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PRODUCTION OF METHYL ESTERS FROM PALM OIL WITH HIGH CONTENT OF FREE FATTY ACIDS

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
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วัชรัตน์ งามสอาด : การผลิตเมทิลเอสเทอร์จากน้ำมันปาล์มที่มีปริมาณกรดไขมันสูง. (PRODUCTION OF METHYL ESTERS FROM PALM OIL WITH HIGH CONTENT OF FREE FATTY ACIDS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : อ.ดร.เจิดศักดิ์ ไชยคุนา, 77 หน้า.

งานวิจัยนี้เป็นการศึกษาการผลิตเมทิลเอสเทอร์ด้วยวิธีสองขั้นตอนโดยใช้ของผสมของน้ำมันปาล์มโอเลอินและกรดไขมันเป็นสารตั้งต้นในอัตราส่วนร้อยละ 4.5 โดยน้ำหนักของกรดไขมันในน้ำมันปาล์มโอเลอิน การทดลองเป็นการทำปฏิกิริยาระหว่างน้ำมันผสมกับเมทานอลในถังปฏิกรณ์แบบกะ การทดลองขั้นตอนแรกเป็นการทดลองแบบไม่ใช้ตัวเร่งปฏิกิริยา ทำการทดลองที่อุณหภูมิ 60 150 200 และ 250 องศาเซลเซียส ที่ความดัน 14.7 500 และ 1000 ปอนด์ต่อตารางนิ้ว และที่อัตราส่วนโดยโมลของเมทานอลต่อน้ำมันเท่ากับ 3:1 6:1 และ 9:1 การทดลองขั้นตอนที่สองเป็นการทำปฏิกิริยาทรานเอสเทอร์ริฟิเคชันเพื่อผลิตเมทิลเทอร์ โดยใช้โซเดียมเมทิลเลทเป็นตัวเร่งปฏิกิริยา ทำปฏิกิริยาที่อัตราส่วนโดยโมลของเมทานอลต่อน้ำมันคือ 6:1 ที่อุณหภูมิ 60 องศาเซลเซียส และความดันบรรยากาศ

ผลการทดลองแสดงว่าปฏิกิริยาเอสเทอร์ริฟิเคชันของกรดไขมันอิสระในน้ำมันปาล์มสามารถเกิดขึ้นได้เมื่ออุณหภูมิสูงกว่า 150 องศาเซลเซียส และความดันสูงกว่า 1000 ปอนด์ต่อตารางนิ้ว สภาวะที่เหมาะสมที่สามารถลดปริมาณกรดไขมันจากร้อยละ 4.5 เหลือน้อยกว่าร้อยละ 2 คือที่อุณหภูมิสูงกว่า 150 องศาเซลเซียส ความดันสูงกว่า 1000 ปอนด์ต่อตารางนิ้ว และที่ปริมาณอัตราส่วนโดยโมลของเมทานอลต่อน้ำมันคือ 6:1 ภายใน 1 ชั่วโมง ผลการทดลองในขั้นตอนที่สองแสดงค่าผลได้ของเมทิลเอสเทอร์สูงถึงร้อยละ 90 ในเวลา 1 ชั่วโมง

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต วัชรัตน์ งามสอาด
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WATCHARAT NGAMSA-ARD : PRODUCTION OF METHYL ESTERS FROM PALM OIL WITH HIGH CONTENT OF FREE FATTY ACIDS. ADVISOR : JIRDSAK TSCHEIKUNA, Ph.D, 77 pp.

The objective of this study is to investigate the production of methyl esters by two step method. Palm olein oil and palm fatty acids distillate were used as raw materials and were mixed at a ratio of 4.5% of free fatty acids. The experiments were carried out in a batch reactor using an oil mixture and methanol. A non-catalytic esterification reaction is used in the first step. The experiments were conducted at temperatures of 60, 150, 200 and 250°C, at pressures of 14.7, 500 and 1000 psia and at methanol to oil molar ratio of 3:1, 6:1 and 9:1. In the second step, methyl esters was produced by transesterification reaction using sodium methylate as an alkaline catalyst. The reactions were conducted at a molar ratio of methanol to oil of 6:1 and at a temperature of 60°C and at ambient pressure.

The results indicate that esterification reaction of free fatty acid content in palm oil can occur when temperature is higher than 150°C and pressure is higher than 1000 psia. The suitable conditions of esterification reaction reduce free fatty acid content from 4.5% to less than 2% are a temperature of at least 150°C, a pressure of at least 1000 psia and at methanol to oil molar ratio of at least 6:1 in 1 hr. The second step, the results indicate that the final yield of methyl esters was achieved at 90% in 1 hr.

Department : Chemical Engineering Student's Signature Ng. Watcharat.
Field of Study : Chemical Engineering Advisor's Signature
Academic Year : 2008

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CHAPTER I

INTRODUCTION

Fatty acid methyl esters are aliphatic organic esters used extensively as intermediates in manufacture of detergents, emulsifiers, textile treatment and waxes among other applications. It can also be used as an alternative fuel (biodiesel) and lubricant. Vegetable oils and animal fats are normally used as raw materials along with suitable alcohols such as methanol. The reaction is called transesterification reaction. Alkalines such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) are used as catalyst. In order for the reaction to proceed effectively, free fatty acids content in oil must be less than 2wt%. Several types of vegetable oils such as crude palm oil, crude jatropha oil and tobcco seed oil have free fatty acids content of 4-15 wt%. Two step method is employed to produce fatty acids methyl esters from these oils. The method consists of an esterification reaction to reduce free fatty acids content followed by a transesterification reaction to convert tryiglycerides to fatty acids methyl esters. Esterification reaction is a chemical reaction between free fatty acids and alcohol to produce fatty acids methyl esters. Acids such as sulfuric acid (H_2SO_4) are used as catalyst. Berchmans H.J. and Hirata S. conducted experiment to reduce free fatty acids content in crude jatropha oil by esterification reaction. The experiments were carried out using methanol to oil weight ratio of 0.60 w/w and at H_2SO_4 catalyst of 1% w/w. They found that free fatty acids content was reduced from 15% to less than 1%. Their experiments were conducted for 1 hour. Veljkovic V.B. et al. conducted experiment to reduce free fatty acids content of tobacco seed oil by esterification reaction. The experiments were carried out with methanol and sulfuric acid was used as catalyst. Free fatty acids level was reduced from 35% to less than

2% in 25 min at molar ratio of methanol to oil of 18:1, in the presence of 2% w/w H_2SO_4 and at temperature of 60 °C.

Even though two step method can be used with high free fatty acids content oil, several problems in production also arise. The oil must be purified to remove acid catalyst and water before it can be processed in the second step. Corrosion of equipment because of acid catalyst is also another problem. High temperature and pressure (supercritical condition) transesterification of vegetable oils with methanol without catalysts have been successfully performed by several researches such as Kusdiana D. and Saka S. The experiments were carried out in a batch-type supercritical biomass conversion system. Rapeseed oil and methanol were used as raw materials and the reactions were conducted at temperature of 250 to 550 °C and at pressure of 1-20 MPa. They found that the conversion of methyl ester was increased with increasing pressure. Developing under the same basics, this work investigates an esterification reaction of free fatty acids in palm oil with methanol under high temperature and pressure conditions at various methanol to oil ratio.

CHAPTER II

LITERATURE REVIEWS

Methyl ester is compound of ester has structure CH_3COOR when R depend on the type of FFA such as palmitic acid, stearic acid and oleic acid etc. When palmitic acid reacts with methanol the product is methyl palmitate, stearic acid reacts with methanol the product is methyl state, oleic acid reacts with methanol the product is methyl oleate. Methyl ester product from vegetable oils or fat from animals. The reaction carry out with alcohol, the product is alkyl ester and glycerol is by product. The present methyl esters can convert to other products such as alkanolamine, isopropyl ester, fatty alcohol and sucrose polyester etc. Furthermore methyl esters can use in surfactant industrial and fuel gas is biodiesel. The process of methyl ester use vegetable oils, fat from animals and waste cooking oils. The vegetable oils to production methyl ester have many type such as palm oil, soybean oil, coconut oil, sunflower oil and rapeseed oil etc. In another part of the world use different materials show in Table 2.1. In America use soybean oil, in Europe use rapeseed oil and in Asia use palm oil. Especially South East Asia palm oil is industrial drop. This research advertent palm oil because it abound in Thailand.

Table 2.1 Major of materials of biodiesel fuel

	Palm oil	Soybean oil	Rapeseed oil
Area	Asia	U.S.	Europa
Major component	Palmitic acid	Linoleic acid	Oleic acid
Production (kton)	33,328	32,857	15,734
Oil Yield at 1 ha (kg)	5,000	375	1,000

Palm Oil

The palm fruit is the source of both palm oil and palm kernel oil. Palm oil extracted from palm fruit flesh and palm kernel or seed oil. They are composed of fatty acids esterified with glycerol just like any ordinary fat. Both are high in saturated fatty acids. Saturated fat, also found in coconut oil, beef fat, and milk fat are correlated with an increased incidence of atherosclerosis and coronary heart disease. The palm oil gives its name to the 16 carbon saturated fatty acid palmitic acid found in palm oil; monosaturated oleic acid is also a constituent of palm oil, It shows in Table 2.2.

Table2.2 Fatty Acid composition of palm oil and other vegetable oils

Fatty Acid	Palm	Jatropha	Coconut	Rapeseed	Soybean	Sunflower
Caprylic acid (C8:0)	-	-	8.30	-	-	-
Capric acid (C10:0)	-	-	5.80	-	-	-
Lauric acid (C12:0)	-	-	48.70	-	-	-
Myristic acid (C14:0)	1.0	-	18.00	-	-	-
Palmitic acid (C16:0)	44.2	14.0	8.60	4.0	10.3	6.7
Stearic acid (C18:0)	4.5	8.0	2.60	1.7	3.8	3.7
Oleic acid (C18:1)	39.3	34.0	6.50	58.6	24.3	19.0
Linoleic acid (C18:2)	9.6	43.0	-	21.8	52.7	69.9
Linolenic acid(C18:3)	0.3	-	-	10.8	7.9	0.7

Objective of this research point to reduce free fatty acid in palm oil, normally palm oil have fatty acids 4 – 6 %wt of palm oil Chonghong et al. (2007) and Veljkovic et al. (2006). Generally of method for product methyl esters from palm oil is 2 step method. The first step of the process is to reduce free fatty acids content in vegetable oil by esterification reaction show in Figure 2.1.

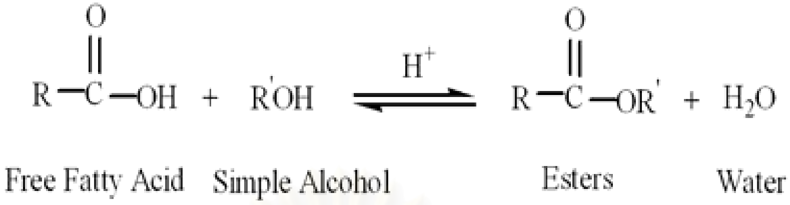

Figure 2.1 Esterification equation

The second step is transesterification reaction show in Figure 2.2, in which triglyceride portion of the oil reacts with methanol and alkaline catalyst to form alkyl ester and glycerol.

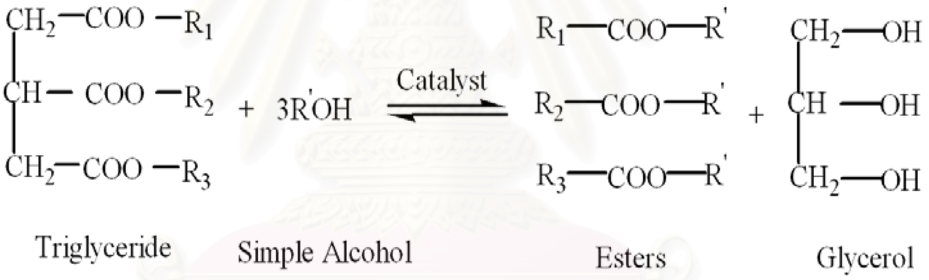

Figure 2.2 Transesterification equation

Literature review for esterification reaction of palm oil by acid catalyst

A.K. Tiwari et al. (2007) studied response surface methodology (RSM) based on central composite rotatable design (CCRD). They was used to optimize the three important reaction variables-methanol quantity (*M*), acid concentration (*C*) and reaction time (*T*) for reduction of free fatty acid (FFA) content of the oil to around 1% as compared to methanol quantity (*M′*) and reaction time (*T′*) and for carrying out transesterification of the pretreated oil. Using RSM, quadratic polynomial equations were obtained for predicting acid value and transesterification. Verification experiments confirmed the validity of both the predicted models. The optimum combination for reducing the FFA of *Jatropha curcas* oil from 14% to less than 1% was found to be 1.43% v/v H_2SO_4 acid catalyst, 0.28 v/v methanol-to-oil ratio and 88-min reaction time at a reaction temperature of 60 °C as compared to 0.16 v/v methanol-to-pretreated oil ratio and 24 min of reaction time at a reaction temperature of 60 °C for producing biodiesel. This process gave an average yield of biodiesel more than 99%. The fuel properties of jatropha biodiesel so obtained were found to be comparable to those of diesel and confirming to the American and European standards.

A.S. Ramadhas et al. (2005) studied biodiesel production. Most of the biodiesel is produced from the refined/edible type oils using methanol and an alkaline catalyst. However, large amount of non-edible type oils and fats are available. The difficulty with alkaline-esterification of these oils is that they often contain large amounts of free fatty acids (FFA). These free fatty acids quickly react with the alkaline catalyst to produce soaps that inhibit the separation of the ester and glycerin. A two-step transesterification process is developed to convert the high FFA oils to its mono-esters. The first step, acid catalyzed esterification reduces the FFA content of the oil to less than 2%. The second step, alkaline catalyzed transesterification process converts the products of the first step to its mono-esters and glycerol. The major factors affect the conversion efficiency of the process such as molar ratio, amount of catalyst, reaction temperature and reaction duration is analyzed. The two-step esterification procedure converts rubber seed oil to its methyl esters. The viscosity of biodiesel oil is nearer to that of diesel and the calorific value is about 14% less than that of diesel. The important properties of biodiesel such as specific gravity, flash point, cloud point and pour point are found out and compared with that of diesel. This study supports the production of biodiesel from unrefined rubber seed oil as a viable alternative to the diesel fuel.q 2004 Elsevier Ltd. All rights reserved.

H.J. Berchmans and S. Hirata (2007) studied technique to produce biodiesel from crude Jatropha curcas seed oil (CJCO). Crude jatropha curcas seed oil having high free fatty acids (15%FFA) has been developed. 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 H2SO4 as an acid catalyst in 1-h reaction at 50 °C. After the reaction, the mixture was allowed to settle for 2 h 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 ca. 90% in 2 h.

J.F. Reyes and M.A. Sepu´lveda (2006) studied power response and level of particulate emissions. They were assessed for blends of Diesel-crude Biodiesel and Diesel-refined Biodiesel. Crude Biodiesel and refined Biodiesel or methyl ester, were made from salmon oil with high content of free fatty acids, throughout a process of acid esterification followed by alkaline transesterification. Blends of Diesel-crude Biodiesel and Diesel-refined Biodiesel were tested in a diesel engine to measure simultaneously the dynamometric response and the particulate material (PM-10) emission performance. The results indicate a maximum power loss of about 3.5% and also near 50% of PM-10 reduction with respect to diesel when a 100% of refined Biodiesel is used. For blends with less content of either crude Biodiesel or refined Biodiesel, the observed power losses are lower but at the same time lower reduction in PM-10 emissions are attained.

J.M. Marchetti et al. (2007) studied production of methyl ester from frying oils. Frying oils have become the newest raw material for the transesterification reaction for the production of biodiesel. However, these compounds usually come with a certain amount of free fatty acids. These impurities can be transformed into esters and the production of biodiesel could be increased. The use of basic resins to perform the esterification reaction into biodiesel is studied in this work. The effect of the most relevant variables of the process such as reaction temperature, molar ratio between alcohol and oil, amount of catalyst and amount of free fatty acids fed with the oil have been analyzed. For this purpose, an ideal frying oil using oleic acid and soybean oil was made. The alcohol used was ethanol. The esterification of free fatty acid using this heterogeneous catalyst appears as a great alternative to purify frying oil; in this case, the final conversion achieved was around 80%.

S. Chongkhong et al. (2007) studied production of fatty acid methyl ester (FAME) from palm fatty acid distillate (PFAD). Palm fatty acid distillate having high free fatty acids (FFA) was investigated in this work. Batch esterifications of PFAD were carried out to study the influence of: including reaction temperatures of 70–100 1C, molar ratios of methanol to PFAD of 0.4:1–12:1, quantity of catalysts of 0–5.502% (wt of sulfuric acid/wt of PFAD) and reaction times of 15–240 min. The optimum condition for the continuous esterification process (CSTR) was molar ratio of methanol to PFAD at 8:1 with 1.834wt% of H2SO4 at 70 1C under its own pressure with a retention time of 60 min. The amount of FFA was reduced from 93wt% to less than 2wt% at the end of the esterification process. The FAME was purified by neutralization with 3M sodium hydroxide in water solution at a reaction temperature of 80 1C for 15 min followed by transesterification process with 0.396M sodium hydroxide in methanol solution at a reaction temperature of 65 1C for 15 min. The final FAME product met with the Thai biodiesel quality standard, and ASTM D6751-02.

S.V. Ghadge and H. Raheman (2005) studied a technique to produce biodiesel from mahua oil (Madhuca indica). Mahua oil having high free fatty acids (19% FFA) has been developed. 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 H2SO4 as an acid catalyst in 1-hour reaction at 601C. 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. The fuel properties of mahua biodiesel were found to be comparable to those of diesel and conforming to both the American and European standards.

V.B. Veljkovic et al. (2006) studied production of fatty acid methyl esters (FAME) from crude tobacco seed oil (TSO). Crude tobacco seed oil having high free fatty acids (FFA) was investigated. Due to its high FFA, the TSO was processed in two steps: the acid-catalyzed esterification (ACE) followed by the base-catalyzed methanolysis (BCM). 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 tobacco biodiesel obtained had the fuel properties within the limits prescribed by the latest American (ASTM D 6751-02) and European (DIN EN14214) standards, except a somewhat higher acid value than that prescribed by the latter standard (<0.5). Thus, tobacco seeds (TS), as agricultural wastes, might be a valuable renewable raw material for the biodiesel production.

Y. Wang et al. (2006) studied the traditional acid and the new two-step catalyzed processes for synthesis of biodiesel expressed as fatty acid methyl ester (FAME). They were comparatively studied to achieve an economic and practical method for utilization of waste cooking oil (WCO) from Chinese restaurants. WCO samples with the acid value of 75.92 ± 0.04 mgKOH/g mixed with methanol were catalyzed under 95 ◦C for various reaction time, followed by methanol recovery under vacuum (10 ±1 mmHg) at 50 ◦C with a rotational evaporation. FAME analyzed by gas chromatography (GC) was obtained directly from sulfuric acid catalyzed reaction in the traditional acid method, whereas in the two-step method it was produced from ferric sulfate (2.0%) catalyzed reaction followed by alkali (1.0% potassium hydroxide) transesterification. The conversion of free fatty acids of WCO into FAME in the two-step method was 97.22% at the reaction time of 4 h, mole ratio of methanol to TG of 10:1, compared in the acid method with 90%, 10 h, and 20:1, respectively, showing much higher catalyzed activity of ferric sulfate. This new two-step process showed advantages of no acidic wastewater, high efficiency, low equipment cost, and easy recovery of catalyst compared with the limitations of acidic effluent, no reusable catalyst and high cost of equipment in the traditional acid process.

Y. Wang et al. (2007) studied production of methyl esters from waste cooking oils (WCO). It contain large amounts of free fatty acids produced in restaurants, are collected by the environmental protection agency in the main cities of China and should be disposed in a suitable way. In this research, a two step catalyzed process was adopted to prepare biodiesel from waste cooking oil whose acid value was 75.92 0.036 mgKOH/g. The free fatty acids of WCO were esterified with methanol catalyzed by ferric sulfate in the first step, and the triglycerides (TGs) in WCO were transesterified with methanol catalyzed by potassium hydroxide in the second step. The results showed that ferric sulfate had high activity to catalyze the esterification of free fatty acids (FFA) with methanol. The conversion rate of FFA reached 97.22% when 2 wt% of ferric sulfate was added to the reaction system containing methanol to TG in10:1 (mole ratio) composition and reacted at 95 °C for 4 h. The methanol was vacuum evaporated, and transesterification of the remained triglycerides was performed at 65 °C for 1 h in a reaction system containing 1 wt% of potassium hydroxide and 6:1 mole ratio of methanol to TG. The final product with 97.02% of biodiesel, obtained after the two step catalyzed process, was analyzed by gas chromatography. 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

Literature review for non-catalytic reaction in palm oil

Fatty acids can eradicate by non-catalytic at high pressure and high temperature condition.

Ayhan Demirbas (2006) studied production of methyl esters from vegetable oil. Methyl esters, commonly referred to as ‘‘biodiesel,’’ are prominent candidates as alternative Diesel fuels. Biodiesel is technically competitive with or offers technical advantages compared to conventional petroleum Diesel fuel. The vegetable oils, as alternative engine fuels, are all extremely viscous with viscosities ranging from 10 to 20 times greater than that of petroleum Diesel fuel. The purpose of the transesterification process is to lower the viscosity of the oil. Transesterifications of vegetable oils in supercritical methanol are performed without using any catalyst. The most important variables affecting the methyl ester yield during the transesterification reaction are the molar ratio of alcohol to vegetable oil and the reaction temperature. Biodiesel has become more attractive recently because of its environmental benefits. The cost of biodiesel, however, is the main obstacle to commercialization of the product. With cooking oils used as raw material, the viability of a continuous transesterification process and recovery of high quality glycerol as a biodiesel by product are primary options to be considered to lower the cost of biodiesel. Supercritical methanol has a high potential for both transesterification of triglycerides and methyl esterification of free fatty acids to methyl esters for a Diesel fuel substitute. In the supercritical methanol transesterification method, the yield of conversion increases to 95% in 10 min. The viscosity values of vegetable oils are between 27.2 and 53.6 mm2/s, whereas those of vegetable oil methyl esters are between 3.59 and 4.63 mm2/s. The flash point values of vegetable oil methyl esters are much lower than those of vegetable oils. An increase in density from 860 to 885 kg/m3 for vegetable oil methyl esters or biodiesels increases the viscosity from 3.59 to 4.63 mm2/s. Biodiesel is an environmentally friendly fuel that can be used in any Diesel engine without modification.

L. Wang and J. Yang (2007) Nano-MgO can apparently improve the transesterification reaction of soybean oil with supercritical/subcritical methanol. The variables affecting the yield of methyl ester during the transesterification reaction, such as the catalyst content, reaction temperature and the molar ratio of methanol to soybean oil were investigated and compared with those of non-catalyst. When nano-MgO was added from 0.5 wt% to 3 wt%, the transesterification rate increased evidently, while the catalyst content was further enhanced to 5 wt%, little increased in yield. It was observed that increasing the reaction temperature had a favorable influence on methyl ester yield. In addition, for molar ratios of methanol to soybean oil ranging from 6 to 36, the higher molar ratios of methanol to oil was charged, the faster transesterification rate was obtained. When the temperature was increased to 533 K, the transesterification reaction was essentially completed within 10 min with 3 wt% nano-MgO and the methanol/oil molar rate 36:1. Such high reaction rate with nano-MgO was mainly owing to the lower activation energy (75.94 kJ/mol) and the higher stirring.

S. Saka and D. Kusdiana (2001) studied transesterification reaction of rapeseed oil in supercritical methanol. The experiments were investigated without using any catalyst. An experiment has been carried out in the batch-type reaction vessel preheated at 350 and 400°C and at a pressure of 45±65 MPa, and with a molar ratio of 1:42 of the rapeseed oil to methanol. It was consequently demonstrated that, in a preheating temperature of 350°C, 240 s of supercritical treatment of methanol was sufficient to convert the rapeseed oil to methyl esters and that, although the prepared methyl esters were basically the same as those of the common method with a basic catalyst, the yield of methyl esters by the former was found to be higher than that by the latter. In addition, it was found that this new supercritical methanol process requires the shorter reaction time and simpler purification procedure because of the unused catalyst.

S. Saka et al. (2004) studied a catalyst-free biodiesel production method with supercritical methanol. They have been developed that allows a simple process and high yield because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids. From these lines of evidence, we expected that similar results would be attained with the use of various alcohols by the supercritical treatment. However, it still remains unclear which type of reaction, transesterification or alkyl esterification, is faster. This parameter would be important in designing the optimum reaction conditions of the supercritical alcohol method. Therefore, we studied the effect of transesterification of triglycerides and esterification of fatty acids in rapeseed oil. Reaction temperature was set at 300°C, and methanol, ethanol, 1-propanol, 1-butanol or 1-octanol was used as the reactant. The results showed that transesterification of triglycerides (rapeseed oil) was slower in reaction rates than alkyl esterification of fatty acids for any of the alcohols employed. Furthermore, saturated fatty acids such as palmitic and stearic acids had slightly lower reactivity than that of the unsaturated fatty acids; oleic, linoleic and linolenic.

W. Cao et al. (2005) studied transesterification of soybean oil in supercritical methanol. The experiment has been carried out in the absence of catalyst. A co-solvent was added to the reaction mixture in order to decrease the operating temperature, pressure and molar ratio of alcohol to vegetable oil. With propane as cosolvent in the reaction system, there was a significant decrease in the severity of the conditions required for supercritical reaction, which makes the production of biodiesel using supercritical methanol viable as an industrial process. A high yield of methyl esters (biodiesel) was observed and the production process is environmentally friendly. Furthermore the co-solvent can be reused after suitable pretreatment.

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

3.1 Material

3.1.1 Palm Fatty Acids and Palm Olein Oil

Feed stock used in this study is a mixture of 5%wt palm fatty acids distillate and palm olein. Palm fatty acids distillate was obtained from local palm oil industry. Commercial edible-grade palm olein oil was obtained from the supermarket.

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	98% (industrial grade)
Ethanol	Fisher Scientific	98% (industrial grade)
Iso-Propanol	Fisher Scientific	99.99%(analytical reagent grade)
Toluene	Ajax Chemicals	99.8% (analytical reagent grade)
Sodium Hydroxide	Ajax Chemicals	98% (analytical reagent grade)
Potassium Hydroxide	Ajax Chemicals	85% (analytical reagent grade)
Sodium Methylate	ACROS	N/A
Sulfuric Acid	J:T Baker	95% (analytical reagent grad)
Hydrochloric Acid	J:T Baker	36.5-38%
Heptane	QREC	99%
Methyl Decanoate	ALDRICH	99%
Mix Fatty Acids Methyl Ester	RESTEK	99.5%+

3.2 Equipment

3.2.1 Ambient Condition

The acid-catalyzed experiments were conducted in a flask equipped with a reflux condenser as shown in Figure 3.1. The system temperature was controlled by a water bath which is set at 60 °C. All experiments are conducted at ambient pressure and at methanol to oil ratios of 3:1, 6:1 and 9:1. Samples were taken at 30, 60, 120 and 180 minutes

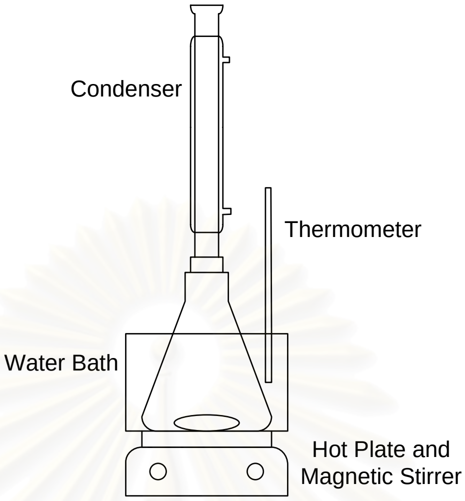

Figure 3.1 Condenser and hot plate magnetic stirrer set

3.2.2 High Pressure Condition

The non-catalytic experiments were conducted in a 2 litre batch reactor as shown in Figure 3.2. The experiments are conducted at temperatures and pressures as shown in Table 3.2 and at methanol to oil ratios of 3:1, 6:1 and 9:1. Samples were taken at 30, 60, 120 and 180 minutes

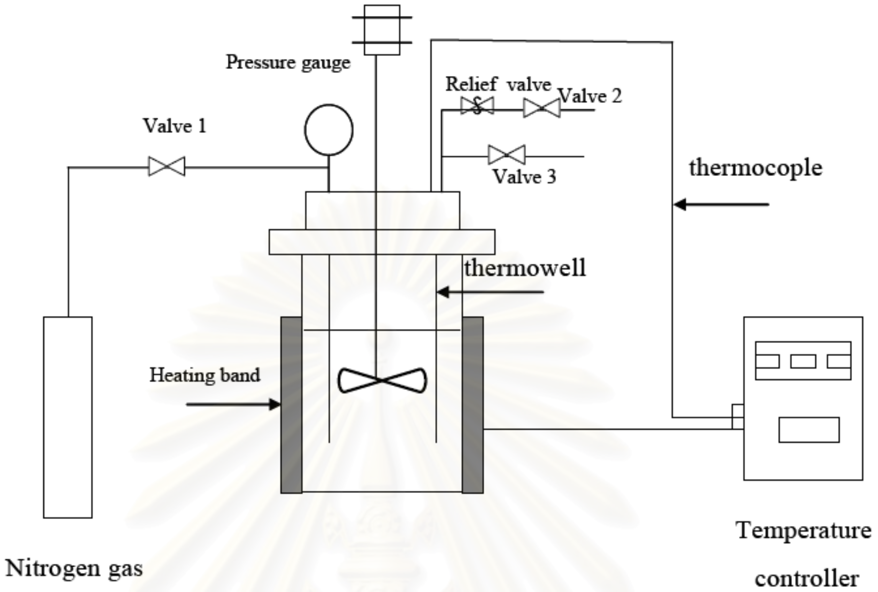

Figure 3.2 High pressure reactor

3.3 Methodology

3.3.1 Characterization of Palm Fatty Acids and Palm Olein Oils

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

3.3.2 Investigation the effect of acid catalyst and non-catalytic on esterification

3.3.2.1 Acid catalyst

1. Heat palm fatty acids and palm olein oil at 100°C to eradicate moisture.
2. Blend palm fatty acids and palm olein oil ratio of 5:95%wt.
3. Prepare catalyst for experiment.
   - 3.1 The molar ratio of methanol to oil of 3:1, 6:1 and 9:1 put in the flask.
   - 3.2 The concentration of acid catalyst used is 2% of oil weight.

3.3 Mix the catalyst, sulfuric acid and methanol.

4. Pour catalyst mixture in mix oils thoroughly in the reactor.
5. Heat sample until reach the desired temperature (60°C) and stirrer.
6. Leave the reaction continue for 2 hours mixed thoroughly.
7. Wash oils by water for purify oils.

3.3.2.2 Non-catalytic

1. Heat palm fatty acids and palm olein oil at 100°C to evaporate moisture.
2. Blend palm fatty acids and palm olein oil ratio of 5:95%wt.
3. The molar ratio of methanol to oil of 3:1, 6:1 and 9:1 pour methanol in mix oils thoroughly in the reactor.
5. Heat sample until reach the desired temperature and add pressure follow in Table 3.2 and stirrer.
6. Leave the reaction continue for 3 hours mixed when temperature and pressure is constant.

3.3.3 Alkaline-catalyzed on transesterification reaction

1. Bring oils from 3.3.2.1 and 3.3.2.2
2. Prepare catalyst for experiment.
    2.1 The molar ratio of methanol to oil used is 6:1 and put in the flask.
    2.2 The concentration of basic catalyst used is 0.5% of oil weight.
    3.3 Mix the catalyst, sodium methylate and methanol, together until they were all dissolved.
3. Pour catalyst mixture in mix oils thoroughly in the reactor.
4. Heat sample until reach the desired temperature (60°C) and stirrer.
5. Leave the reaction continue for 1 hours mixed thoroughly.

6. Wash oils by warm water for purify oils.

Table 3.2 Temperature and pressure for non-catalytic

Temperature (°C)	Pressure (psia)
60	14.7
150	500
	1000
250	500
	1000

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 must be less than 2%wt of oil. Free fatty acids content was determined by a standard titration method 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 heptanes was solvent. Therefore, the type of methyl ester was compared retention time of each methyl esters with methyl esters standard in Figure 3.3 and Table 3.3.

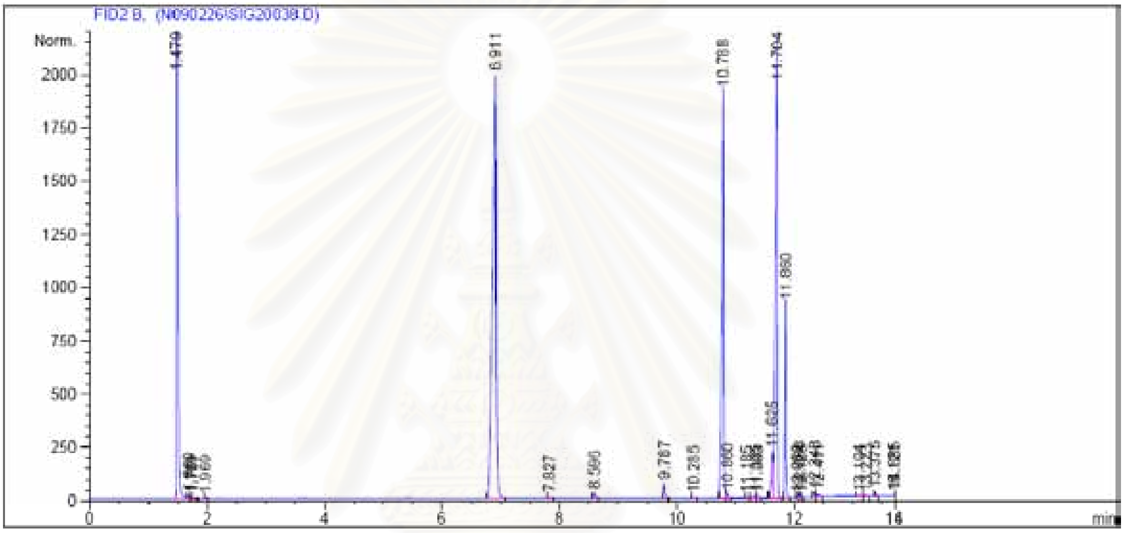

Figure 3.3 GC chromatogram of methyl esters

Table 3.3 Retention time of methyl ester in GC chromatogram

Retention time (min)	Peak of sample
1.479	N-Heptane
6.911	Methyl Decanoate
9.787	Methyl Myristate
10.788	Methyl Palmitate
10.860	Methyl Palmitoleate
11.625	Methyl Stearate
11.704	Methyl Oleate
11.860	Methyl Linoleate
11.088	Methyl Linolenate

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.

$$\%\text{Metyl Ester} = \frac{\text{Weight of Methyl Ester}}{\text{Weight of Sample}} \times 100 \qquad (3.1)$$

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

3.5 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.

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

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

CHAPTER IV

Results and Discussion

This chapter presents the results of methyl ester production from the mixtures of palm olein oil and palm fatty acids distillate. Feed stock used in this study is a mixture of 5%wt palm fatty acids distillate and palm olein oil. The experiments were carried out between mixed oils and methanol by a two-step method. Acid-catalyzed and non-catalytic experiments were conducted in the first step to reduce free fatty acid content in mixed oils. Effects of different operating conditions such as reaction time, molar ratio of methanol to oils, operating temperature and operating pressure were determined. In the second step, methyl esters was produced by transesterification reaction using sodium methylate as an alkaline catalyst. Results and discussions are presented in seven parts:

4.1 Characterization of palm fatty acids distillate and palm olein oil

4.2 The effect by non-catalytic esterification reaction at ambient pressure

4.3 The effect by acid catalyst esterification reaction at ambient pressure

4.4 The effect at high temperature

4.5 The effect at high pressure

4.6 The effect of molar ratio of methanol to oil

4.7. Percent yield of methyl esters

4.1 Characterization of palm fatty acids distillate and palm olein oil

Palm fatty acids distillate was obtained from refinery process of crude palm oil. It is brown solid at room temperature and melts into brown liquid on heating. Commercial edible-grade palm olein oil was obtained from supermarket. It is light yellow liquid at room temperature. Table 4.1 shows properties of palm fatty acids distillate, palm olein oil and mixture of 5%wt palm fatty acids distillate and palm olein oil. Free fatty acid value was a measure of free fatty acid concentration. The quantity of free fatty acids is an important parameter in production of methyl esters because free fatty acid value higher than 2% which cause soap formation, Chonghong et al. (2007) and Veljkovic et al. (2006). The analysis results showed that free fatty acids value of palm fatty acids distillate, palm olein oil and mixed oils were 90.05, 0.11 and 4.6 %, respectively. Palm fatty acids distillate and mixed oils indicated easily soap formation because free fatty acid value of both oil are more than 2%wt. Palm olein oils indicated difficultly soap formation because free fatty acid value was less than 2%wt. The molecular weight of palm fatty acids distillate, palm olein oil and mixed oils are calculated based on acid value and saponification value. They are found that the molecular weight of oils are 273, 801 and 749 g/mole, respectively.

Fatty acid composition of palm fatty acids distillate and palm olein oil can be analyzed in terms of fatty acid methyl esters by gas chromatography (GC). Table 4.2 shows the main saturated and unsaturated fats in both palm fatty acids distillate and palm olein oil. The molecular weight of palm fatty acids distillate, palm olein oil could recheck by fatty acids composition. The molecular weight are 269 and 813 g/mol, respectively. This molecular weight values are nearly molecular weight values were determined by acids value and sponification value show in Table 4.1.

Table 4.1. Properties of Palm Fatty Acids Distillate, Palm Olein Oil and Mixed Oils.

Properties	PFAD*	POO*	Mixed Oils
Free Fatty Acid, %	90.05	0.11	4.6
Acid Value, mgKOH/g	176	0.47	5.02
Saponification Value, mgKOH/g	204	210	225
Melting Point, °C	43	N/A	N/A
MW, g/mol	273	802	749

*PFAD mean palm fatty acids distillate, POO mean Palm Olein Oil

Table 4.2 Composition of Palm Fatty Acids and Palm Olein Oil

Composition		Palm Fatty Acid (%Composition)	Palm Olein Oil (%Composition)
Myristate Acid	C14:0	1.1	1.1
Palmitate Acid	C16:0	46.6	39.9
Palmitoleate Acid	C16:1	0.2	0.3
Stearate Acid	C18:0	4.2	N/D
Oleate Acid	C18:1	39.0	38.3
Linoleate Acid	C18:2	8.7	10.1
Linolenate Acid	C18:3	0.2	0.4
Molocular Weight (g/mol)		269	813

The acid-catalyzed experiments were conducted in a flask equipped with a reflux condenser. The system temperature was controlled by a water bath which is set at 60 °C. All experiments are conducted at ambient pressure and at methanol to oil ratios of 3:1, 6:1 and 9:1. The non-catalytic experiments were conducted in a 2 liters batch reactor. The experiments are conducted at various temperatures and pressures and at methanol to oil ratios of 3:1, 6:1 and 9:1. Samples were taken at 30, 60, 120 and 180 minutes and free fatty acid content was determined by a standard titration method AOCS Ca 5a-20 for the first step. The second step, samples were determined by gas chromatography followed by EN 13103. The percentage of methyl esters was defined as the ratio of the weight methyl esters to weight of sample and was determined by gas chromatography as shown in Equation 4.1.

$$\%\text{Metyl Ester} = \frac{\text{Weight of Methyl Ester}}{\text{Weight of Sample}} \times 100 \qquad (4.1)$$

4.2 The effect of non-catalytic esterification reaction at ambient pressure

In this part composed studies on effect of non-catalytic esterification reaction at ambient pressure. Figure 4.1 shows free fatty acid content and reaction time of non-catalytic experiments which were conducted at ambient pressure and at temperature of 60°C. The experimental results are summarized in Table C-1.1 in Appendix C. The results indicate that esterification reaction of free fatty acid cannot proceed without acid catalyst at low temperature and pressure.

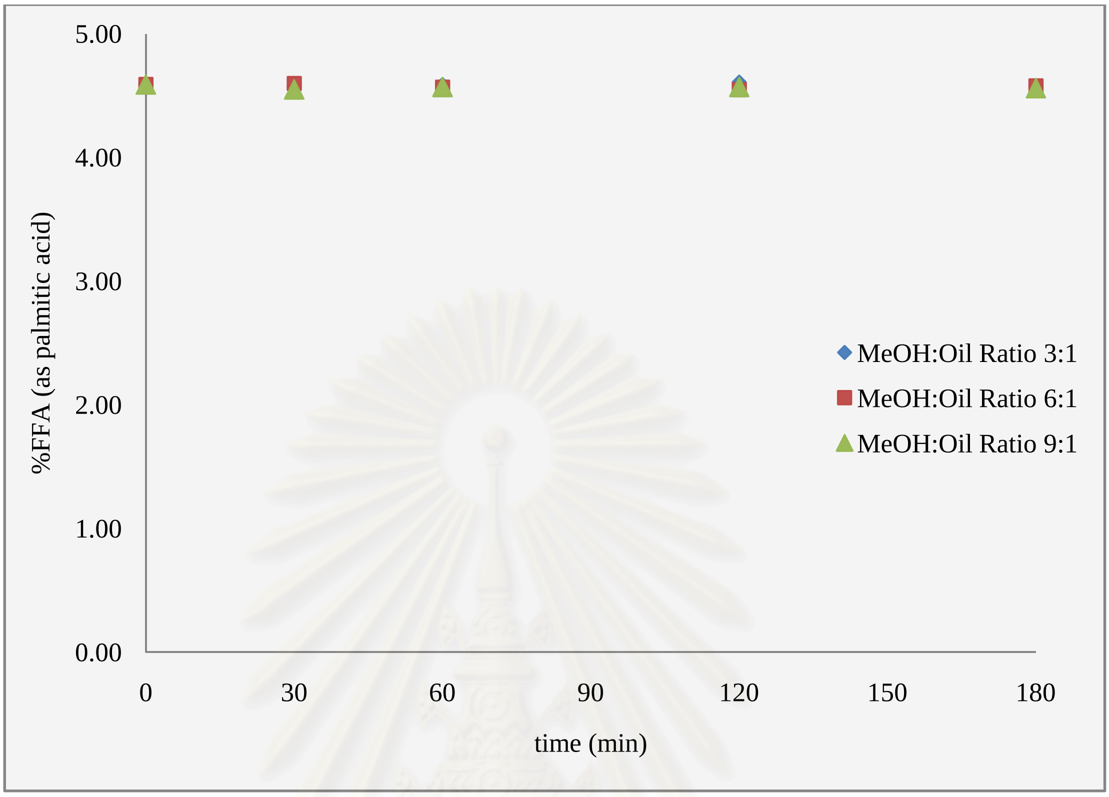

Figure 4.1. The effect of non-catalytic esterification reaction at ambient pressure and temperature of 60°C

4.3 The effect of acid catalyst esterification reaction at ambient pressure

In this part composed studies on effect of acid catalyst esterification reaction and amount of methanol to oil molar ratio at ambient pressure. Figure 4.2 shows free fatty acid content and reaction time of acid-catalyzed experiments. The analysis results are summarized in Table C-2.1 in Appendix C. When acid catalyst, sulfuric acid, was added to the system, the reaction proceeds very well resulting in reduction of free fatty acid content in oil. The reaction was also shown to be a function of time. Free fatty acid content in oil drops quickly during the first thirty minutes and remains constant after sixty minutes. S.V. Ghadge and H. Raheman, (2005) conducted experiment to reduce free fatty acids content in mahua oil (Madhuea india) by esterification reaction. The experiments were carried out using H_2SO_4 as a catalyst and at methanol to oil volume ratio of 0.30. They found that free fatty acids content was reduced from 19% to less than 1% in 1 hour. H.J. Berchmans and S. Hirata, (2007) conducted experiment to reduce free fatty acids content in Jatropha oil by acid-catalyzed. The experiments were carried out using H_2SO_4 as a catalyst and at methanol to oil weight ratio of 60 at temperature of 50°C. They found that free fatty acids content was reduced from 15% to less than 1% in 1 hour. Chonghong et al. (2007) studied esterification reaction of palm fatty acid distillate (PFAD) in a batch reactor. The experiments were carried out using H_2SO_4 as a catalyst at molar ratios of methanol to PFAD of 0.4:1-12:1and at temperatures of 70-100°C. After the experiment, they found that a rapid formation of methyl esters 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 4.3:1 with 1.834 %wt of H_2SO_4 in which a conversion of over 90% was obtained. The experimental results conclude that esterification reaction of free fatty acid could reduce free fatty acid content very well at low temperature and pressure when the acid catalyst was added in the reaction.

Esterification reaction of free fatty acid was also found to depend on amount of methanol in the system. When the molar ratio of methanol to oil increased from 3:1 to 6:1 and 9:1, amount of free fatty acid in oil significant reduced to less than 2% and 1%, respectively. A.S. Ramadhas et al. (2005) studied the effect of amount of methanol to oil ratio on the free fatty acids content in rubber seed oil. The experiments were carried out using H_2SO_4 catalyst at temperature 50°C in 120 minutes. They found that free fatty acids content decreased when the amount of methanol to oil ratio was increased. Amount of methanol to oil molar ratio of 6:1 was able to reduced free fatty acids content from 14% to less than 2%. The experimental results conclude that esterification reaction of free fatty acid can proceed very well at low temperature and pressure when the molar ratio of methanol to oil was increased.

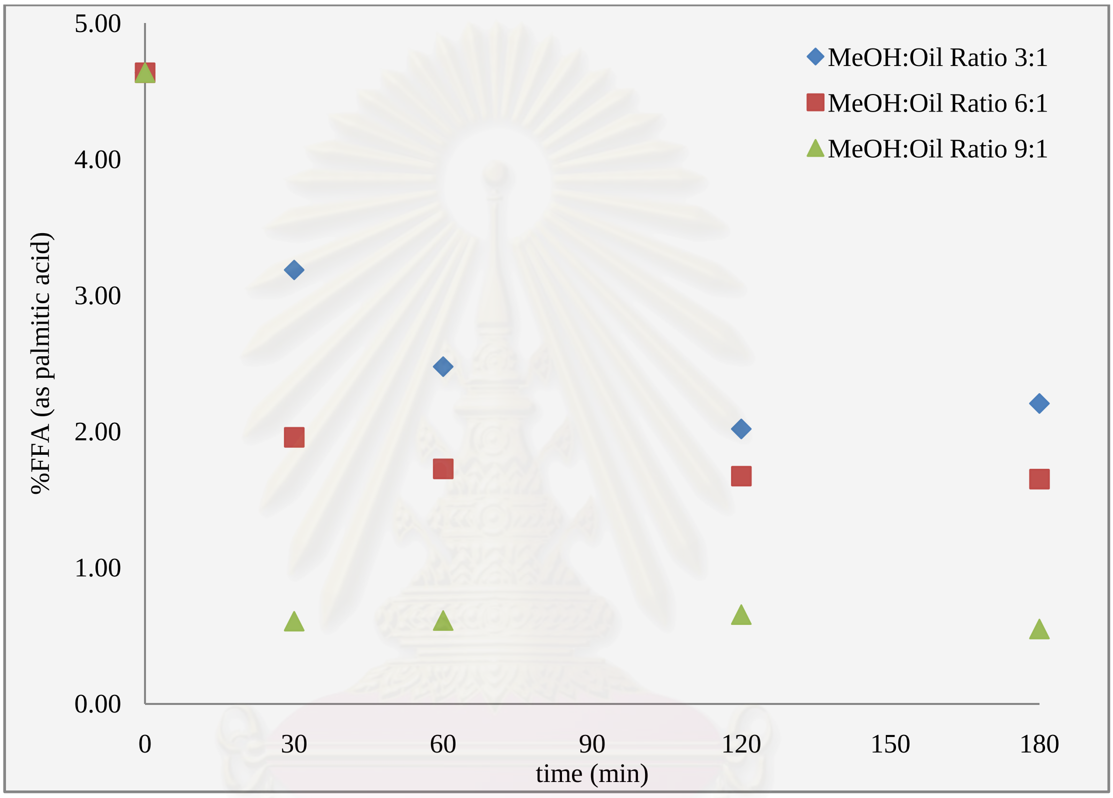

Figure 4.2. The effect of acid catalyst esterification reaction at ambient pressure and temperature of 60°C

4.4 The effect at high temperature

This section is composed studies on effect of temperature by non-catalytic esterication reaction. Figures 4.3 to 4.5 show free fatty acids content and reaction time of non-catalytic experiments which were conducted at various temperatures at pressure 1000 psia and methanol to oil molar ratio of 3:1, 6:1 and 9:1, respectively. The experimental results are show in Table C-3.1 to C-3.3 in Appendix C. The results indicate that non-catalytic esterification reaction of free fatty acids can proceed at high temperature of 150, 200 and 250°C. Increasing reaction temperature from 150 to 250°C increase conversion of free fatty acids. Reaction temperature also has an important role in the reaction. There is no known research work on non-catalytic esterification reaction available. Most of non-catalytic studieds are emphasized on transesterification reaction. Madras et al. (2004) studied the effect of temperature on the conversion of sunflower oil. The reaction carried out of sunflower oil with the molar ratio of methanol to oil 40:1. The experiments were conducted for 40 minutes of reaction time at temperatures of 200-400°C and pressure of 200 bar. They found that the conversion to methyl esters increased with increasing temperature. The optimum temperature was 400°C by non-catalytic reaction between sunflower oil and methanol. The results conclude that esterification reaction of free fatty acid with non-catalytic can proceed when the reaction was increase temperature.

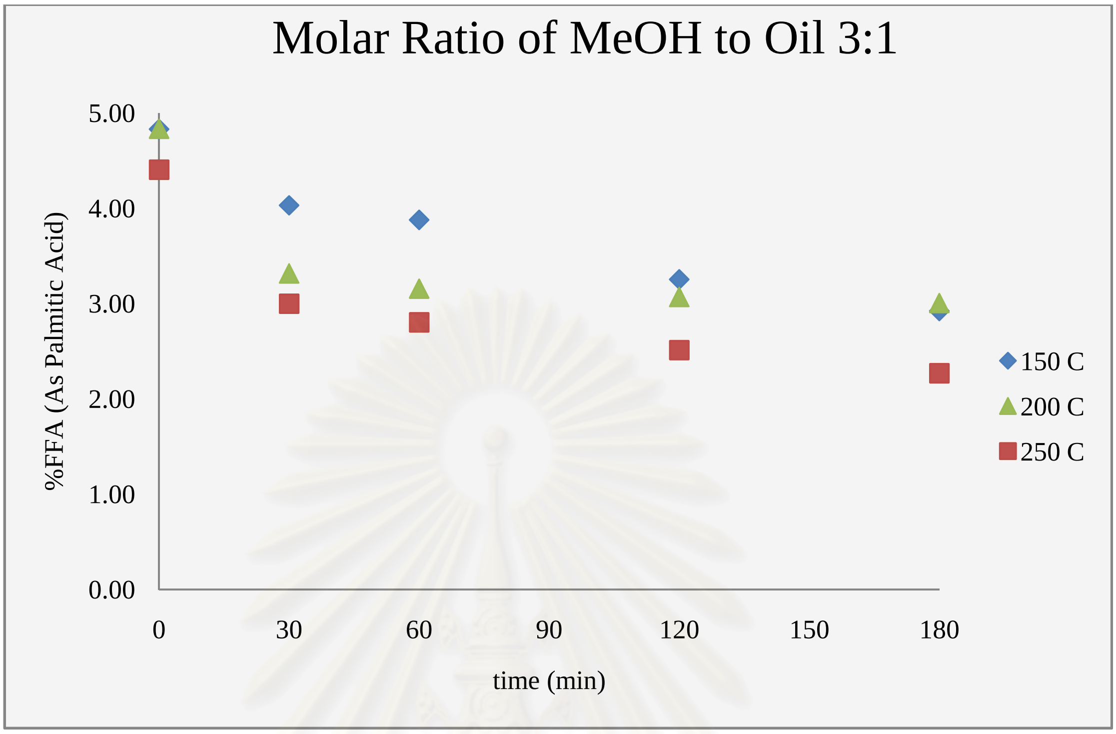

Figure 4.3. The effect of temperature by non-catalytic esterification reaction at pressure of 1000 psia and molar ratio of methanol to oil of 3:1

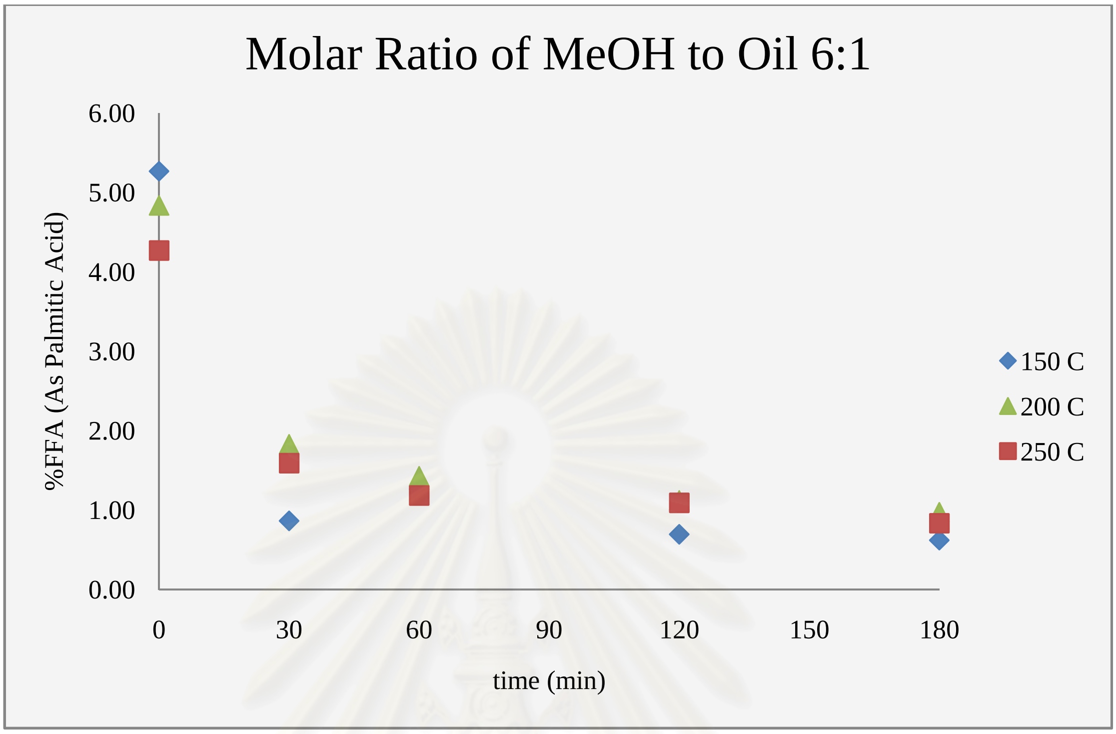

Figure 4.4. The effect of temperature by non-catalytic esterification reaction at pressure of 1000 psia and molar ratio of methanol to oil of 6:1

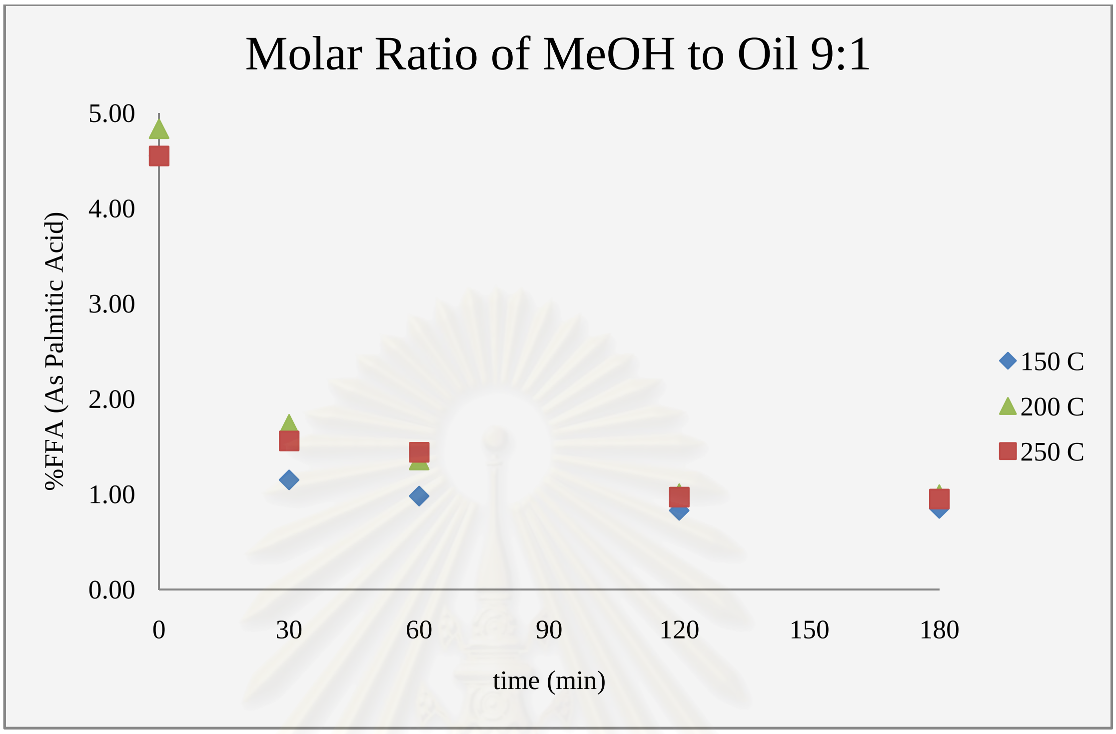

Figure 4.5. The effect of temperature by non-catalytic esterification reaction at pressure of 1000 psia and molar ratio of methanol to oil of 9:1

4.5 The effect at high pressure

In this section composed studies on effect of pressure by non-catalytic esterification reaction. Figures 4.6 to 4.8 show free fatty acid content and reaction time of non-catalytic experiments which were conducted at various pressure at temperature of 250°C and methanol to oil molar ratio of 3:1, 6:1 and 9:1, respectively. The experimental results are show in Table C-4.1 to C-4.3 in Appendix C. The results indicate that non-catalytic esterification reaction of free fatty acid can proceed at high pressure of 500 to 1000 psia. Increasing reaction pressure from 500 to 1000 psia increase conversion of free fatty acid. Reaction pressure also has an important role in the reaction. Pressure was increase boiling point of methanol increasing. At pressure of 500 psia, boiling point of methanol is 191°C and at pressure of 1000 psia, boiling point of methanol is 229°C. S. Saka and D. Kusdiana, (2001) conducted experiment to product methyl esters from rapeseed oil by supercritical methanol condition. The experiments were carried out in a batch-type supercritical biomass conversion system. Rapeseed oil and methanol were used as raw materials and the reactions were conducted at temperature of 250 to 550°C and at pressure of 1-20 MPa. They found that the conversion of methyl ester was increased with increasing pressure. The experimental results conclude that esterification reaction of free fatty acid with non-catalytic can occurred at high pressure. When the pressure was increase the reaction can proceed more than lower pressure.

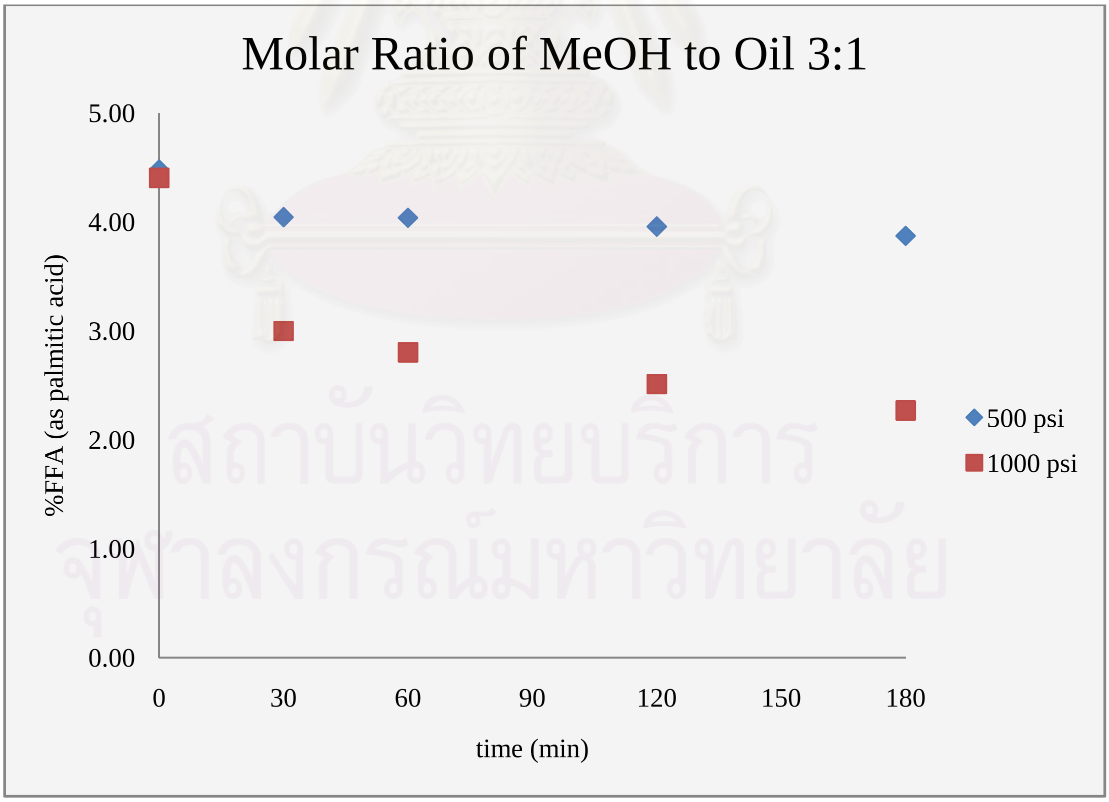

Figure 4.6. The effect of pressure by non-catalytic esterification reaction at temperature of 250°C and molar ratio of methanol to oil of 3:1

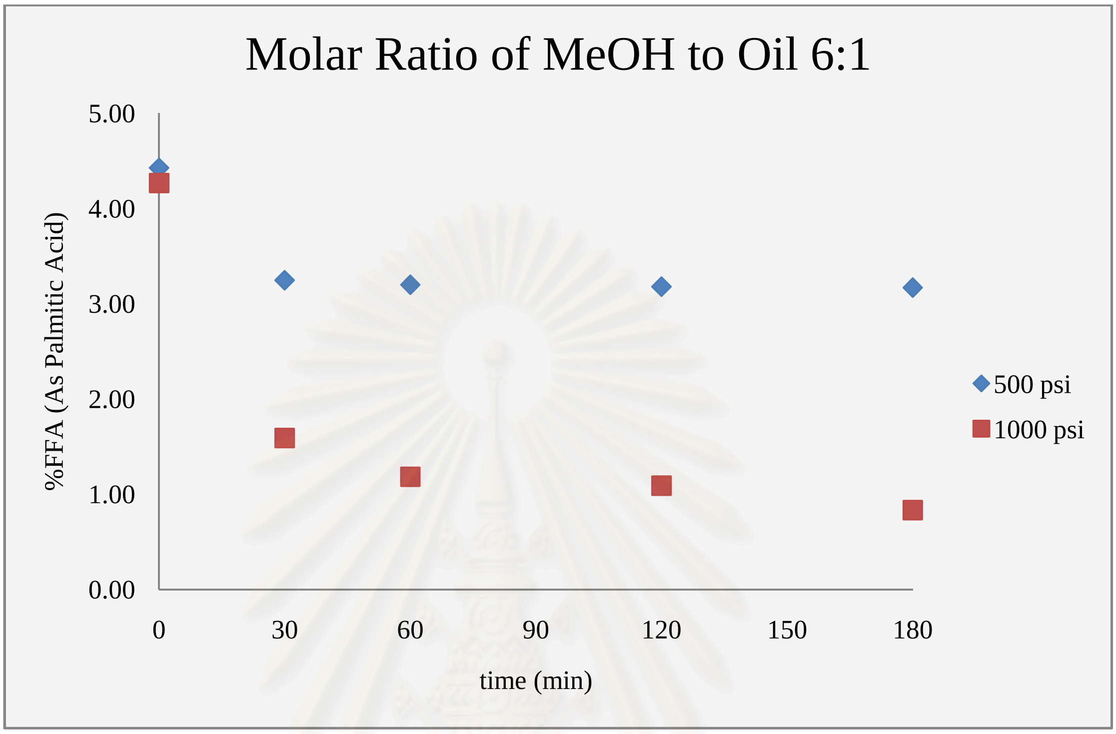

Figure 4.7. The effect of pressure by non-catalytic esterification reaction at temperature of 250°C and molar ratio of methanol to oil of 6:1

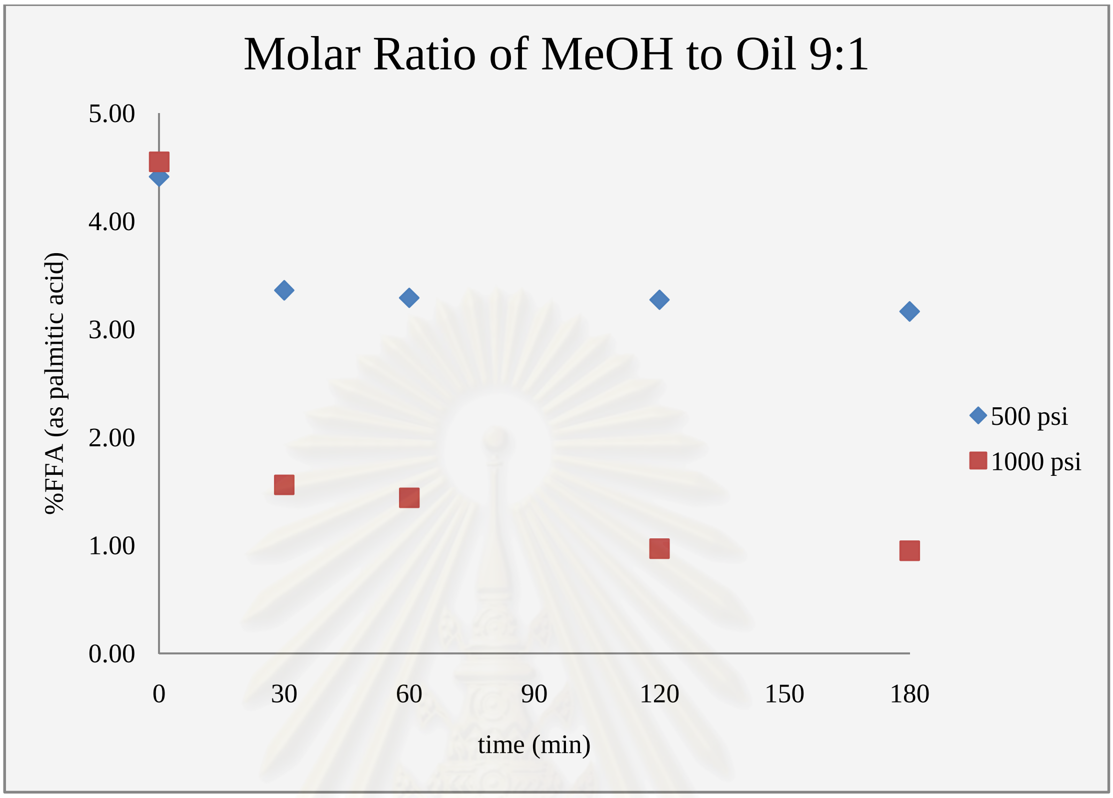

Figure 4.8. The effect of pressure by non-catalytic esterification reaction at temperature of 250°C and molar ratio of methanol to oil of 9:1

4.6 The effect of amount of molar ratio of methanol to oil

In this part composed studies on effect of amount of methanol to oil molar ratio by non-catalytic esterification reaction. Figures 4.9 to 4.14 show free fatty acids content and reaction time of non-catalytic experiments which were conducted at various molar ratio of methanol to oil. The experimental results are summarize in Table C-5.1 to C-5.4 in Appendix C. Esterification reaction of free fatty acid in palm oil also depended on amount of methanol in the system. When the molar ratio of methanol to oil was increased from 3:1 to 6:1 and 9:1, amount of free fatty acid in oil significant reduced to less than 2%. The experimental results conclude that esterification reaction of free fatty acid with non-catalytic can proceed very well when the molar ratio of methanol to oil was increased, the content of free fatty acid significant were equilibrium.

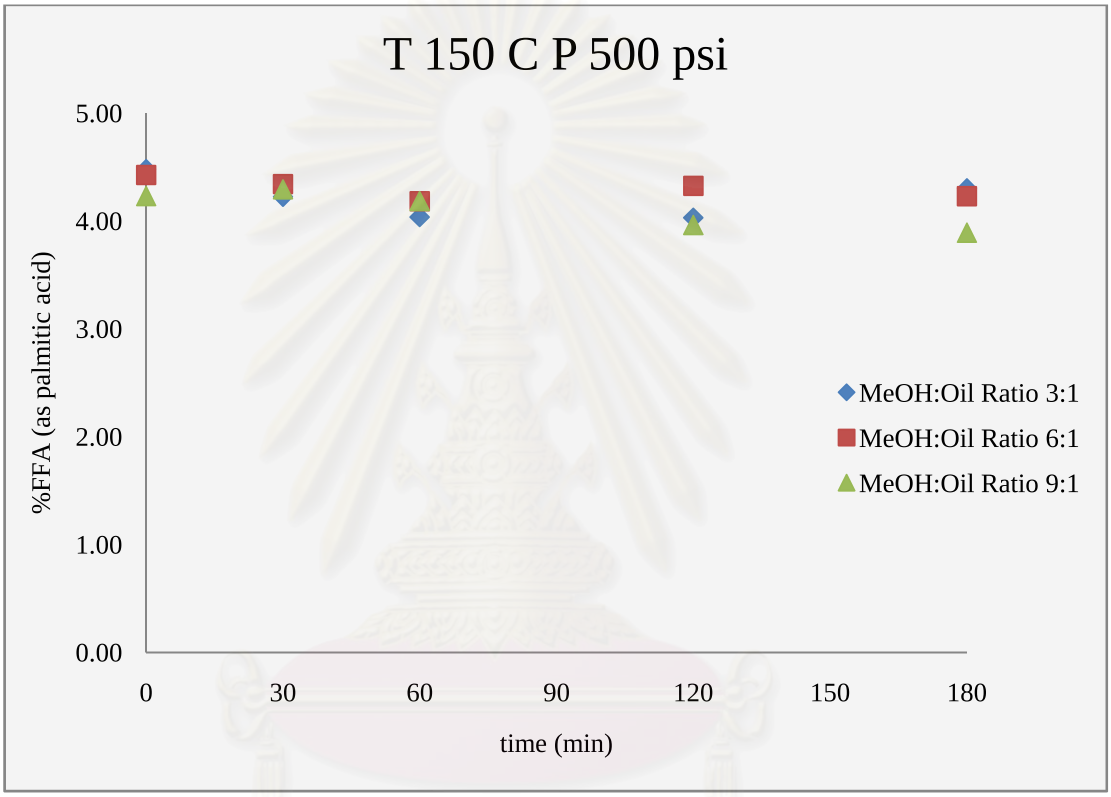

Figure 4.9. The effect of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at temperature of 150°C and pressure of 500 psia

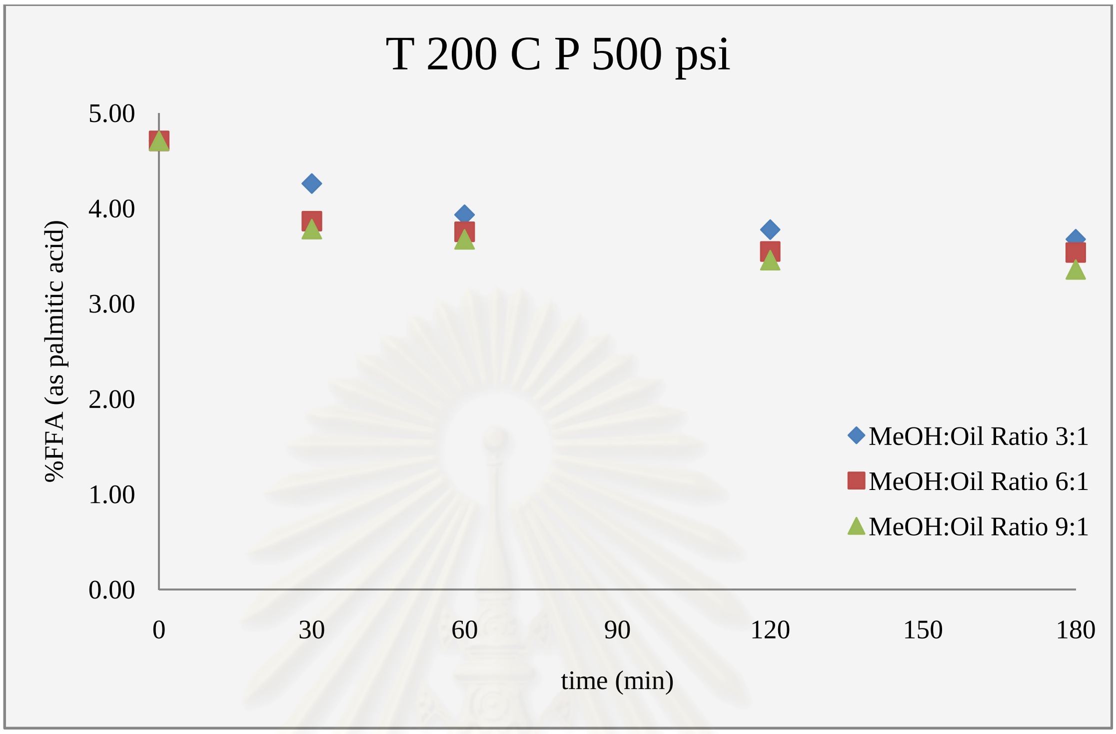

Figure 4.10. The effect of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at temperature of 200°C and pressure of 500 psia

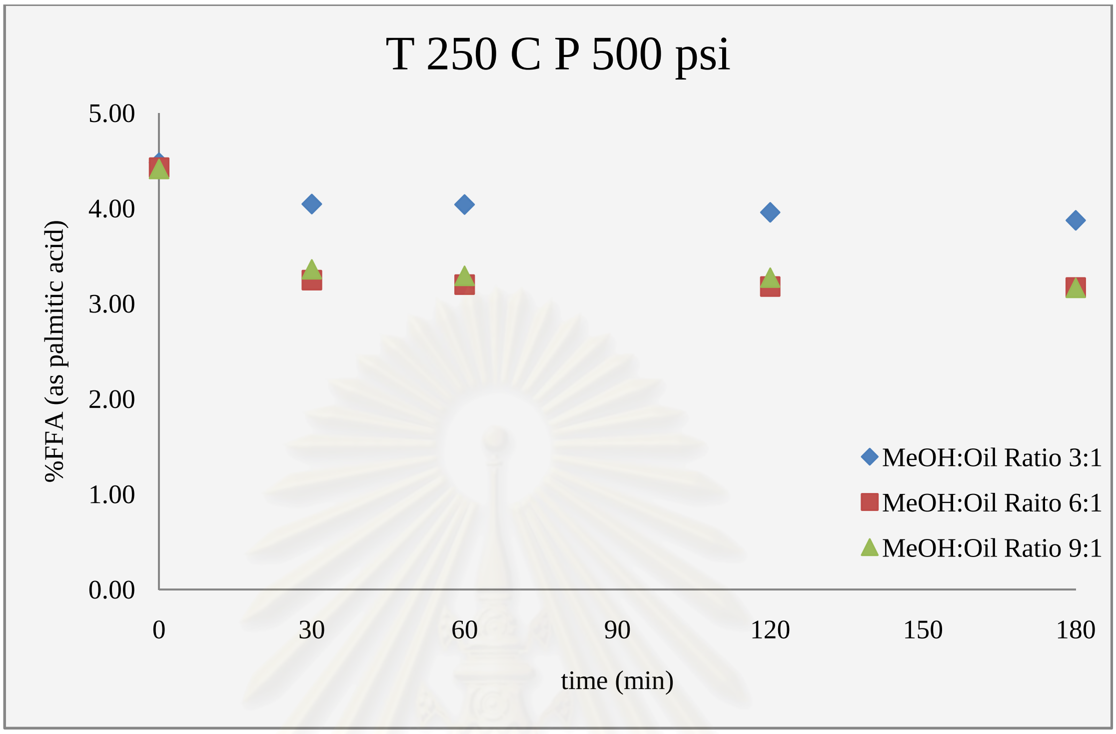

Figure 4.11. The effect of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at temperature of 250°C and pressure of 500 psia

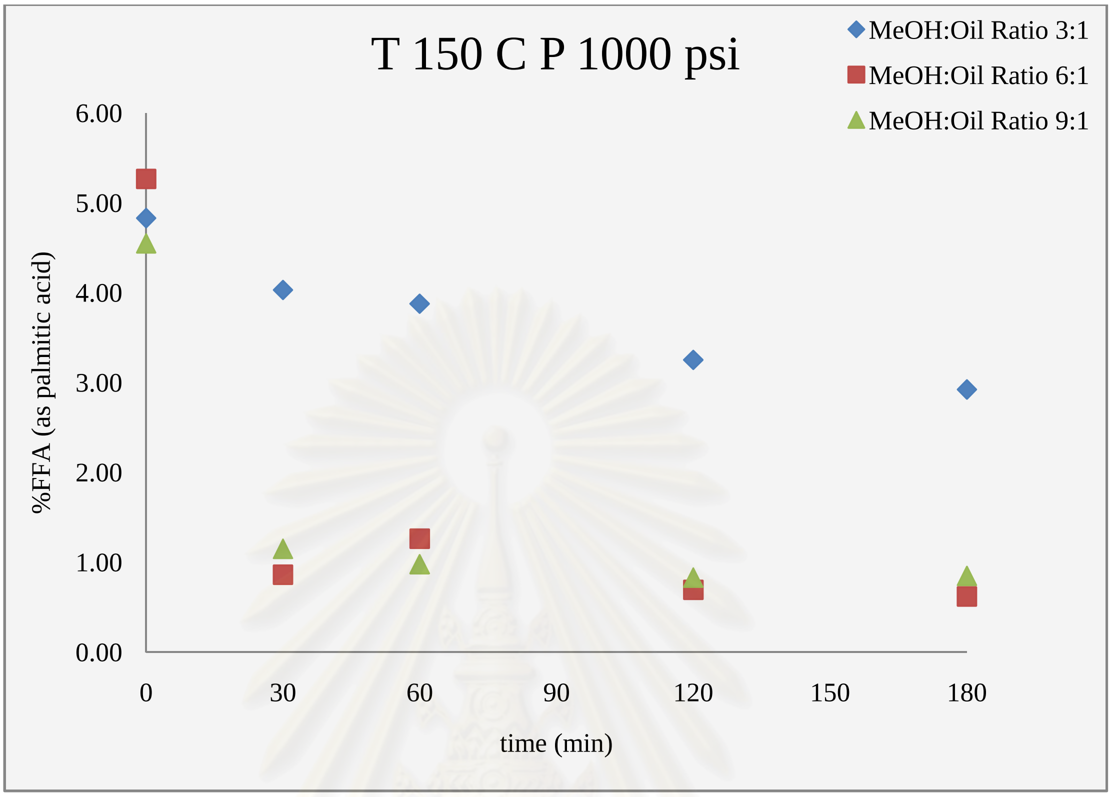

Figure 4.12. The effect of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at temperature of 150°C and pressure of 1000 psia

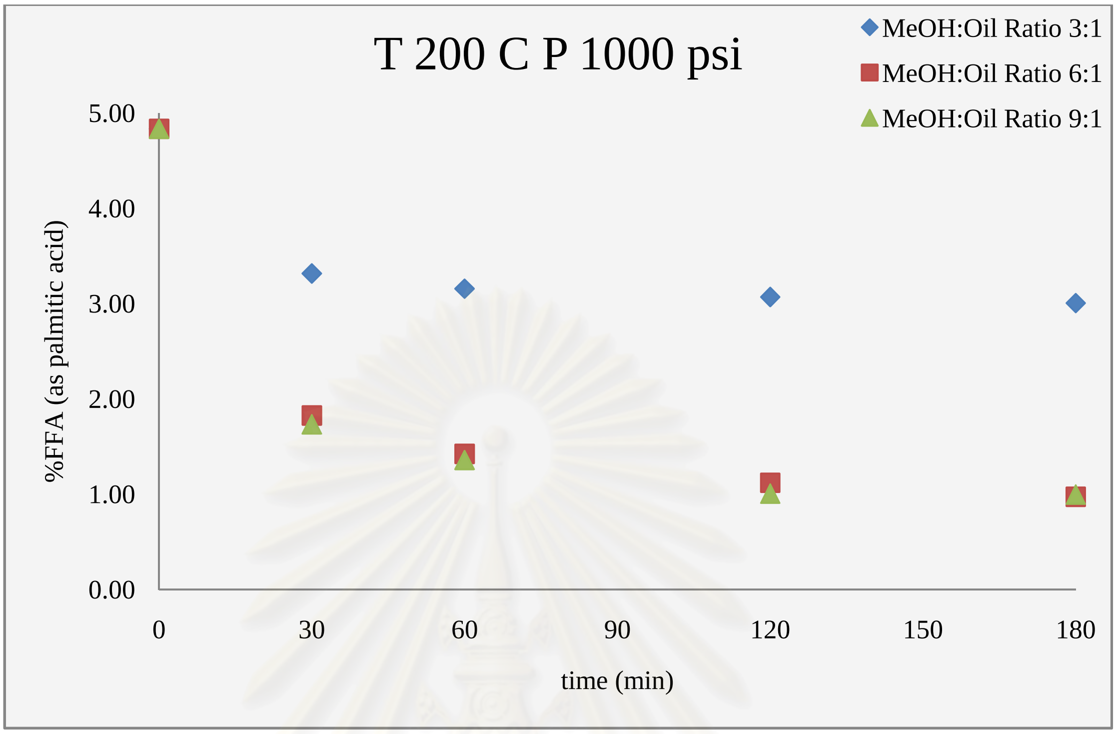

Figure 4.13. The effect of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at temperature of 200°C and pressure of 1000 psia

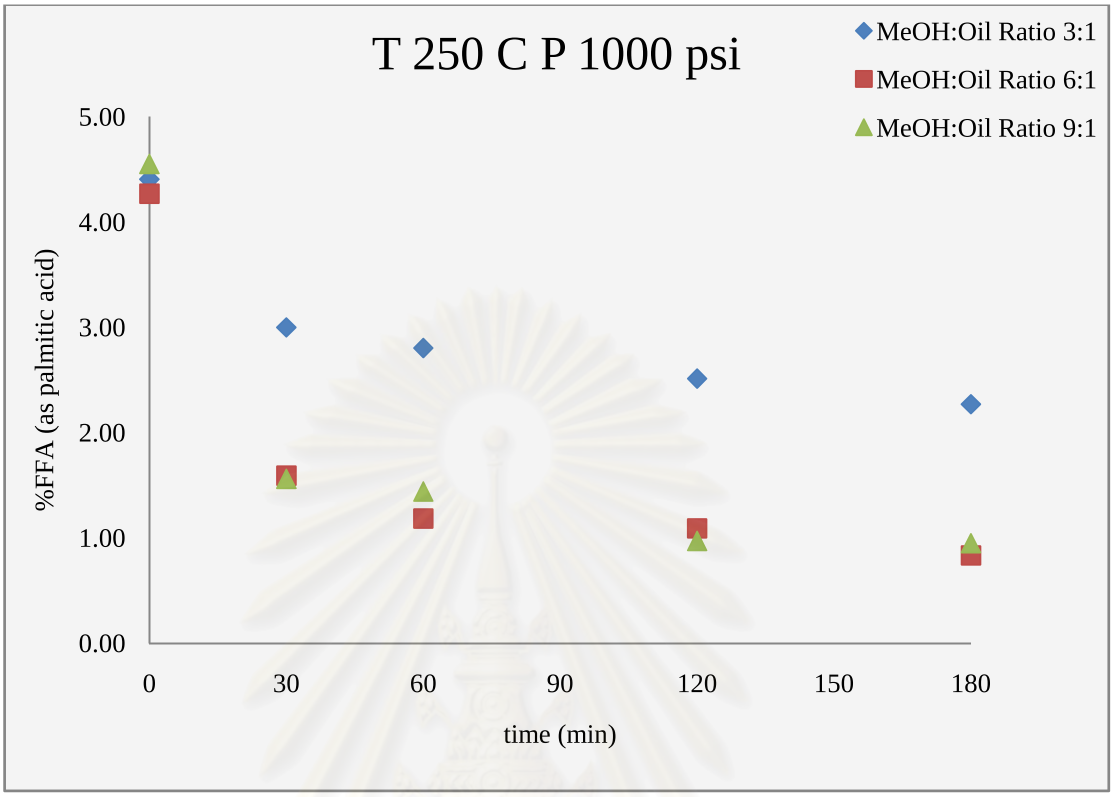

Figure 4.14. The effect of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at temperature of 250°C and pressure of 1000 psia

4.7. Percent yield of methyl esters by

4.7.1. Esterification reaction

When the free fatty acid content reduced from 4.5% to less than 2% from the first step by esterification reaction using acid catalyst and without catalyst. The samples were analyst by gas chromatography to determined methyl esters content. Table 4.3 shows methyl ester content of acid catalyst experiments which were conducted at various molar ratio of methanol to oil at temperature 60°C and at ambient pressure. Esterification reaction of methyl esters was also found to depend on amount of methanol in the system. When the molar ratio of methanol to oil increased from 3:1 to 6:1 and 9:1, amount of methyl esters increasing. H.J. Berchmans and S. Hirata, (2007) studied the effect of amount of methanol by acid catalyst esterification reaction. The experiments were carried out jatropha oil, palm oil and coconut oil with various molar ratio of methanol to oil. They found that methyl ester content depend on amount of methanol in the system, the amount of methyl esters significant were equilibrium.

Figure 4.15 shows methyl esters content of non-catalytic experiments which were conduct at high temperature and high pressure. The results show that the amount of molar ratio of methanol to oil independent on methyl esters content at the same condition, but when temperature was increased the methyl esters content increasing. Methyl esters content depend on temperature. S. Saka and D. Kusdiana, (2001) conducted experiment to produced 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 and at pressure of 1-20 MPa. They studied the effect of temperature and pressure of methyl esters. They found that the conversion of methyl esters increased with increasing temperature and pressure.

Table 4.3 Percent yield of methyl esters by acid catalyst esterification reaction at ambient pressure and at temperature of 60°C

Molar Ratio of MeOH to Oil	%yeild
3:1	8.7
6:1	11.3
9:1	15.9

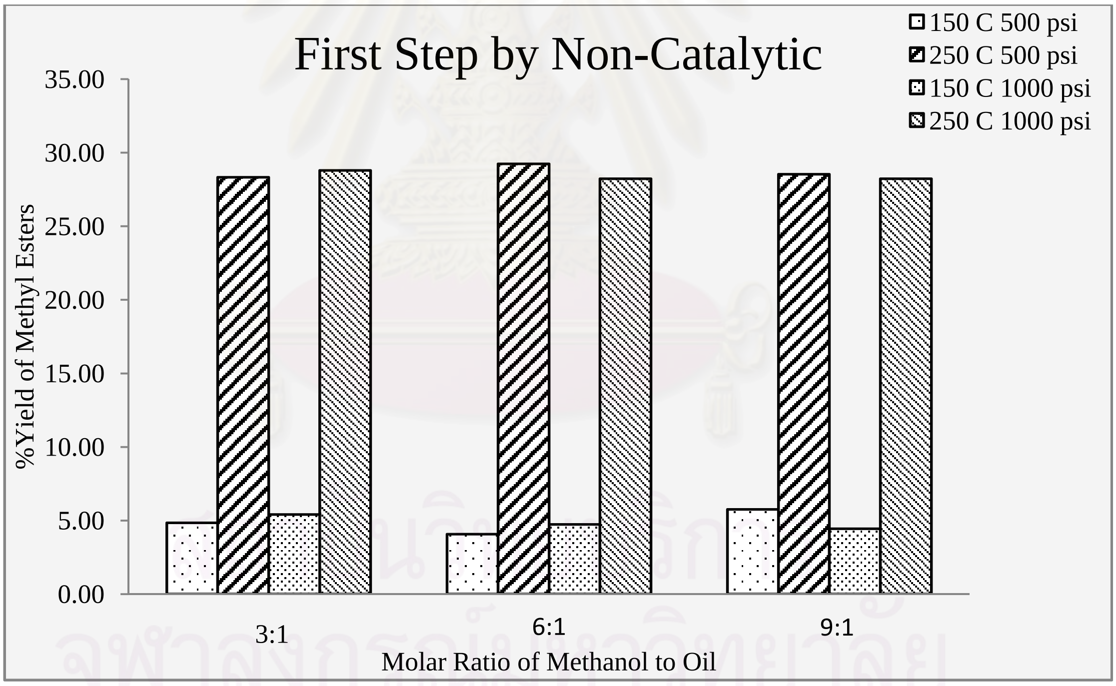

Figure 4.15. Percent yield of methyl esters by non-catalytic esterification reaction.

In this section composed studies on effect of methanol to oil molar ratio. The experiments were conducted to produce methyl esters from palm fatty acids and palm olein oil by acid catalyzed and non-catalytic esterification reaction. Table 4.4 and 4.5 show methyl esters content by acid-catalyzed esterification reaction which were conducted at various molar ratio of methanol to oil at temperature of 60°C and ambient pressure. The results indicate that esterification reaction of palm fatty acids can proceed very well at ambient pressure when the system was added acid catalyst. Transesterification reaction of palm olein oil proceed very low when the acid catalys was used be a catalyst because transesterification reaction by acid catalyst has long time reaction and large amount of methanol to oil molar ratio.

Table 4.4 Percent yield of methyl esters of palm fatty acids by acid-catalyzed esterification reaction at temperature of 60°C and ambient pressure

Molar Ratio of MeOH	%yield
3:1	97.4
6:1	98.2
9:1	99.5

Table 4.5 Percent yield of methyl esters of palm fatty acids by non-catalytic esterification reaction at temperature of 60°C and ambient pressure

Molar Ratio of MeOH	%yield
3:1	1.47
6:1	2.04
9:1	5.96

Table 4.6 and 4.7 show methyl esters content of non-catalytic experiments which were conducted at various molar ratio of methanol to oil at temperature of 250°C and pressure of 1000 psia. The results indicate that non-catalytic experiment of palm fatty acids can proceed at temperature of 250°C and pressure of 1000 psia. But palm olein oil cannot proceed at the same condition. S. Saka et al., (2004) conducted experiment to produce methyl esters

from rapeseed oil by supercritical methanol condition. Rapeseed oil and methanol were used as raw materials and the reactions were conducted at methanol to oil molar ratio of 42:1 at temperature of 550°C and at pressure of 6600 psia. They found that yield of methyl esters was obtained to 98% in 4 min. Y. Cao et al., (2004) conducted experiment to produce methyl esters from soybean oil. The experiments were carried out using non-catalytic at methanol to oil molar ratio of 33:1 at temperature of 450°C and at pressure of 14700 psi. They found that yield of methyl esters was obtained to 99% in 10 min. The experimental results conclude that esterification reaction of palm fatty acids without catalyst can be occur at high temperature and pressure, but palm olein oil without catalyst cannot be occur at the same condition.

Table 4.6 Percent yield of methyl esters of palm fatty acids by non-catalytic esterification reaction at temperature of 250°C and at pressure 1000 psia

Molar Ratio of MeOH to Oil	%yield
3:1	92.2
6:1	88.6
9:1	98.6

Table 4.7 Percent yield of methyl esters of palm olein oil by non-catalytic esterification reaction at temperature of 250°C and at pressure 1000 psia

Molar Ratio of MeOH to Oil	%yield
3:1	1.21
6:1	1.62
9:1	6.22

4.7.2. Transesterification Reaction

In this part composed studies on percent yield of methyl ester by transesterification reaction by second step. Table 4.8 and 4.9 show percent yield of methyl ester by transesterification reaction. When free fatty acids was reduce from 4.5% to less than 2% from the first step. The second step used oil was treated from the first step. The experiments were carried out using sodium methylate as a catalyst at temperature of 60°C at ambient pressure and at methanol to oil molar ratio of 6:1. The results indicate that the final yield of methyl esters was achieved at 90% in 1 hr. Wang et al. (2007) conducted experiment to product methyl esters from waste cooking oil by two step method. The second step were carried out using KOH as a catalyst and at methanol to oil molar ratio of 6:1 at temperature of 60°C. They found that yield of methyl esters was obtained to 97%. S.V. Ghadge and H. Raheman, (2005) conducted experiment to product methyl esters from mahua oil (Madhuea india) by two step method. The second step were carried out using KOH as a catalyst and at methanol to oil volume ratio of 0.23 at temperature of 60°C. They found that yield of methyl esters was obtained to 98% in 1 hour. The results indicate that transesterification reaction of methyl esters can proceed very well with alkaline catalyst, molar ratio of methanol to oil of 6:1, at temperature of 60°C and at ambient pressure in 1 hr.

Table 4.8 Percent yield of methyl esters by alkaline catalyst transesterification reaction at temperature of 60 °C and at ambient pressure from first step by acid catalyst at temperature of 60 °C and at ambient pressure

Molar Ratio of MeOH to Oil	%yeild
6:1	92.1
9:1	92.7

Table 4.9 Percent yield of methyl esters by alkaline catalyst transesterification reaction at temperature of 60 °C and at ambient pressure from first step by non-catalytic at high temperature and high pressure

Molar Ratio of MeOH to Oil	Temperature (°C)	Pressure (psia)	%yeild
6:1	150	1000	96.5
	250	1000	98.4
9:1	150	1000	95.0
	250	1000	97.9

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The study of palm olein oil and palm fatty acids distillate by the two-step method can be concluded as follows:

5.1.1 The first step, esterification reaction of free fatty acid can reduce free fatty acids content very well at low temperature and pressure when the acid catalyst is added in the reaction.

5.1.2 The optimum conditions for non-catalytic esterification reaction are methanol to oil molar ratio of 6:1, at temperature of 150°C and at pressure of 1000 psia in 1 hr. Under these conditions the free fatty acid concentration can reduce from 4.5% to less than 2%.

5.1.3 The second step, transesterification reaction to produced methyl esters, requires the use of alkaline catalyst. The final yield of methyl esters was achieved at 90% in 1 hr.

5.2 Recommendations

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

Reagents

1. Ethyl alcohol, 95%. The alcohol must give a definite, distinct and sharp end point with 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.

Procedure

1. Sample must be well mixed and entirely liquid before weighing; however, do 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.

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

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.

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

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

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

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 10-20 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-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 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

$$\text{Sponification Value} = \frac{56.1\text{N}(\text{v}_2\text{-v}_1)}{\text{w}}$$

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:

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

Where

SV = saponification value of the fat

AV = acid value of the fat

Note: The saponification value (SV), which is related to the molecular 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-4 Calculation molecular weight of palm olein oil

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

Calculation

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

Calculation

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

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

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

Normality of hydrochloric acid = N

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

$$SV = \frac{(56.1 \times 0.485)(28.7 - 11.7)}{2.2}$$

$$S.V. = 210.25$$

Where

SV = saponification value of the fat

AV = acid value of the fat

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

$$MW = \frac{[56108 - 12.67\ (210.25 - 0.47)]}{210.25}$$

$$\mathrm{MW} = 254.82$$

Mean Molecular weight of triglyceride

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

M.MW = (3) (254.82) + 38

M.MW = 802.47

APPENDIX B

CALCULATION OF CONCENTRATION OF METHYL ESTER

B-1 Response factor of methyl ester and fatty acid

The response factor is defined as

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

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

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

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

$$\text{Response Factor of methyl palmitate} = \frac{4814 \times 0.075}{10142 \times 0.029910}$$

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

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

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

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

$$\text{Response Factor of methyl stearate} = 1.28$$

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

$$\text{Response Factor of methyl oleate} = 1.22$$

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

$$\text{Response Factor of methyl linoleate} = 1.22$$

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

$$\text{Response Factor of methyl linolenate} = 1.23$$

B-2 Analysis of methyl ester

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 Gas Chromatogram

Nunber of peak	Retention time (min)	Peak of sample
1	1.479	N-Heptane
2	6.911	Methyl Decanoate
3	9.787	Methyl Myristate
4	10.788	Methyl Palmitate
5	10.860	Methyl Palmitoleate
6	11.625	Methyl Stearate
7	11.704	Methyl Oleate
8	11.860	Methyl Linoleate
9	11.088	Methyl Linolenate

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.

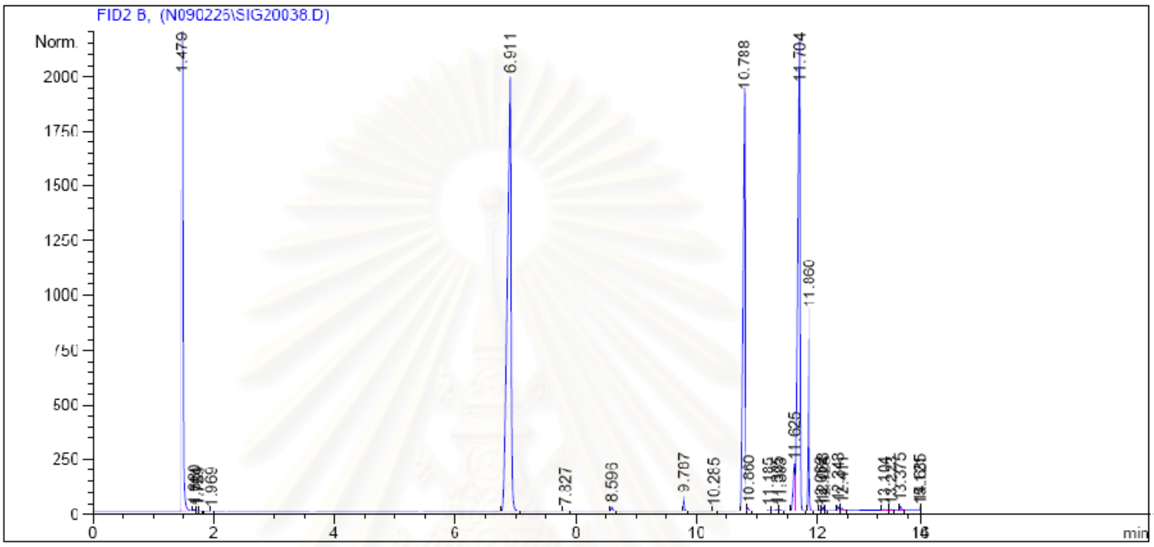

Figure B-1 Chromatogram for methyl ester and fatty acid at condition: Palm oils reactant, molar ratio of methanol to oil of 6:1, 0.5% wt $NaOCH_3$, 60 min at temperature of 60 °C and at ambient pressure

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

Retention Time	Peak of Sample	Area	%Area
6.911	Methyl Decanoate	8168	40.34
9.787	Methyl Myristate	120	0.59
10.788	Methyl Palmitate	4479	22.12
10.86	Methyl Palmitoleate	27	0.13
11.625	Methyl Stearate	429	2.12
11.704	Methyl Oleate	5587	27.59
11.86	Methyl Linoleate	1411	6.97
11.088	Methyl Linolenate	27	0.13

Example1. From figure B-1, find concentration of methyl ester molar ratio of methanol to oil of 6:1, 0.5% wt $NaOCH_3$, 60 min at temperature of 60 °C and at ambient pressure. Product of 0.1066 added to 1.5078 g of methyl decanoate solution in n-heptane.

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

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

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

$$\text{g of methyl myristate} = \frac{120}{8168} \times \frac{0.0750}{1.15}$$

$$= 9.58 \times 10^{-4}$$

$$\text{g of methyl palmitate} = \frac{4479}{8168} \times \frac{0.0750}{1.20}$$

$$= 3.43 \times 10^{-2}$$

$$\text{g of methyl palmitoleate} = \frac{27}{8168} \times \frac{0.0750}{1.20}$$

$$= 2.47 \times 10^{-4}$$

$$\text{g of methyl stearate} = \frac{429}{8168} \times \frac{0.0750}{1.28}$$

$$= 3.08 \times 10^{-3}$$

$$\text{g of methyl oleate} = \frac{5587}{8168} \times \frac{0.0750}{1.22}$$

$$= 4.20 \times 10^{-2}$$

$$\text{g of methyl linoleate} = \frac{1411}{8168} \times \frac{0.0750}{1.22}$$

$$= 1.06 \times 10^{-2}$$

$$\text{g of methyl linolenate} = \frac{27}{8168} \times \frac{0.0750}{1.23}$$

$$= 2.02 \times 10^{-4}$$

Also; g of total methyl esters $= 9.14 \times 10^{-2}$

$$\%\text{Methyl esters} = \frac{9.14 \times 10^{-2}}{0.10} \times 100$$

$$= \mathbf{91.38\%}$$

APPENDIX C

EXPERIMENTAL DATA ANALYSIS

C-1 Experimental data of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at ambient pressure

Table C-1.1 The effect of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at ambient pressure and temperature of 60 °C

time (min)	%FFA (as palmitic acid)		
	3:1	6:1	9:1
0	4.59	4.59	4.59
30	4.57	4.60	4.55
60	4.59	4.57	4.57
120	4.61	4.55	4.57
180	4.58	4.58	4.56

C-2 Experimental data of amount of molar ratio of methanol to oil by acid catalyst esterification reaction at ambient pressure

Table C-2.1 The effect of amount of molar ratio of methanol to oil by acid catalyst esterification reaction at ambient pressure and temperature of 60 °C

time (min)	%FFA (as palmitic acid)		
	3:1	6:1	9:1
0	4.64	4.64	4.64
30	3.19	1.96	0.61
60	2.48	1.73	0.61
120	2.02	1.67	0.65
180	2.21	1.65	0.55

C-3 Experimental data of temperature by non-catalytic esterification reaction at high temperature

Table C-3.1 The effect of temperature by non-catalytic esterification reaction at pressure of 1000 psia and molar ratio of methanol to oil of 3:1

time (min)	%FFA (as palmitic acid)		
	150 (°C)	200 (°C)	250 (°C)
0	4.83	4.84	4.41
30	4.03	3.32	3.00
60	3.88	3.16	2.80
120	3.25	3.07	2.51
180	2.92	3.01	2.27

Table C-3.2 The effect of temperature by non-catalytic esterification reaction at pressure of 1000 psia and molar ratio of methanol to oil of 6:1

time (min)	%FFA (as palmitic acid)		
	150 (°C)	200 (°C)	150 (°C)
0	5.27	4.84	4.27
30	0.86	1.83	1.59
60	1.26	1.42	1.18
120	0.70	1.12	1.09
180	0.62	0.97	0.83

Table C-3.3 The effect of temperature by non-catalytic esterification reaction at pressure of 1000 psia and molar ratio of methanol to oil of 9:1

time (min)	%FFA (as palmitic acid)		
	150 (°C)	200 (°C)	250 (°C)
0	4.55	4.84	4.55
30	1.15	1.73	1.56
60	0.98	1.36	1.44
120	0.83	1.01	0.97
180	0.85	0.99	0.95

C-4 Experimental data of pressure by non-catalytic esterification reaction at high temperature

Table C-4.1 The effect of pressure by non-catalytic esterification reaction at temperature of 250 °C and molar ratio of methanol to oil of 3:1

time (min)	%FFA (as palmitic acid)	
	500 psia	1000 psia
0	4.48	4.41
30	4.04	3.00
60	4.04	2.80
120	3.96	2.51
180	3.87	2.27

Table C-4.2 The effect of pressure by non-catalytic esterification reaction at temperature of 250 °C and molar ratio of methanol to oil of 6:1

time (min)	%FFA (as palmitic acid)	
	500 psia	1000 psia
0	4.43	4.27
30	3.25	1.59
60	3.20	1.18
120	3.18	1.09
180	3.17	0.83

Table C-4.3 The effect of pressure by non-catalytic esterification reaction at temperature of 250 °C and molar ratio of methanol to oil of 9:1

time (min)	%FFA (as palmitic acid)	
	500 psia	1000 psia
0	4.41	4.55
30	3.36	1.56
60	3.29	1.44
120	3.27	0.97
180	3.16	0.95

C-5 Experimental data of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at high temperature and high pressure

Table C-5.1 The effect of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at temperature of 150 °C and pressure of 500 psia

time (min)	%FFA (as palmitic acid)		
	3:1	6:1	9:1
0	4.48	4.43	4.43
30	4.23	4.34	4.29
60	4.04	4.18	4.19
120	4.03	4.33	3.96
180	4.30	4.23	3.89

Table C-5.2 The effect of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at temperature of 200 °C and pressure of 500 psia

time (min)	%FFA (as palmitic acid)		
	3:1	6:1	9:1
0	4.71	4.71	4.71
30	4.26	3.87	3.78
60	3.93	3.75	3.67
120	3.78	3.55	3.46
180	3.68	3.54	3.36

Table C-5.3 The effect of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at temperature of 250 °C and pressure of 500 psia

time (min)	%FFA (as palmitic acid)		
	3:1	6:1	9:1
0	4.48	4.43	4.41
30	4.04	3.25	3.36
60	4.04	3.20	3.29
120	3.96	3.18	3.27
180	3.87	3.17	3.16

Table C-5.4 The effect of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at temperature of 150 °C and pressure of 1000 psia

time (min)	%FFA (as palmitic acid)		
	3:1	6:1	9:1
0	4.83	5.27	4.55
30	4.03	0.86	1.15
60	3.88	1.26	0.98
120	3.25	0.70	0.83
180	2.92	0.62	0.85

Table C-5.5 The effect of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at temperature of 200 °C and pressure of 1000 psia

time (min)	%FFA (as palmitic acid)		
	3:1	6:1	9:1
0	4.84	4.84	4.84
30	3.32	1.83	1.73
60	3.16	1.42	1.36
120	3.07	1.12	1.01
180	3.01	0.97	0.99

Table C-5.6 The effect of amount of molar ratio of methanol to oil by non-catalytic esterification reaction at temperature of 250 °C and pressure of 1000 psia

time (min)	%FFA (as palmitic acid)		
	3:1	6:1	9:1
0	4.41	4.27	4.55
30	3.00	1.59	1.56
60	2.80	1.18	1.44
120	2.51	1.09	0.97
180	2.27	0.83	0.95

C-6 Experimental data of first step by esterification reaction

Table C-6.1 Percent yield of methyl esters by acid catalyst esterification reaction at ambient pressure and at temperature of 60 °C

Molar Ratio of MeOH to Oil	%Concentration of Esters								%yeild
	MM	MP	MPT	MS	MO	MLA	MLN	SUM	
3:1	74.9	2629.1	0.0	210.2	2492.5	613.2	15.6	6035.6	8.74
6:1	85.0	3049.8	14.1	268.2	2872.2	714.7	20.1	7024.1	11.28
9:1	122.6	4422.3	20.4	382.2	4060.3	981.5	25.4	10014.6	15.93

Table C-6.2 Percent yield of methyl esters by non-catalytic esterification reaction at high temperature and high pressure

Molar Ratio of MeOH to Oil	Temperature (°C)	Pressure (psia)	%Concentration of Esters								%yeild
			MM	MP	MPT	MS	MO	MLA	MLN	SUM	
3:1	150	500	37.5	1296.3	0.0	121.3	1262.7	305.7	6.3	3029.8	4.84
	250	500	217.7	7264.1	39.6	662.5	7549.6	1875.7	51.9	17661.2	28.33
	150	1000	41.4	1442.8	0.0	135.7	1399.3	338.2	6.8	3364.2	5.41
	250	1000	216.6	7241.6	39.9	676.3	7512.5	1871.4	47.3	17605.5	28.80
6:1	150	500	30.6	1091.8	0.0	105.5	1049.4	248.8	16.9	2542.9	4.07
	250	500	215.5	7520.0	40.6	707.8	7849.9	1912.9	52.6	18299.2	29.24
	150	1000	35.5	1287.5	0.0	123.6	1229.1	289.2	5.7	2970.7	4.73
	250	1000	199.2	7130.6	37.9	683.0	7545.0	1850.1	44.6	17490.5	28.23
9:1	150	500	37.4	1429.8	0.0	100.1	1745.2	262.7	5.3	3580.5	5.76
	250	500	219.8	7354.0	40.8	688.7	7602.7	1891.4	48.1	17845.4	28.54
	150	1000	33.6	1207.0	0.0	117.4	1159.4	271.6	5.3	2794.3	4.44
	250	1000	201.2	7188.8	38.1	685.5	7596.1	1860.7	43.4	17613.8	28.24

C-7 Experimental data of second step by transesterification reaction

Table C-7.1 Percent yield of methyl esters by alkaline catalyst transesterification reaction at temperature of 60 °C and at ambient pressure from first step by acid catalyst at temperature of 60 °C and at ambient pressure

Molar Ratio of MeOH to Oil	%Concentration of Esters								%yeild
	MM	MP	MPT	MS	MO	MLA	MLN	SUM	
6:1	608.9	21786.4	134.4	1950.6	26672.2	6740.6	129.0	58022.1	92.07
9:1	647.5	21978.1	147.2	1939.4	26568.2	6815.5	132.6	58228.6	92.66

Table C-7.2 Percent yield of methyl esters by alkaline catalyst transesterification reaction at temperature of 60 °C and at ambient pressure from first step by non-catalytic at high temperature and high pressure

Molar Ratio of MeOH to Oil	Temperature (°C)	Pressure (psia)	%Concentration of Esters								%yeild
			MM	MP	MPT	MS	MO	MLA	MLN	SUM	
6:1	150	1000	671.2	23016.8	0.0	1777.9	27856.8	7078.9	161.7	60563.4	96.51
	250	1000	604.2	22639.3	0.0	1769.9	28205.7	7007.6	156.7	60383.3	98.38
9:1	150	1000	647.2	22447.3	149.9	2047.1	27248.7	6996.9	135.8	59672.9	94.96
	250	1000	665.0	23005.0	153.2	2048.7	27944.5	7167.9	139.6	61123.8	97.92

Where; MM = Methyl Myristate (C14:0)

MP = Methyl Palmitate (C16:0)

MPT = Methyl Palmitoleate (C16:1)

MS = Methyl Stearate (C18:0)

MO = Methyl Oleate (C18:1)

MLA = Methyl Linoleate (C18:2)

MLN = Methyl Linolenate (C18:3)

VITA

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