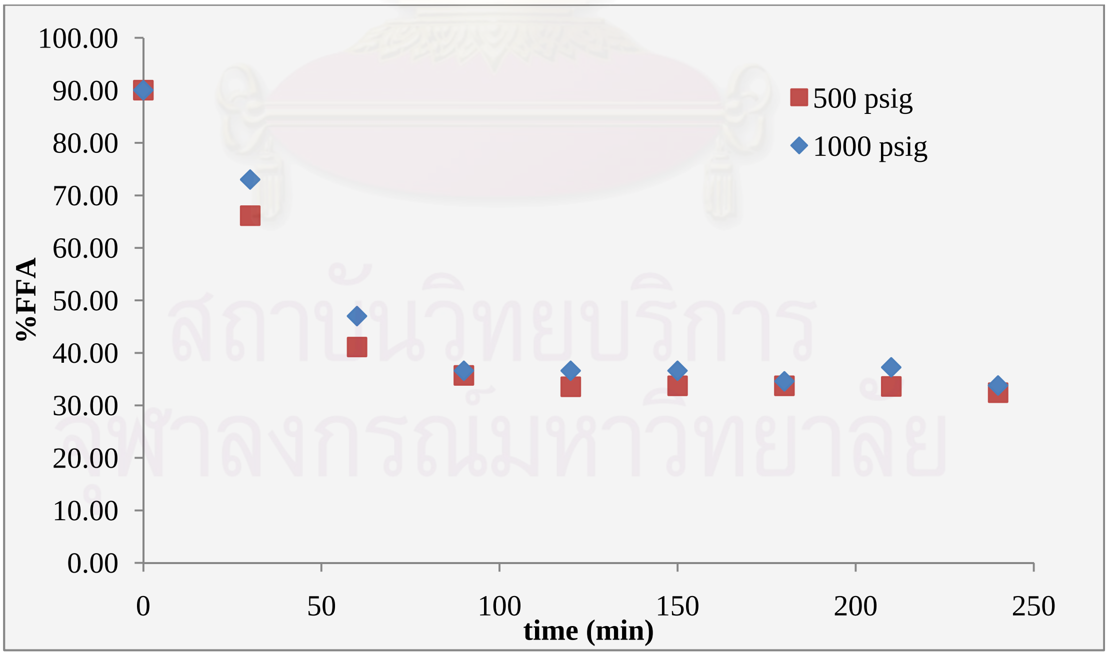


Figure 4.7 Effect of pressure on esterification reaction without catalyst at a temperature of 300°C and molar ratio of methanol to palm fatty acids of 1:1

4.6 Effect of methanol to palm fatty acids distillate ratios

The experiments were conducted at a temperature of 200, 250 and 300^{o}C and a molar ratio of methanol to palm fatty acids distillate of 1:1, 5:1, and 10:1. Figures 4.8 to 4.10 shows analysis results of fatty acid content at various times and molar ratio of methanol to palm fatty acids distillate. It can be seen clearly that rate of non-catalytic esterification reaction does not depend on molar ratio of methanol to palm fatty acids distillate. The reaction proceeds quickly during the first 90 minutes. Reaction equilibrium is reached at approximately 100 minutes. The results also show that equilibrium conversion of free fatty acid depend slightly on amount of methanol. Increasing molar ratio of methanol to palm free fatty acid distillate slightly shifts the remaining of free fatty acid content except in an experiment conducted at temperature of 300 ^{o}C. Y. Dongkamol (2006) studied production of methyl esters from palm fatty acids in supercritical methanol. The experiments conducted using palm fatty acids in supercritical methanol, molar ratio of methanol to palm fatty acids distillate of 1:1 to 12:1 and found that high conversion of 94% was obtained at the molar ratio of 6:1 and at a temperature of 300°C after 30 minute.

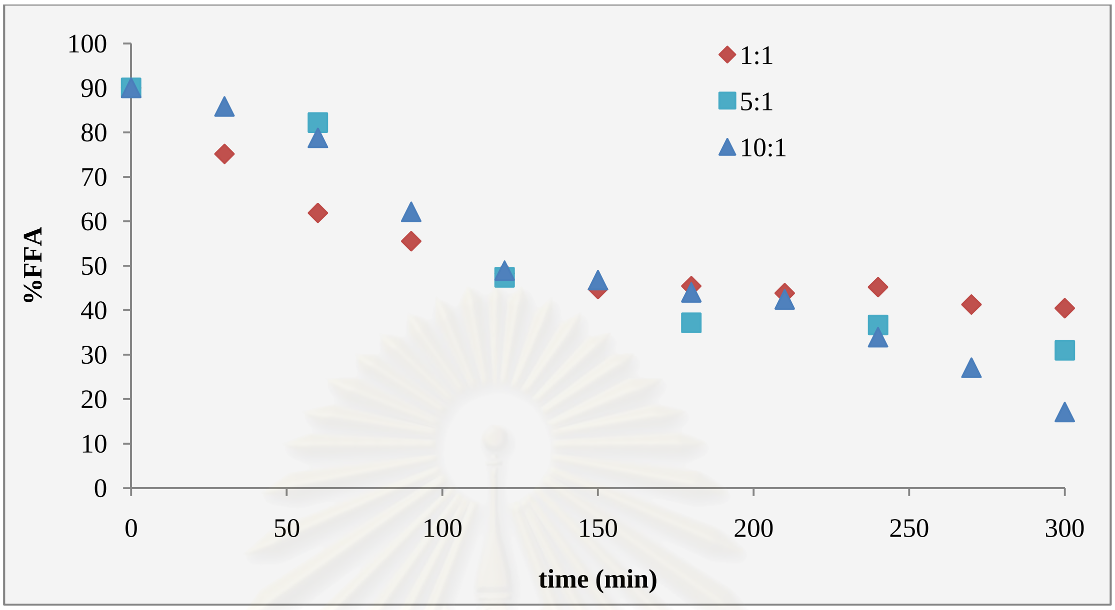


Figure. 4.8 Effect of molar ratio of methanol to free fatty acids in non-catalytic esterification reaction, as treated at 200°C

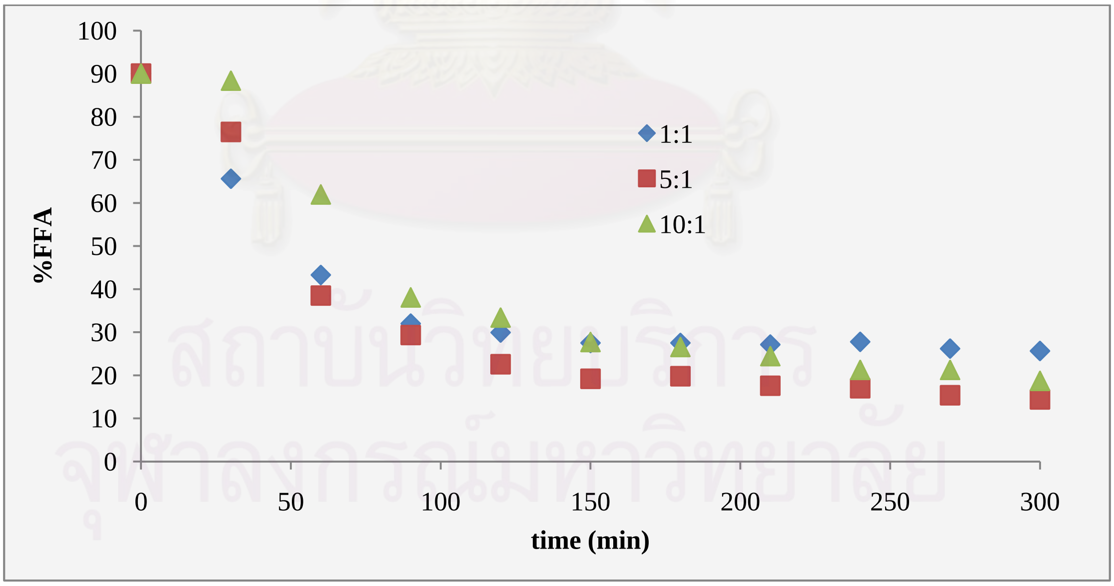


Figure. 4.9 Effect of molar ratio of methanol to free fatty acids in non-catalytic esterification reaction, as treated at 250°C

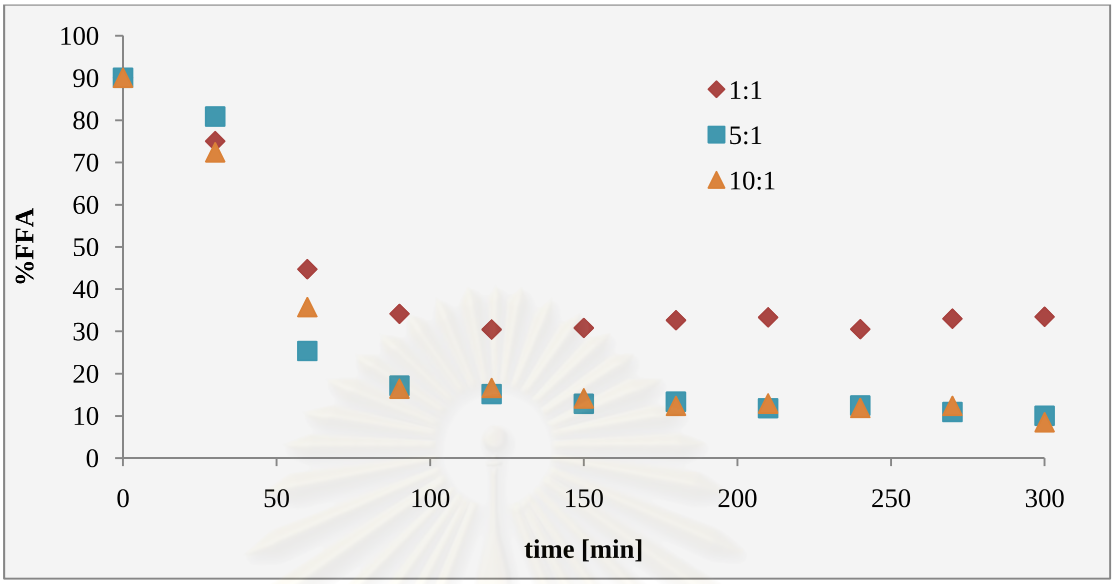


Figure. 4.10 Effect of molar ratio of methanol to free fatty acids in non-catalytic esterification reaction, as treated at 300°C

4.7 Kinetic of non-catalytic esterification reaction

The commonly esterification reaction of free fatty acids with alcohol follows the reaction:

$$R_1\text{-COOH} \quad + \quad R_2\text{-OH} \quad \rightleftarrows \quad R_1\text{-COOH-}R_2 \quad + \quad H_2O \qquad (1)$$

Where R_1 was a linear chain of carbon atoms containing a variable number of unsaturations depending on the particular origin of the raw material, and R_2 was a methyl radical. Berrios, M et al (2007) and Aumnad, B et al (2007) studied kinetic of esterification reaction from biodiesel processed. In this work, esterififcation reaction of palm fatty acids distillate with methanol without catalyst can be presented by the following stoichiometric equation:

$$\text{FFA} \quad + \quad \text{MeOH} \quad \rightleftarrows \quad \text{ME} \quad + \quad H_2O \qquad (2)$$

Where FFA was free fatty acids of Palm fatty acids distillate, MeOH was methanol and ME was methyl ester.

This reaction is homogeneous reaction. It is physical reactions in which the reactants are in the same phase. The rate of reaction does not influence from shape of reactor or from surface area of reactor Heat and mass transfer has not in reaction. The reaction rate for reactant A is then

$$\text{Rate of disappearance of A } (-r) = -\frac{1}{v}\frac{dN_A}{dt}$$

$$= \frac{(\text{amount of A disappearing})}{(\text{volume})(\text{time})}$$

Thus, rate of reaction can write

$r = f$ [temperature dependent terms, concentration dependent terms]

In this study, the model of kinetic reaction based on overall reaction and esterification reaction was assumed to proceed in the second order reaction as a function of the concentration of free fatty acids, methanol, and reaction time, as shown below.

$$\text{rate } (-r_{FFA}) = \frac{dC_{FFA}}{dt} = k \; C_{FFA} C_{MeOH} \qquad (3)$$

Where C_{FFA} refer to the concentration of palm fatty acid distillate used in this study. k is the rate constant of reaction.

Figures 4.11 to 4.13 shows the relation between concentration of free fatty acids and time at molar ratio methanol to palm fatty acids distillate of 1:1, 5:1 and 10:1, a temperature of 200, 250 and 300^{o}C. The analysis results are summarized in Table C.1.1 to Table C.1.9 in Appendix C.

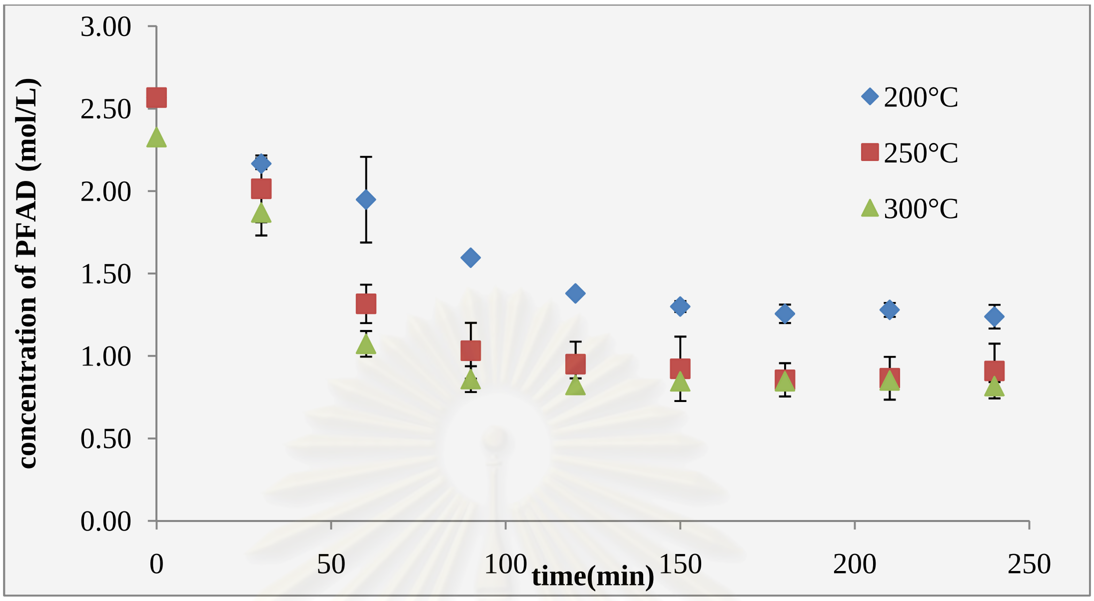


Figure. 4.11 Concentrations of free fatty acids versus time at molar ratio methanol to palm fatty acids distillate of 1:1 and a temperature of 200, 250 and 300^{o}C.

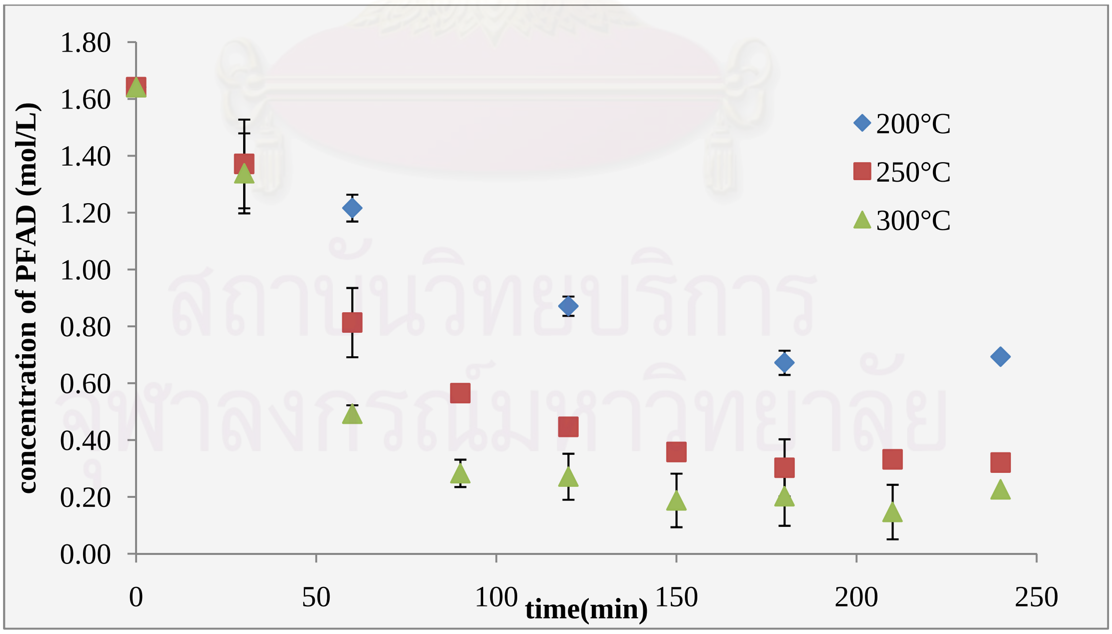


Figure. 4.12 Concentrations of free fatty acids versus time at molar ratio methanol to palm fatty acids distillate of 5:1 and a temperature of 200, 250 and 300^{o}C.

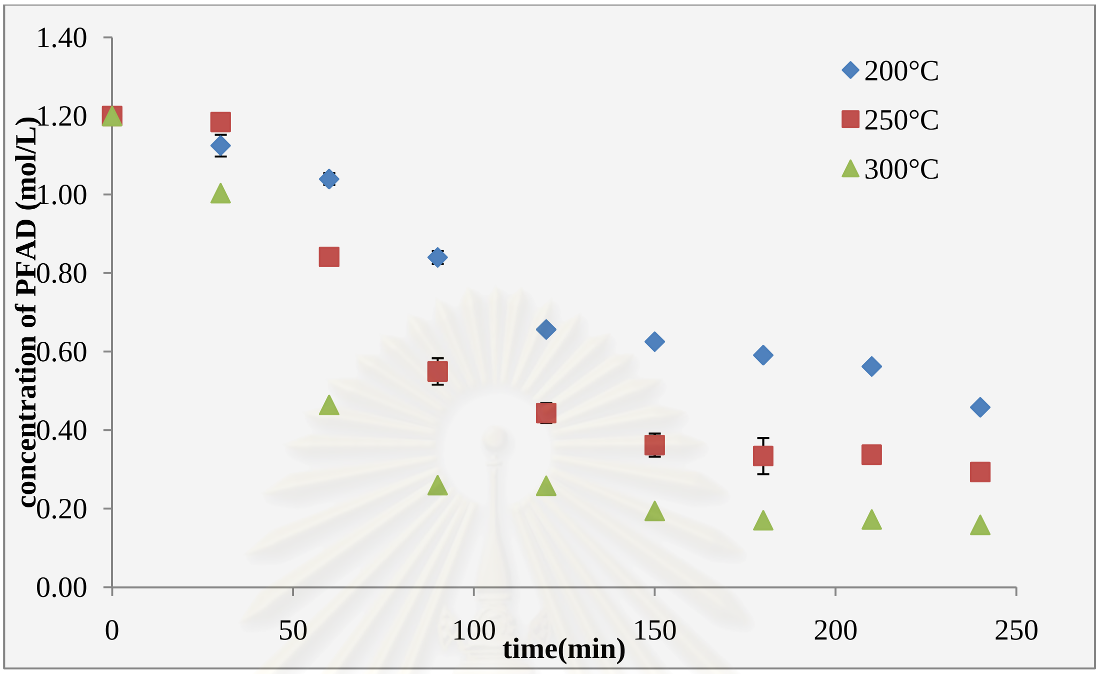


Figure. 4.13 Concentrations of free fatty acids versus time at molar ratio methanol to palm fatty acids distillate of 10:1 and a temperature of 200, 250 and 300^{o}C.

The rate constant of the reaction can be determined based on the decreased amount of reactant, this is percent of fatty acid in palm fatty acid, was chosen. Therefore, the rate constant of reaction can be give by Eq. (3). The experimental result as show from a straight line plot of ln C_{PFAD}/C_{MeOH} versus time in Figure 4.14. It shows the fitting of the experimental data obtained at a methanol to palm fatty acids distillate molar ratio of 1:1, 5:1 and 10:1 and a temperature of 200, 250 and 300^{o}C. The straight line was determined to fit the data in order to adopt the second order rate equation. Summary of the rate constant for each temperature could be evaluated from the slope of each line in Figure 4.13, and the results (k) are tabulated in Table 4.3. The result found that rate constant increases when increases temperature. Chanin, J et al (2007) studied kinetic reduction of free fatty acid in palm oil. The experiment used sulfuric was catalyst (0.05wt %), at temperature of 30 to

60°C and molar ratio of methanol to oil of 1:1. They found that rate constant were increases from 0.0125 to 0.0704 mol/(L·min) when increases temperature. The results indicate that rate constant dependent on temperature.

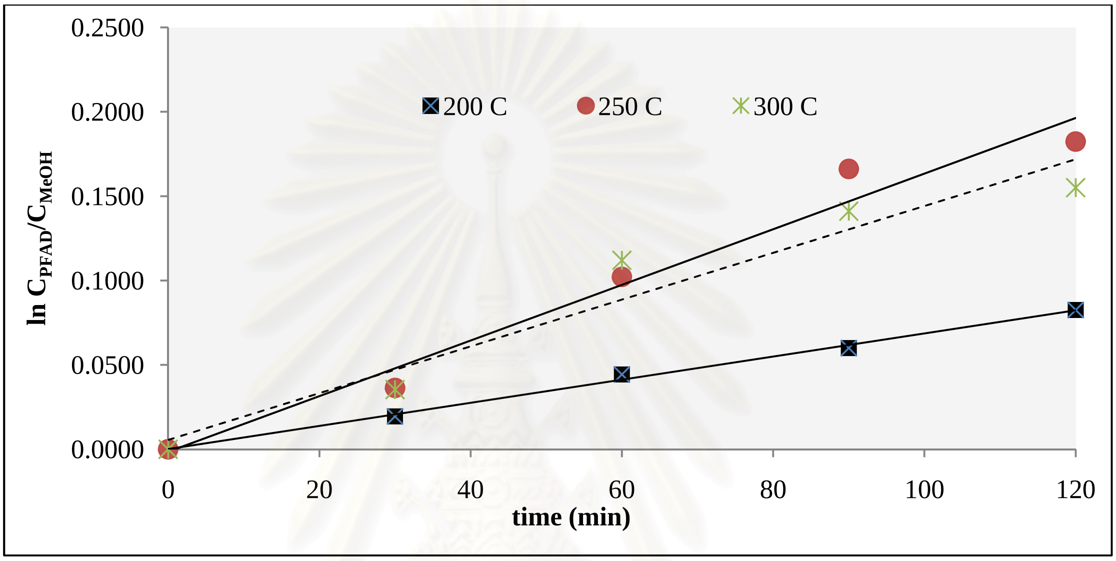


Figure. 4.14 Determination of the kinetic constants at a methanol/palm fatty acid mole ratio of 1:1 and a temperature of 200, 250 and 300 ^{o}C

Table 4.3 The rate constant of palm fatty acid distillate, non-catalystic esterification at different molar ratios of methanol to palm oil.

Reaction temperature (^{o}C)	k [L/(mol·min)]		
	1:1	1:5	1:10
200	0.0027	0.005	0.0042
250	0.0053	0.0115	0.0088
300	0.0107	0.0206	0.0179

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

$$k = k_0 e^{-\frac{E}{RT}} \tag{4}$$

Arrhenius type relationship of the form could describe the relationship between the kinetic constant and the temperature and the activation energy of the reaction (E) was determined from the slope of ln k and 1/T as shown in Figures 4.15 to 4.17. The activation energy of non-catalytic esterification reaction of palm fatty acids distillate was approximate 31.5 kJ/mol.

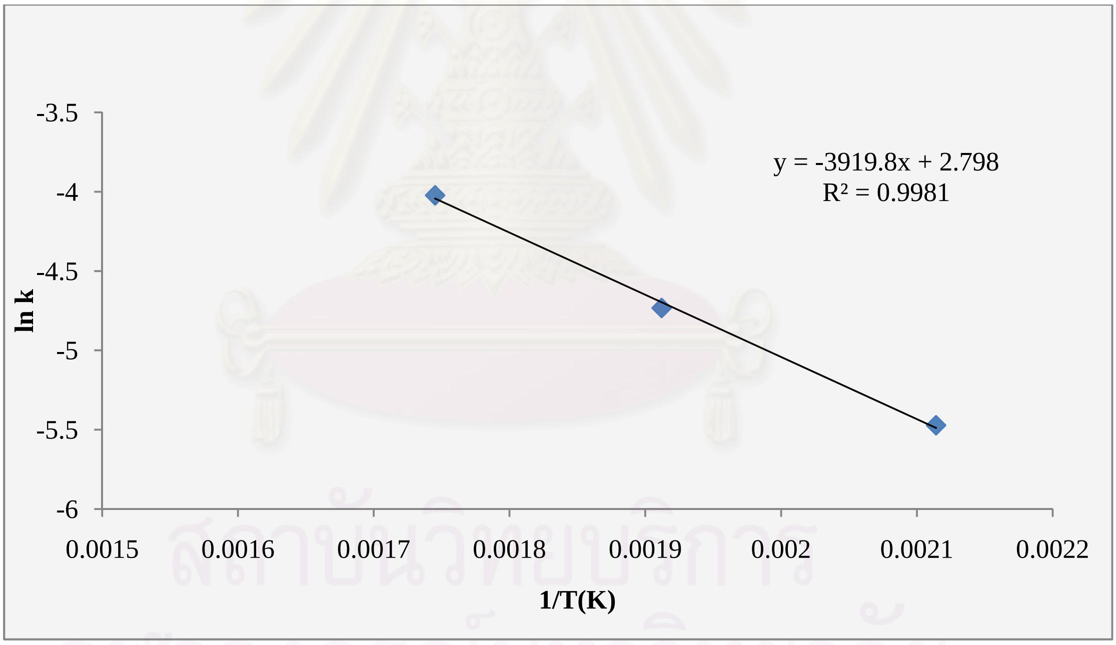


Figure 4.15 Arrhenius plot of palm fatty acid distillate in methanol during non-catalytic esterification reaction. At molar ratio of methanol to palm fatty acids of 1:1

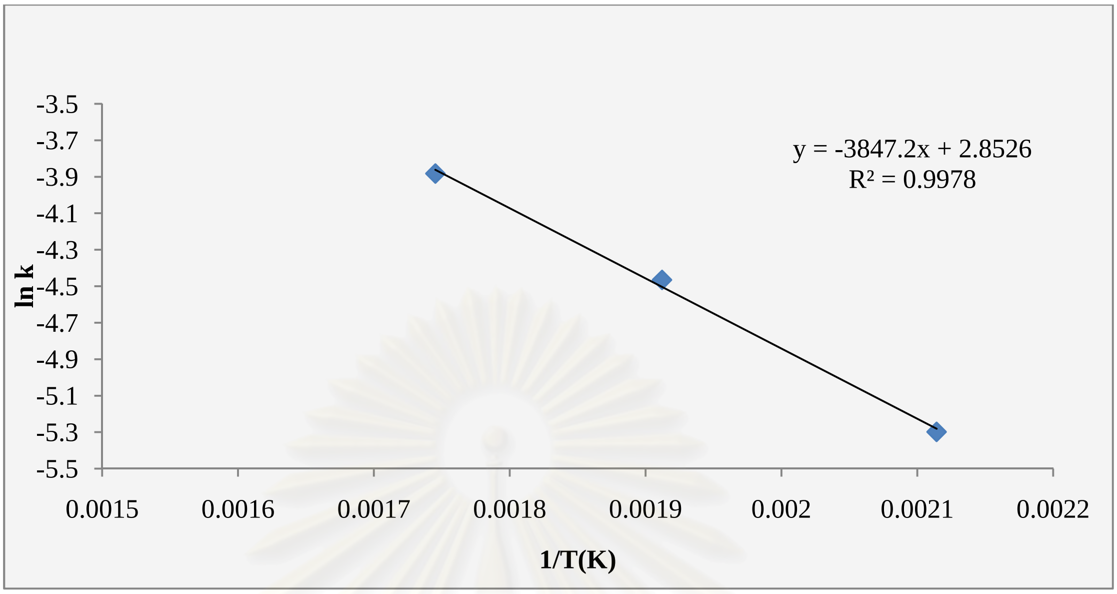


Figure 4.16 Second order reaction rate constant in Arrhenius plot of palm fatty acid distillate in methanol during non-catalytic esterification reaction. At molar ratio of methanol to palm fatty acids of 5:1

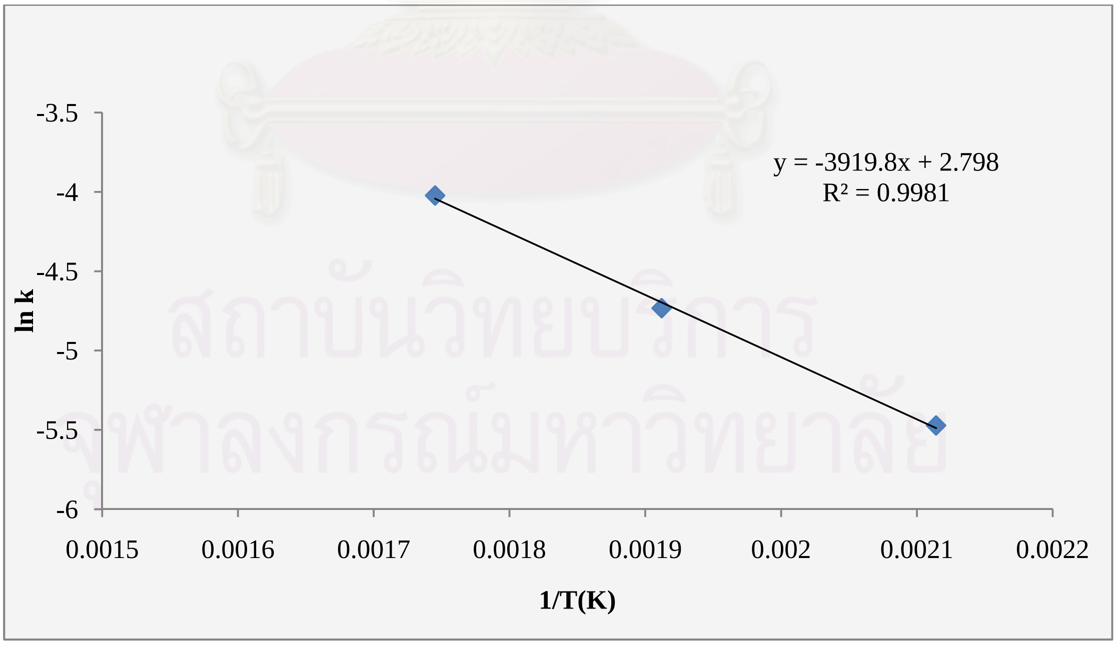


Figure 4.17 Second order reaction rate constant in Arrhenius plot of palm fatty acid distillate in methanol during non-catalytic esterification reaction. At molar ratio of methanol to palm fatty acids of 10:1

4.8 Percent yield of methyl esters by non-catalytic esterification reaction

The samples were analyst by gas chromatography to determined methyl esters content. Figure 4.18 shows percent yield of methyl esters from conducted at molar ratio of methanol to palm fatty acids distillate of 1:1, 5:1 and 10:1, at a temperature of 250 and 300°C. From the result, when increased molar ratio of methanol to palm fatty acids distillate and temperature percent yield of methyl esters are increase. The optimum condition is a molar ratio of methanol to palm fatty acids of 10:1 and temperature of 300°C to give highest yield of 83% Kusdiana, D. and Saka, S. (2001) conducted experiment to product methyl esters from rapeseed oil by supercritical methanol condition. Rapeseed oil and methanol were used as raw materials and the reactions were conducted at temperature of 250 to 550°C. They studied the effect of temperature and pressure of methyl esters. They found that the conversion of methyl ester was increased with increasing temperature and pressure.

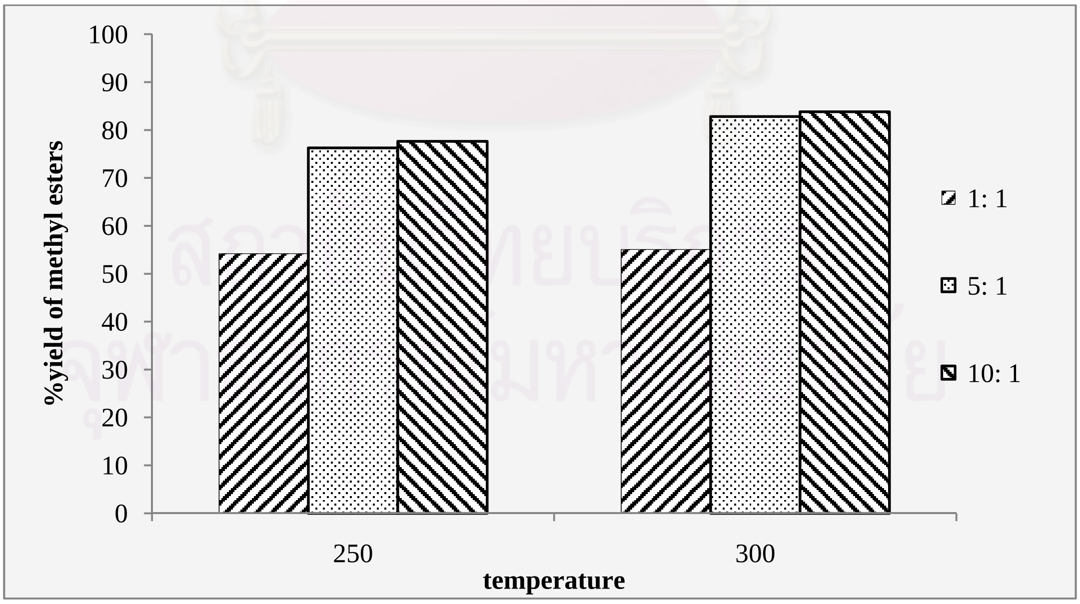


Figure 4.18 Percent yield of methyl esters by non-catalytic esterification reaction.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Esterification reaction of palm fatty acids distillate with methanol without catalyst to find the optimal condition and kinetic of esterification reaction in batch reactor can be concluded as follows:

1. Esterification reaction cannot occur at low temperature of 60°C, but at high temperature esterification reaction can process very well.
2. Effect of increase temperature, the reaction processed quickly during the first 90 minutes. Reaction equilibrium is reached at approximately 100 minutes.
3. Non-catalytic esterification reaction of palm fatty acid distillate can be performed at temperature of higher the 250°C, and at methanol to palm fatty acid distillate molar ratio of high than 5:1, and reaction time of 100 minute. Reaction is reached equilibrium.
4. Rate of reaction non-catalytic esterification reaction of palm fatty acid distillate is second order reaction as a function of the concentration of free fatty acids, methanol, and reaction time and the activation energy of the reaction was approximate 31.5 kJ/mol.

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APPENDICES

APPENDIX A

EXPERIMENTAL AND DATA ANALYSIS

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

This method determines the free fatty acids existing in the sample.

Reagents

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

Table A.1 Free fatty acid range, alcohol volume and strength of alkali

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

Procedure

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

Calculations

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

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

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

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

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

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

1. Weigh of sample 10 g. in conical flasks 250 ml.
2. Add mix equal volumes of 95% toluene and iso-propanol ratio 1:1 50 ml.
3. Solution is titrated with 1.0 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-3 Saponification Value, AOCS official Method Cd-3b-76

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

Reagents

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

Calculation

Let; Weight (in g.) of oil or fat taken = w

Volume (in ml.) of hydrochloric acid used in test = v_1

Volume (in ml.) of hydrochloric acid used in blank = v_2

Normality of hydrochloric acid = N

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

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

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

$$M = \frac{[56108-12.67(S.V.-A.V.)]}{S.V.}$$

Where

S.V. = saponification value of the fat

A.V. = acid value of the fat

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

A-4 Calculation molecular weight of palm fatty acids distillate

Saponification value of palm fatty acids distillate, 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 $= N$

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

$$\text{S.V.} = \frac{56.1 \times 0.5 \times (22 - 7.45)}{2}$$

$$= 204 \ \text{mgKOH/g}$$

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

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

Where

S.V. = saponification value of the fat

A.V. = acid value of the fat

$$\text{M.W.} = \frac{[56108 - 12.67(\text{S.V.} - \text{A.V.})]}{\text{S.V.}}$$

$$\text{M.W.} = \frac{[56108 - 12.67(204 - 176)]}{204}$$

$$\text{M.W.} = 273.3 \ \text{g/mol}$$

APPENDIX B

CALCULATION OF CONCENTRATION OF METHYL ESTER

B-1 Response factor of methyl ester and fatty acid

The response factor is defined as

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

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

$$\text{Response Factor of methyl myristate} = \frac{309 \times 0.075}{10142 \times 0.001996}$$

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

$$\text{Response Factor of methyl myristate} = \frac{309 \times 0.075}{10142 \times 0.001996}$$

$$\text{Response Factor of methyl palmitate} = 1.20$$

$$\text{Response Factor of methyl palmitoleate} = \frac{484 \times 0.075}{10142 \times 0.002991}$$

Response Factor of methyl palmitoleate = 1.20

$$\text{Response Factor of methyl stearate} = \frac{2413 \times 0.075}{10142 \times 0.013986}$$

Response Factor of methyl stearate = 1.28

$$\text{Response Factor of methyl oleate} = \frac{6703 \times 0.075}{10142 \times 0.040877}$$

Response Factor of methyl oleate = 1.22

$$\text{Response Factor of methyl linoleate} = \frac{1142 \times 0.075}{10142 \times 0.06972}$$

Response Factor of methyl linoleate = 1.22

$$\text{Response Factor of methyl linolenate} = \frac{492 \times 0.075}{10142 \times 0.02985}$$

Response Factor of methyl linolenate = 1.23

B-2 Analysis of methyl ester and free fatty acid

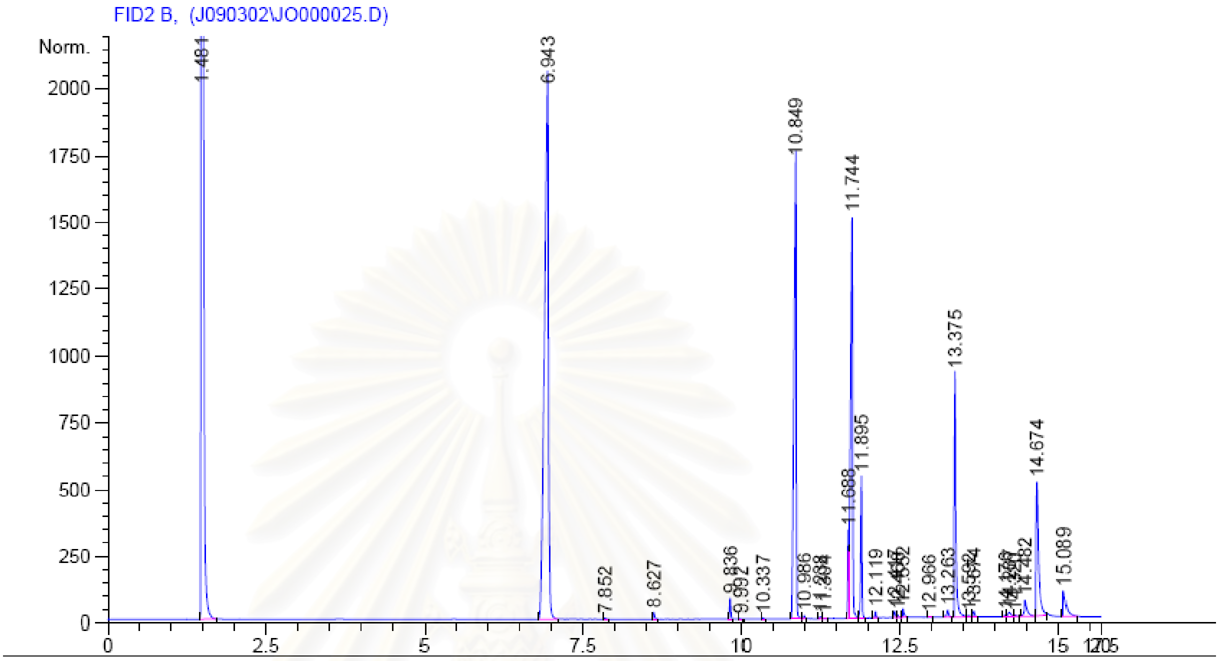
Analysis of methyl ester and free fatty acids in product by used gas chromatography (GC). The retention time of each methyl esters are different. Therefore, for find the type of methyl ester by compare retention time of each methyl ester with methyl ester standard. The retention time are shown in Table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

Table B.1 Retention time of methyl esters in GC chromatogram

Number of peak	Reaction time (min)	Peak of sample
1	1.481	N-Heptane
2	6.943	Methyl Decanoate
3	9.836	Methyl Myristate
4	10.849	Methyl Palmitate
5	10.986	Methyl Palmitoleate
6	11.688	Methyl Stearate
7	11.744	Methyl Oleate
8	11.895	Methyl Linoleate
9	12.119	Methyl Linolenate

B-3 GC chromatogram of methyl ester

From experiment of non-catalytic esterification reaction can see main methylester



```
Name                Total Area   Amount
                     [pA*s]       [ppm]
-----------------|-----------|-----------|
Heptane          1.89307e5     0.0000
Methyl Decanoat  8955.84570 4.838e4
Methyl Myristat   106.40306 512.7503
Methyl Palmitat  4106.98096 1.810e4
Methyl Palmitol    15.46154 293.8093
Methyl Stearate   393.11337 1.495e3
Methyl Oleate    3376.09424 1.390e4
Methyl Linoleat   765.30811 3.401e3
Methyl Linolena    26.69904 141.3040
```

Figure B-1 Chromatogram for methyl ester and fatty acid at condition: Palm fatty acids reactant, molar ratio of methanol to fatty acids distillate of 1:1, at temperature of 300 °C

Example1. From figure B-1, find concentration of methyl ester molar ratio of methanol to oil of 10:1, 300 min at temperature of 300°C and 500 psi. Product of 0.1025 added to 1.4939 g of methyl decanoate solution in n-heptane.

Note that: In methyl decanoate solution 1.4939 g has 0.0750 g of methyl decanoate.

$$\%\text{Metyl Esters} = \frac{\text{Weight of Methyl Ester}}{\text{Weight of Sample}} \times 100$$

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

$$\text{g of methyl myristate} = \frac{106.4}{8955} \times \frac{0.0750}{1.15}$$

$$= 7.72 \times 10^{-4}$$

$$\text{g of methyl palmitate} = \frac{4106.98}{8955} \times \frac{0.0750}{1.20}$$

$$= 2.87 \times 10^{-2}$$

$$\text{g of methyl palmitoleate} = \frac{15.46}{8955} \times \frac{0.0750}{1.20}$$

$$= 1.07 \times 10^{-4}$$

$$\text{g of methyl stearate} = \frac{393.11}{8955} \times \frac{0.0750}{1.28}$$

$$= 2.57 \times 10^{-3}$$

$$\text{g of methyl oleate} = \frac{3376.09}{8955} \times \frac{0.0750}{1.22}$$

$$= 2.32 \times 10^{-2}$$

$$\text{g of methyl linoleate} = \frac{765.308}{8955} \times \frac{0.0750}{1.22}$$

$$= 5.26 \times 10^{-3}$$

$$\text{g of methyl linolenate} = \frac{26.7}{8955} \times \frac{0.0750}{1.23}$$

$$= 1.82 \times 10^{-4}$$

Also; g of total methyl esters $= 6.08 \times 10^{-2}$

$$\%\text{Methyl esters} = \frac{6.08 \times 10^{-2}}{0.10} \times 100$$

$$= 60.80\%$$

APPENDIX C

EXPERIMENTAL DATA ANALYSIS

C-1 Experimental data of non-catalytic esterification reaction time

Table C.1.1 %FFA and concentration at molar ratio methanol to palm fatty acids distillate of 1:1, at temperature of 200 °C and pressure 500 psig

time	%FFA				Concentration(mole/L)			
	Ex1	Ex2	Average	S.D	Ex1	Ex2	Average	S.D
0	90.05	90.05	90.05	0.00	2.57	2.57	2.57	0.00
30	75.18	76.80	75.99	1.14	2.14	2.19	2.17	0.03
60	61.90	74.80	63.45	2.19	1.76	2.13	1.95	0.26
90	55.55	56.43	55.99	0.62	1.58	1.61	1.60	0.02
120	48.32	48.47	48.39	0.11	1.38	1.38	1.38	0.00
150	44.78	46.42	45.60	1.16	1.28	1.32	1.30	0.03
180	45.45	42.68	44.07	1.96	1.30	1.22	1.26	0.06
210	43.86	45.95	44.90	1.48	1.25	1.31	1.28	0.04
240	45.24	41.67	43.45	2.52	1.29	1.19	1.24	0.07
270	41.31	-	-	-	1.18			
300	40.47	-	-	-	1.15			

Table C.1.2 %FFA and concentration at molar ratio methanol to palm fatty acids distillate of 1:1, at temperature of 250 °C and pressure 500 psig

time	%FFA				Concentration(mole/L)			
	Ex1	Ex2	Average	S.D	Ex1	Ex2	Average	S.D
0	90.05	90.05	90.05	0.00	2.57	2.57	2.57	0.00
30	65.63	63.00	64.32	1.86	1.87	2.16	2.01	0.20
60	43.29	49.06	46.17	4.08	1.23	1.40	1.32	0.12
90	31.99	35.00	33.50	2.13	0.91	1.15	1.03	0.17
120	29.93	33.00	31.47	2.17	0.85	1.05	0.95	0.14
150	27.51	29.00	28.26	1.05	0.78	1.06	0.92	0.20
180	27.51	30.00	28.76	1.76	0.78	0.93	0.86	0.10
210	27.13	29.00	28.07	1.32	0.77	0.96	0.87	0.13
240	27.78	27.00	27.39	0.55	0.79	1.03	0.91	0.17
270	26.19	28.00	27.09	1.28	-	-	-	-
300	25.64	28.00	26.82	1.67	-	-	-	-

Table C.1.3 %FFA and concentration at molar ratio methanol to palm fatty acids distillate of 1:1, at temperature of 300 °C and pressure 500 psig

time	%FFA				Concentration(mole/L)			
	Ex1	Ex2	Average	S.D	Ex1	Ex2	Average	S.D
0	90.05	90.05	90.05	0.00	2.33	2.33	2.33	0.00
30	75.03	75.89	75.46	0.60	1.94	1.96	1.95	0.02
60	44.73	38.75	41.74	4.23	1.16	1.00	1.08	0.11
90	34.19	29.86	32.02	3.06	0.88	0.77	0.83	0.08
120	30.45	31.61	31.03	0.82	0.79	0.82	0.80	0.02
150	30.84	33.59	32.21	1.94	0.80	0.87	0.83	0.05
180	32.65	31.87	32.26	0.55	0.84	0.82	0.83	0.01
210	33.33	31.87	32.60	1.03	0.86	0.82	0.84	0.03
240	30.54	31.87	31.20	0.94	0.79	0.82	0.81	0.02
270	33.02	34.37	33.70	0.95	-	-	-	-
300	33.48	33.17	33.32	0.22	-	-	-	-

Table C.1.4 %FFA and concentration at molar ratio methanol to palm fatty acids distillate of 5:1, at temperature of 200 °C and pressure 500 psig

time	%FFA				Concentration(mole/L)			
	Ex1	Ex2	Average	S.D	Ex1	Ex2	Average	S.D
0	90.05	90.05	90.05	0.00	1.64	1.64	1.64	0.00
30	-	-	-	-	-	-	-	-
60	66.80	64.89	65.84	1.35	1.25	1.18	1.22	0.05
90	-	-	-	-	-	-	-	-
120	49.11	46.48	47.80	1.86	0.90	0.85	0.87	0.03
150	-	-	-	-	-	-	-	-
180	38.53	35.23	36.88	2.34	0.70	0.64	0.67	0.04
210	-	-	-	-	-	-	-	-
240	38.03	35.00	36.51	2.14	0.69	-	0.69	-
270	-	-	-	-	-	-	-	-
300	32.11	33.00	32.55	0.63	0.59	-	-	-

Table C.1.5 %FFA and concentration at molar ratio methanol to palm fatty acids distillate of 5:1, at temperature of 250 °C and pressure 500 psig

time	%FFA				Concentration(mole/L)			
	Ex1	Ex2	Average	S.D	Ex1	Ex2	Average	S.D
0	90.05	90.05	90.05	0.00	1.64	1.64	1.64	0.00
30	69.19	73.30	71.25	2.90	1.26	1.48	1.37	0.16
60	39.90	42.00	40.95	1.48	0.73	0.90	0.81	0.12
90	30.40	31.60	31.00	0.84	0.55	0.58	0.57	0.02
120	23.39	25.60	24.50	1.56	0.43	0.47	0.45	0.03
150	19.89	19.40	19.64	0.34	0.36	0.35	0.36	0.01
180	20.50	17.20	18.85	2.33	0.37	0.23	0.30	0.10
210	18.22	-	18.22	-	0.33	-	0.33	-
240	17.61	-	17.61	-	0.32	-	0.32	-
270	15.94	-	15.94	-	0.29	-	-	-
300	14.91	-	14.91	-	0.27	-	-	-

Table C.1.6 %FFA and concentration at molar ratio methanol to palm fatty acids distillate of 5:1, at temperature of 300 °C and pressure 500 psig

time	%FFA				Concentration(mole/L)			
	Ex1	Ex2	Average	S.D	Ex1	Ex2	Average	S.D
0	90.05	90.05	90.05	0.00	1.64	1.64	1.64	0.00
30	68.54	65.00	67.65	2.34	1.25	1.50	1.34	0.14
60	25.36	28.67	27.03	1.66	0.46	0.52	0.49	0.03
90	17.14	17.01	15.55	2.64	0.31	0.31	0.28	0.05
120	15.18	18.20	14.57	3.98	0.28	0.35	0.27	0.08
150	6.00	8.00	6.12	1.82	0.23	0.25	0.19	0.09
180	5.50	5.60	5.25	0.52	0.24	0.28	0.20	0.10
210	5.00	-	4.68	0.45	0.22	-	0.15	0.10

Table C.1.7 %FFA and concentration at molar ratio methanol to palm fatty acids distillate of 10:1, at temperature of 200 °C and pressure 500 psig

time	%FFA				Concentration(mole/L)			
	Ex1	Ex2	Average	S.D	Ex1	Ex2	Average	S.D
0	90.05	90.05	90.05	0.00	1.20	1.20	1.20	0.00
30	85.86	80.00	82.93	4.15	1.14	1.10	1.12	0.03
60	78.79	75.60	77.20	2.26	1.05	1.03	1.04	0.02
90	62.16	65.60	63.88	2.43	0.83	0.85	0.84	0.02
120	48.92	50.20	49.56	0.90	0.65	0.66	0.66	0.01
150	46.78	47.30	47.04	0.36	0.62	0.63	0.63	0.00
180	44.03	45.20	44.62	0.83	0.59	0.59	0.59	0.01
210	42.46	41.30	41.88	0.82	0.57	0.56	0.56	0.01
240	33.94	35.60	34.77	1.17	0.45	0.46	0.46	0.01

Table C.1.8 %FFA and concentration at molar ratio methanol to palm fatty acids distillate of 10:1, at temperature of 250 °C and pressure 500 psig

time	%FFA				Concentration(mole/L)			
	Ex1	Ex2	Average	S.D	Ex1	Ex2	Average	S.D
0	90.05	90.05	90.05	0.00	1.20	1.20	1.20	0.00
30	75.60	89.70	84.46	7.71	1.17	1.20	1.18	0.02
60	60.30	62.03	62.18	1.96	0.86	0.83	0.84	0.02
90	34.60	43.01	39.02	4.22	0.53	0.57	0.55	0.03
120	32.30	31.95	32.95	1.44	0.46	0.43	0.44	0.02
150	27.70	25.60	27.34	1.59	0.38	0.34	0.36	0.03
180	26.80	22.61	25.64	2.65	0.37	0.30	0.33	0.05
210	24.30	-	-	-	0.34	-	-	-
240	23.20	-	-	-	0.29	-	-	-
270	22.60	-	-	-	0.29	-	-	-
300	20.40	-	-	-	0.26	-	-	-

Table C.1.9 %FFA and concentration at molar ratio methanol to palm fatty acids distillate of 10:1, at temperature of 300 °C and pressure 500 psig

time	%FFA				Concentration(mole/L)			
	Ex1	Ex2	Average	S.D	Ex1	Ex2	Average	S.D
0	90.05	90.05	90.05	0.00	1.20	1.20	1.20	0.00
30	72.40	78.20	75.30	4.10	0.96	1.04	1.00	0.05
60	35.74	33.94	34.84	1.27	0.48	0.45	0.46	0.02
90	16.45	22.53	19.49	4.30	0.22	0.30	0.26	0.06
120	16.63	22.12	19.37	3.88	0.22	0.29	0.26	0.05
150	14.17	14.96	14.56	0.56	0.19	0.20	0.19	0.01
180	12.39	13.17	12.78	0.55	0.17	0.18	0.17	0.01

Table C.1.10 %FFA at molar ratio methanol to palm fatty acids distillate of 1:1, at temperature of 200 °C and pressure 1000 psig

Sample No.	Time (min)	%FFA	Concentration(mole/L)
0	0	90.05	2.33
1	30	82.94	2.14
2	60	64.77	1.67
3	90	56.32	1.46
4	120	53.01	1.37
6	180	47.99	1.24
7	210	47.31	1.22
8	240	45.06	1.16

Table C.1.11 %FFA at molar ratio methanol to palm fatty acids distillate of 1:1, at temperature of 250 °C and pressure 1000 psig

Sample No.	Time (min)	%FFA	Concentration(mole/L)
0	0	90.05	2.33
1	30	78.85	2.04
2	60	46.93	1.21
3	90	41.59	1.08
4	120	36.44	0.94
5	150	35.50	0.92
6	180	35.73	0.92
7	210	36.04	0.93

Sample No.	Time (min)	%FFA	Concentration(mole/L)
8	240	37.55	0.97

Table C.1.12 %FFA at molar ratio methanol to palm fatty acids distillate of 1:1, at temperature of 300 °C and pressure 1000 psig

Sample No.	Time (min)	%FFA	Concentration(mole/L)
0	0	90.05	2.33
1	30	73.02	1.89
2	60	47.01	1.22
3	90	36.61	0.95
4	120	36.61	0.95
5	150	36.61	0.95
6	180	34.60	0.89
7	210	37.26	0.96
8	240	33.79	0.87

Table C.1.13 %FFA at molar ratio methanol to palm fatty acids distillate of 5:1, at temperature of 200 °C and pressure 1000 psig

Sample No.	Time (min)	%FFA	Concentration(mole/L)
0	0	90.05	1.64
1	30	79.51	1.45
2	60	64.03	1.17

Sample No.	Time (min)	%FFA	Concentration(mole/L)
3	90	48.81	0.89
4	120	36.95	0.67
5	150	29.57	0.54
6	180	34.33	0.63
7	210	31.74	0.58
8	240	24.33	0.44

Table C.1.14 %FFA at molar ratio methanol to palm fatty acids distillate of 5:1, at temperature of 250 °C and pressure 1000 psig

Sample No.	Time (min)	%FFA	Concentration(mole/L)
0	0	90.05	1.64
1	30	67.58	1.23
2	60	38.62	0.70
3	90	28.16	0.51
4	120	21.66	0.39
5	150	18.30	0.33
6	180	19.31	0.35
7	210	16.22	0.30
8	240	13.81	0.25

Table C.1.15 %FFA at molar ratio methanol to palm fatty acids distillate of 5:1, at temperature of 300 °C and pressure 1000 psig

Sample No.	Time (min)	%FFA	Concentration(mole/L)
0	0	90.05	1.64
1	30	60.59	1.10
2	60	19.59	0.36
3	90	13.35	0.24
4	120	11.68	0.21
5	150	9.56	0.17
6	180	13.31	0.24
7	210	10.51	0.19
8	240	12.13	0.22

Table C.1.16 %FFA at molar ratio methanol to palm fatty acids distillate of 10:1, at temperature of 200 °C and pressure 1000 psig

Sample No.	Time (min)	%FFA	Concentration(mole/L)
0	0	90.05	1.20
1	30	90.48	1.21
2	60	71.97	0.96
3	90	63.90	0.85
4	120	53.25	0.71
5	150	45.64	0.61
6	180	46.26	0.62

Sample No.	Time (min)	%FFA	Concentration(mole/L)
7	210	37.51	0.50

Table C.1.17 %FFA at molar ratio methanol to palm fatty acids distillate of 10:1, at temperature of 250 °C and pressure 1000 psig

Sample No.	Time (min)	%FFA	Concentration(mole/L)
0	0	90.05	1.20
1	30	87.77	1.17
2	60	45.47	0.61
3	90	44.24	0.59
4	120	23.28	0.31
5	150	14.59	0.19
6	180	16.38	0.22
7	210	15.02	0.20

Table C.1.18 %FFA at molar ratio methanol to palm fatty acids distillate of 10:1, at temperature of 300 °C and pressure 1000 psig

Sample No.	Time (min)	%FFA	Concentration(mole/L)
0	0	90.05	1.20
1	30	71.00	0.95
2	60	31.95	0.43
3	90	16.38	0.22

Sample No.	Time (min)	%FFA	Concentration(mole/L)
4	120	11.06	0.15
5	150	8.51	0.11
6	180	8.19	0.11
7	210	9.62	0.13

VITA

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