ทรานส์เอสเทอร์ริฟิเคชันของน้ำมันปาล์มโอเลอินโดยใช้โซเดียมฟอสเฟตที่เคลือบฝังบนตัวรองรับอะลูมินา

นางสาวกฤษยาพร ทินกร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรดุษฎีบัณฑิต
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TRANSESTERIFICATION OF PALM OLEIN OIL USING SODIUM PHOSPHATE IMPREGNATED ON ALUMINA SUPPORT

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กฤษยาพร ทินกร : ทรานส์เอสเทอร์ริฟิเคชันของน้ำมันปาล์มโอเลอินโดยใช้โซเดียมฟอสเฟตที่เคลือบ ฝังบนตัวรองรับอะลูมินา. (TRANSESTERIFICATION OF PALM OLEIN OIL USING SODIUM PHOSPHATE IMPREGNATED ON ALUMINA SUPPORT) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดร.เจิดศักดิ์ ไชยคุนา , 185 หน้า.

งานวิจัยนี้ทำการศึกษาการใช้โซเดียมฟอสเฟต (Na_3PO_4) เป็นตัวเร่งปฏิกิริยาแบบวิวิธพันธ์ในปฏิกิริยาทรานส์เอสเทอร์ริฟิเคชันของปาล์มโอเลอินและเมทานอล โดยทำการศึกษาการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาโซเดียมฟอสเฟตในรูปแบบผง และทำการเปลี่ยนแปลงพื้นที่ผิวของตัวเร่งปฏิกิริยาโดยการเตรียมบนตัวรองรับชนิดแกมมาอลูมินา (gamma-Al_2O_3) ตัวเร่งปฏิกิริยานำไปตรวจสอบคุณสมบัติด้วยเครื่อง BET, XRD, FTIR, SEM-EDX, TGA และ ICP-OES ทำการศึกษาผลของตัวแปรต่ออัตราการเกิดปฏิกิริยาของตัวเร่งปฏิกิริยา ได้แก่ ความเร็วรอบในการกวน สัดส่วนโดยโมลของเมทานอลต่อน้ำมัน อุณหภูมิในการทำปฏิกิริยา ปริมาณตัวเร่งปฏิกิริยา และปริมาณน้ำและกรดไขมันอิสระที่ปนมากับสารตั้งต้น

ผลการศึกษาแสดงให้เห็นว่าโซเดียมฟอสเฟตสามารถใช้เป็นตัวเร่งปฏิกิริยาที่มีประสิทธิภาพในปฏิกิริยาทรานส์เอสเทอร์ริฟิเคชัน โดยสภาวะของปฏิกิริยามีผลต่ออัตราการเกิดปฏิกิริยาเป็นอย่างมาก เช่น ภายใต้สภาวะที่ศึกษาโดยใช้ตัวเร่งปฏิกิริยาที่อยู่ในรูปแบบผง สัดส่วนโดยโมลของเมทานอลต่อน้ำมัน 18:1 อุณหภูมิ 210 $^{\circ}C$ ปริมาณตัวเร่งปฏิกิริยา 1 % โดยน้ำหนักของปาล์มโอเลอิน ให้ค่าร้อยละผลได้ของผลิตภัณฑ์สูงถึง 98.5 % และจากการศึกษาปริมาณน้ำและกรดไขมันอิสระที่ปนมากับสารตั้งต้นพบว่าทำให้อัตราการเกิดปฏิกิริยาในช่วงต้นช้าลง แต่ระบบจะเข้าสู่สมดุลที่ค่าร้อยละผลได้ของผลิตภัณฑ์สูงใกล้เคียงกับระบบที่ไม่มีน้ำและกรดไขมันอิสระปนอยู่

ในส่วนของการใช้ตัวเร่งปฏิกิริยาโซเดียมฟอสเฟตที่เปลี่ยนแปลงพื้นที่ผิวโดยการเตรียมบนตัวรองรับชนิดแกมมาอลูมินา โดยวิธี incipient-wetness impregnation เมื่อนำตัวเร่งปฏิกิริยาที่เตรียม (Na_3PO_4/Al_2O_3)ไปทดสอบความว่องไวในการเร่งปฏิกิริยาทรานส์เอสเทอร์ริฟิเคชัน พบว่าให้ค่าปริมาณ FAME สูง (>96 %) ในเวลา 30 นาที ที่สัดส่วนโดยโมลของเมทานอลต่อน้ำมัน 18:1 ปริมาณตัวเร่งปฏิกิริยา 1 % โดยน้ำหนักปาล์มโอเลอิน อุณหภูมิ 210 $^{\circ}C$

จากการศึกษาการนำตัวเร่งปฏิกิริยากลับมาใช้ซ้ำ 5 รอบ โดยที่ตัวเร่งปฏิกิริยาไม่ผ่านการกระตุ้นก่อนการนำกลับมาใช้ซ้ำพบว่าความสามารถในการเร่งปฏิกิริยาลดลงเพียงเล็กน้อย ผลการศึกษาจลนพลศาสตร์ของปฏิกิริยาพบว่าเมื่อใช้เมทานอลในปริมาณมากเกินพอปฏิกิริยาสอดคล้องกับปฏิกิริยาลำดับที่ 1 แบบไม่ย้อนกลับ คำนวนพลังงานกระตุ้นของระบบที่ใช้ตัวเร่งปฏิกิริยาโซเดียมฟอสเฟตในรูปแบบผงเท่ากับ 43.6 กิโลจูลต่อโมล

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....

ปีการศึกษา 2556

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KEYWORDS: TRANSESTERIFICATION / HETEROGENEOUS CATALYST / SODIUM PHOSPHATE / PALM OLEIN / ALUMINA

KHRITSAYAPORN THINNAKORN: TRANSESTERIFICATION OF PALM OLEIN OIL USING SODIUM PHOSPHATE IMPREGNATED ON ALUMINA SUPPORT. ADVISOR: JIRDSAK TSCHEIKUNA, Ph.D., 185 pp.

The production of Fatty Acid Methyl Esters (FAMEs) via the transesterification reaction of palm olein and methanol using sodium phosphate (Na_3PO_4) as a heterogeneous catalyst has been investigated. This work studied Na_3PO_4 catalyzed transesterification in powdered form and modified surface area by impregnate on gamma-Al_2O_3. The catalysts were characterized using of BET, XRD, FT-IR, SEM-EDX, and ICP-OES method. The influences of various parameters, such as, the agitation speed, the molar ratio of methanol/oil, the operating temperature, the amount of catalyst, and the presence of water and free fatty acid in raw materials, on the rate of reaction were determined.

The study demonstrated that Na_3PO_4 can be used effectively as a heterogeneous catalyst in transesterification process. The operating conditions have a strong effect on FAME products. Under the study conditions, with powder form of catalyst, with a methanol/oil molar ratio of 18:1 and a reaction temperature of 210 °C, 98.5 % FAME yield was obtained with only 1 wt.% of Na_3PO_4.

The modified surface area of sodium phosphate (Na_3PO_4) as active component is prepared using incipient-wetness impregnation method on gamma-Al_2O_3 support. The prepared catalyst has tested its catalytic activity in transesterification reaction. The results showed that high FAME content (>96%) within 30 minutes of reaction, with methanol/oil molar ratio of 18:1, the catalyst amount is equivalent to 1.0 wt.% Na_3PO_4, and the temperature of 210 $^{\circ}$C.

The catalyst can be easily separated after the reaction and the prepared catalyst exhibited high stability and recyclability, on our test for 5 recycles, FAME product shows slightly reducing from fresh run but not significantly. When a large excess of methanol was used, the experimental results agreed with the irreversible first order kinetic model, while the activation energy was found to be 43.6 kJ/mol of the system used catalyst in powdered form.

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

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

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CHAPTER I

INTRODUCTION

1.1 Introduction

Fatty acid methyl esters (FAME) produced by transesterification of vegetable oil or animal fats with methanol used as a renewable substitute of petroleum-derived diesel fuels. The main advantages of using biodiesel is its biodegradable, it can be used without modifying existing engines. Additionally, compared to diesel, biodiesel is non-toxic and produces less harmful gas emission such as sulfur oxide, nitrous oxide [1, 2]. Biodiesel mixed with diesel can be improved the lubricity properties of diesel [3]. The sources of oil used as raw material for biodiesel production are diverted, depending on the oil availability in each country such as, the United States depends mainly on soybean, while Europe depends on rapeseed oil and jatropha oil most available in India and Indonesia. The main oil resources of Asia are palm and coconut oil. Nevertheless, waste oil and non-edible oils are also studied [4, 5], from the motivation of cheap oil sources. The different kind of oil are varied in fatty acid composition effecting to fuel properties significantly, when used as a fuel, such as, melting point, cetane number, oil stability, and lubricity properties [2, 6].

Various technologies have been studied to convert oil to biodiesel, transesterification with homogeneous base catalyst were the most applied and currently used in industrial scale production. The commonly used homogeneous alkaline catalysts are NaOH, KOH and their methoxides (CH_3ONa, CH_3OK). The advantages of process are attained high conversion in a short time of operating condition [7], but there are suitable for refined oil as a raw material to avoid soap formation. It have been reported, homogeneous base catalyst are limited to use with refined oil as raw material, which the limited amount of water and free fatty acid content is not higher than 0.5 wt.% of water, and 1.0 wt.% of free fatty acid [8, 9]. Moreover, this process required a complex purification step, releasing a large amount of waste water from water washing step. Moreover, glycerine is a by-product from this reaction is not pure and not appropriate to apply in cosmetic industrial.

Several types of catalysts have been developed to reduce the environmental impact from biodiesel production. A homogeneous acid-catalyzed process can avoid soap formation from free fatty acid reacts with base catalyst, but acid catalysts require a large amount of alcohol and a long reaction time to complete the conversion [10]. A supercritical methanol process is an alternative method for a non-catalytic transesterification reaction. The reaction completes in a short time, but requires high temperature (350–400 °C) and high pressure (45-65 MPa) [11]. Enzymatic processes [12] and ion - exchange resins [13] have been the focus of interest in recent years. Since enzymes can tolerate free fatty acid and water contents in raw materials, thus it avoiding soap formation and the purification of biodiesel is easier than the other methods. However, enzymes are expensive, and ion-exchange resins require a long reaction time to obtain high product yields.

Among of these processes, transesterification with heterogeneous catalyst is an attractive. The advantage of heterogeneous catalyst is its easy separation from the reaction products by filtration without requiring the complex purification step, it produces biodiesel which is more environmentally friendly. Avoid soap formation by catalyst reacts with free fatty acid in oil. Many researchers, have been studied with different oils and alcohols catalyzed by a variety of solid base catalyst. However, at the present day, it seem does not possible in industrial process to produce the ester and glycerol economically. There have only one industrial application on the development of biodiesel production using heterogeneous catalyst developed by French Institute of Petroleum (IFP) [14, 15], the process with heterogeneous catalyst consisted of a mixed oxide of zinc and alumina with a spinel structure. At laboratory scale, several compounds have been investigated as a solid catalyst for biodiesel synthesis.

The most commonly studied as heterogeneous basic catalyst is several compound of metal oxide group [16-21], and several compound of alkaline and alkaline-earth groups [22, 23], are considered the most of strong base and were the most applied to the transesterification process. Pure K_2CO_3 was active in the methanolysis of sunflower oil and achieved 90% conversion [24]. Sodium phosphate [25, 26] and potassium phosphate [27] also showed higher conversion of 97%yield [27]. Nevertheless, the other catalysts also catalyzed transesterification reaction of vegetable oil are commercial hydrotalcite [28], zeolites and modified zeolites [29, 30], but do not get much attention because it is quite expensive or complicated to prepare, which limited their industrial application.

However, the main problem of solid catalyst operate at conventional reaction temperature is the rate of reaction lower than homogeneous system, due to the diffusion limitation of three phases. Besides, the most of solid catalyst used are in powder form, which is mixed with the products, thus leads to difficultly separation. Moreover, it also found the leaching active species into the reaction products after the reaction, result in homogeneous and heterogeneous behavior goes together, and complex separation is still required. The developments of heterogeneous catalyst are studied continuously to solve these problems [31, 32]. Normally, a small metal particle is unstable, particularly at the temperatures typical of catalytic reactions. One way to overcome this problem is to use structure promoters or catalyst support, which can provide more specific area and pores for active species, where they can be anchored and react with large triglyceride molecules. The different types of support have been investigated to provide the shape stability, reduce the mass transfer resistant and the catalyst dissolved into the reaction mixture. En-Chin Su et al. [33] studied the influence of supports structure on the activity and adsorption behavior of Na, Ca-based catalysts for biodiesel synthesis from canola oil. Zu et al. [34] prepared using a series of carbon-supported CaO materials [34], and Noiroj et al. [35] showed that the support strongly affect the activity of the heterogeneous catalyst.

Alumina oxide in forms of porous γ- Al_2O_3 has been widely used as a support in catalytic process because it offers high surface area and high thermal stability [36]. Alumina exhibited no activity [37], but when loaded with alkali, alkaline-earth compounds were demonstrated as an efficient solid-base catalyst for the alcoholysis of vegetable oils [32, 37-40]. Alumina loaded potassium compounds were the most investigated, alumina loaded with KI, KF, KNO_3, K_2CO_3 or KOH and activated at high temperature showed catalytic activities [35, 38, 39, 41, 42].

The important variables effect on the rate of reaction of solid catalyst is the immiscible of reactants phases (oil/methanol/solid catalyst), result in long time of operating condition and required high mechanical stirred to promote the miscibility of phase. CaO showed more than 5 hours of reaction to achieved 90 % conversion [43, 44]. The prepared of catalyst onto the porous is slow rate of reaction, because of the surface of support remains porous cause to the internal mass transfer of large molecules of triglycerides into supported pore. Xie et al. [42] reported that 65% obtained with 15 hours of operation. Boz et al. [39] also reported on the activity of KI, KF , K_2CO_3, KNO_3 on Al_2O_3 take at time up to 8 hour to obtained 99% of yield. According to Fernandez et al. [45], the critical diameter of the triglyceride molecule is around 2 nm. Lopez Granados et al. [46] reported that methyl oleate has diameter around 2.5 nm, and the diameter of triglycerides is at least two times larger. This reason is cause from large triglyceride molecule diffuse to micro-pore of support structure. The preparation of catalyst on supported should be bigger pore size than triglycerides molecule. The use of meso-structured supports is shown as a factor improving the catalytic performance as compared with micro-structured supported could be reducing mass transfer resistance. KI loaded on meso-porous silica can solve the problem from internal mass transfer [47, 48]. Moreover, it was found that KOH/NaY, KOH/Al_2O_3 gave a good conversion but 51.26 wt.% of potassium was leached form KOH/Al_2O_3 [35]. Claire. S et al. [49], studied the ability of alkali dope metal oxide and showed $LiNO_3$/CaO, $NaNO_3$/CaO, KNO_3/CaO and $LiNO_3$/MgO exhibited >90% conversion in a standard 3 hours, KNO_3/CaO didn’t drop significantly after 5 cycles. potassium/γ-Al_2O_3 showed excellent catalytic activity in the first run (FAME yield 99%), but significant drop occurs in the second run (33% FAME) due to the leaching of potassium species [50]. The dissolution of solid catalyst resulted in some homogeneous activity.

The conventional production process of transesterification reaction is operated at reflux temperature, CaO showed slow reaction rate at low temperature [43], but when increase reaction temperature to 250 °C showed complete conversion in 6 minutes [51]. As well as, $CaCO_3$ gave low conversion at low temperature, but at 200 °C, the complete conversion in 23 minutes [52]. Lukic et al. [41] studied the reaction temperature between 80–200 °C, they concluded that when increasing reaction temperature increased in product content significantly. The catalytic ability of MgO [53] is quite weak at lower temperature, but increasing the reaction temperature had favorable influence on the methyl ester yield, to achieve high conversion in a few minutes. Transesterification reaction with high temperature can be reduced in the amount of catalyst used in the system and obtained high conversion in the same time [17, 54-57].

Biodiesel produced from supercritical alcohol is a high-efficiency method for noncatalytic reaction. However, this method has limited to practical applications, due to high temperature (250-350 °C) and high pressure (20-30 Mpa) [56, 58, 59]. To improve the operation conditions, developing a mild method of supercritical process has become a new trend for biodiesel production. Transesterification by couple catalyst can be reduce the hard condition of supercritical state to mild condition as well attained high product yield in the same time. Wang et al. [54] added amount of NaOH in to supercritical and subcritical condition, they found that can be promoted the great conversion and helps to reduce the critical state to mild condition as well attained high yield of product in the same time. Jian et al. [60] studied the transesterification reaction of soybean oil in supercritical methanol with sodium silicate compared with those of non-catalyst experiments. Many researchers have been reported on the subcritical and supercritical by adding amount of catalyst couple in the reaction [58, 60, 61].

Generally, the developments of heterogeneous catalyst are in the powder form, results in difficult to separate after the reaction. The commercial catalyst is available in any form of pellets, pills, rings, sphere, and granules or extrudes to facilitate the separation of solid phase from the reactants and products easier. Wan et al. [62] prepared $MgCO_3/ZnO$ and operated at 175 °C showed 91.54% conversion after 1 hour. The preparation of catalyst on a big shape are interested in this work, its easy to separate after the reaction, hence can reuse in many time. Nowadays, a few research on lab scale in a big shape, there only one industrial development with industrial catalyst form [14, 15].

Among of heterogeneous catalyst, Na_3PO_4 showed a potential catalyst. Since the catalyst is insoluble in products and reactants. This work intended to study the catalytic activity with both powder form and facilitate in a big shape form which suitable for industrial scale production in a continuous production process. A new type of catalyst for transesterification of palm olein using Na_3PO_4 loaded on alumina support. The catalyst was prepared using incipient-wetness impregnation of Na_3PO_4 on meso-pores alumina extrudates form. XRD, BET, FT-IR, and SEM method were employed for the catalyst characterization. ICP-OES was used to elemental analysis of the prepared catalyst, the spent catalyst, and the leaching of catalyst. The activity of the prepared catalyst (Na_3PO_4/Al_2O_3) was further tested in transesterification of palm olein with methanol. The stability and the leaching of catalyst in a reaction product also study in this work. The physical and fuel properties of biodiesel produced from the process also studied meet standard of biodiesel of Thailand.

1.2 Objectives of Research

1. To study the activity of sodium phosphate use as a heterogeneous catalyst in transesterification reaction of palm olein and methanol in powdered form.
2. To prepare of sodium phosphate on alumina by impregnation method.

1.3 Scopes of Research

1. Study of Na_3PO_4 in powdered form to catalyzed transesterification reaction.
2. Improve the surface area of Na_3PO_4 by prepare on γ-Al_2O_3 supported catalyst using incipient wetness impregnation method.
3. Characterization of Na_3PO_4 in powdered form and the prepared Na_3PO_4/Al_2O_3 by the following methods.
    - a) Structure and crystallinity of Na_3PO_4 by X-ray diffractometer (XRD).
    - b) Structure of Na_3PO_4 and the prepared Na_3PO_4/Al_2O_3 by FT-IR.
    - b) Thermal gravity analysis by TGA.
    - c) Specific surface area by N_2 adsorption based on BET method (BET)
    - d) Dispersion of the prepared catalyst on alumina by SEM-EDX.
    - e) Quantitative analysis of the prepared catalyst by ICP-OES.
    - f) Basic strength of the catalyst using Hammett indicator method.
4. Study the catalytic activity of Na_3PO_4 in powdered form in transesterification.
    - a) Effect of agitation speed on FAME yield: 100-800 rpm.
    - b) Effect of methanol/oil molar ratio on FAME yield: 3:1-30:1
    - c) Effect of reaction temperature on FAME yield: 150–250 °C.

d) Effect of amount of catalyst on FAME yield: 0-1 wt.%.

e) Effect of the presence of water in raw materials: 0-10 wt.%.

f) Effect of free fatty acid (FFAs) contents in raw materials: 0-10 wt.%.

5. Study the catalytic activity of the prepared Na_3PO_4/Al_2O_3 in transesterification.

a) Effect of agitation speed on FAME yield: 600-1200 rpm.

b) Effect of methanol/oil molar ration on FAME yield: 3:1-30:1.

c) Effect of reaction temperature on FAME yield: 190–250 °C.

d) Effect of amount of catalyst on FAME yield: 0-2 wt.%.

e) Study of the deterioration of catalyst and catalyst reusability.

6. Compares of the use of Na_3PO_4 in powdered form and the prepared catalyst on alumina support.

7. Biodiesel quality analysis follows standard method.

CHAPTER II
THEORY AND LITERATURE REVIEWS

2.1 Properties of biodiesel

At first time, vegetable oils can be used as a fuel direct in diesel engines, but there has a limitation of use cause from its viscosity. In comparison with diesel fuels, vegetable oil fuels have a good heating value but it has high viscosity (nearly 10 times of petroleum-derived diesel fuel) cause to the use of vegetable oil in diesel engines is not satisfactory [63]. Biodiesel or fatty acid methyl ester (FAME) produced from fats and oils has a similar properties to diesel produced from crude oil and can be used directly in diesel engines. Biodiesel mixed with diesel can be improved the lubricity properties of diesel [64].

The main advantages of using biodiesel is its biodegradable, can be used without modifying existing engines, and produces less harmful gas emissions such as sulfur oxide (SO_2), nitrous oxide (NO_X) [3–5]. It reduces net carbon dioxide emissions by 78% on a life-cycle basis when compared to conventional diesel fuel. The combustion of biodiesel decreases carbon monoxide (CO) emissions by 46.7%, particulate matter emissions by 66.7% and unburned hydrocarbons by 45.2% [8][2, 65, 66]. Additionally, biodiesel is non - toxic, compared to diesel fuel, biodiesel has a similar properties like diesel and some properties are better than diesel [67, 68]. The fuel properties of biodiesel show in Table 2.1.

Table 2. 1 Selected Properties of Typical No.2 Diesel and Biodiesel Fuels[6].

Fuel Property	Diesel	Biodiesel
Fuel Standard	ASTM D975	ASTM D6751
Lower Heating Value, Btu/gal	~129,050	~118,170
Kinematic Viscosity, @ 40 °C	1.3-4.1	4.0-6.0
Specific Gravity kg/L @ 60 °F	0.85	0.88
Density, lb/gal @ 15 °C	7.079	7.328
Water and Sediment, %vol.	0.05 max	0.05 max
Carbon, %wt.	87	77
Hydrogen, %wt.	13	12
Oxygen, %wt.	0	11
Sulfur, %wt.	0.05 max	0.0–0.0024
Boiling Point, °C	180-340	315-350
Flash Point, °C	60-80	100-170
Cloud Point, °C	-15 to 5	-3 to 12
Pour Point, °C	-35 to -15	-15 to 10
Cetane Number	40-55	48-65
Lubricity SLBOCLE, g	2000-5000	>7000
Lubricity HFRR, µm	300-600	<300

Biodiesel can be produced commercially from variety of oils and fats react with alcohol to yield biodiesel or fatty acid methyl ester (FAME). The source of triglycerides are diverses, ranging from single fatty acid to waste oil. Biodiesel produced from edible soybean oil be the most research, Table 2.2 show fatty acid composition in each type of vegetale oils.

Other vegetable oil such as rapeseed, sunflower, palm kenel and canola oils are follow in terms of frequency application. Animal fats and waste edible oils are also studied, from the motivation of used cheap oil sources [4, 5]. The different in chemical composition makes it different in application. In chemical terms, the featured of fatty acid are described by carbon number and degree of unsatuation each oil source has a specific composition of fatty acids and there effect on fuel properties of final product.

Table 2. 2 Fatty acid composition of vegetable oils [6].

Oil or Fat	**Fatty acids composition (wt.%)**							
	12:0	**14:0**	**16:0**	**18:0**	**18:1**	**18:2**	**18:2**	**22:1**
Canola	-	-	4-5	1-2	55-63	20-31	9-1	1-2
Coconut	44-51	13-18.5	7.5-10.5	1-3	5-8.2	1-2.6	-	-
Corn	-	-	7-13	2.5-3	30.5-43	39 - 52	1	-
Cottonsee	-	0.8-1.5	22-24	2.6-5	19	50-52.5	-	-
Olive	-	1.3	7-18.3	1.4-3.3	55.5-	4-19	-	-
Palm	-	0.6-2.4	32-46.3	4-6.3	37-53	6-12	-	-
Rapeseed	-	1.5	1-4.7	1 - 3.5	13-38	9.5-22	1-10	40-64
Sesame	-	-	7.2-9.2	5.8-7.7	35-46	35-48	-	-
Soybean	-	-	2.3-11	2.4 -6	22-30.8	49-53	2-10.5	-
Sunflower	-	-	3.5-6.5	1.3 -5.6	14-43	44-68.7	-	-
Tallow	-	3-6	25-37	14-29	26-50	1-2.5	-	-

The main properties that affected by different of fatty acids composition are low temperature operability, oxidative and storage stability, kinemetics viscosity, exhaust emissions, cetane number and heating combusion [69]. For the instance, the fuel properties of biodiesel increase with increasing carbon number and unsaturation degree. Figure 2.1 shows the properties of saturated, monounsaturated and polyunsaturated in different type of oil. Table 2.3 shows the properties of differerent biodisel derived from different of fatty acids.

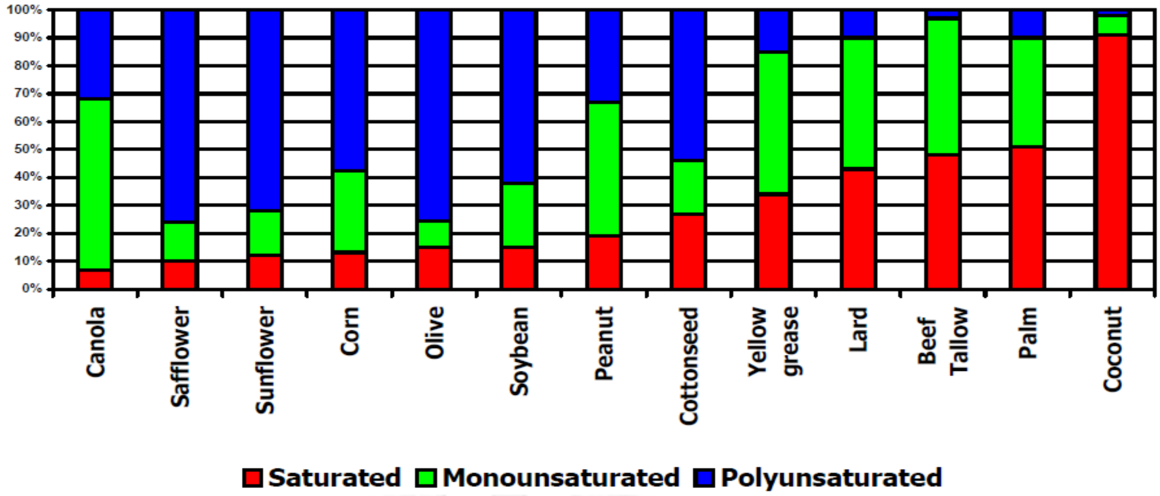


Figure 2. 1 Compared of the propertieds of saturated, monounsaturated, and polyunsaturated [6].

Table 2. 3 Properties of different biodiesel [6].

Fatty acid	Saturated	Monounsaturated	Polyunsaturated
	12:0, 14:0, 16:0, 18:0, 20:0, 22:0	16:1, 18:1, 20:1, 22:1	18:2, 18:3
Cetane Number	High	Medium	Low
Cloud Point	High	Medium	Low
Stability	High	Medium	Low

** Source: Biodiesel Handing and Use Guidelines 2006,U.S. Department of Energy

2.2 Biodiesel technology

Currently, there have various technologies to convert oil to biodiesel, such as, homogeneous base, homogeneous acid, supercritical alcohol, ion exchange resins, enzymatic, hydrotreating and heterogeneous. However, theses technology can convert oil to biodiesel by 2 reactions pathway, transesterification and esterification reaction. Biodiesel productions are different in raw material, catalyst used and reaction condition. Table 2.4 compares the production of biodiesel in each system and summarizes the advantages and the draw back in each production process.

Table 2. 4 Biodiesel Technology [70].

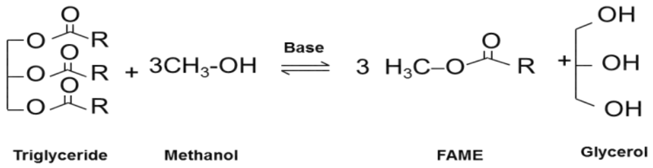
Variable	Alkaline Catalysis	Acid Catalysis	Hetero. Catalysis	Lipase Catalysis	Supercritical Alcohol
Reaction temp.(°C)	60 - 70	55 - 80	180-220	30 - 40	239 - 385
FFA in raw materials	Saponified products	Esters	Not sensitive	Esters	Esters
Water in raw materials	Interference with reaction	Interference with reaction	Not sensitive	No influence	
Yield of ME	Normal	Normal	Normal	Higher	Good
Glycerol recovery	Difficult	Difficult	Easy	Easy	
Purification of ME	Repeated washing	Repeated washing	Easy	None	
Production cost of catalyst	Cheap	Cheap	Potentially cheaper	Relatively expensive	Medium

2.2.1 Homogeneous technology

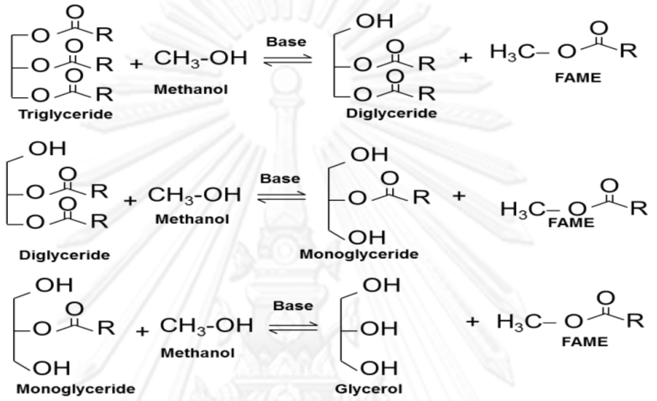
Homogeneous production processes are separated for homogeneous base and homogeneous acid.

Homogeneous base

Basic homogeneous technology is the most common process and currently used to convert vegetable oil to biodiesel. It is available in industrial scale production that it is carried on under regular operational conditions (65 °C). The overall transesterification reaction is as follow in scheme 2.1.



Scheme 2.1 The overall reaction of transesterification.

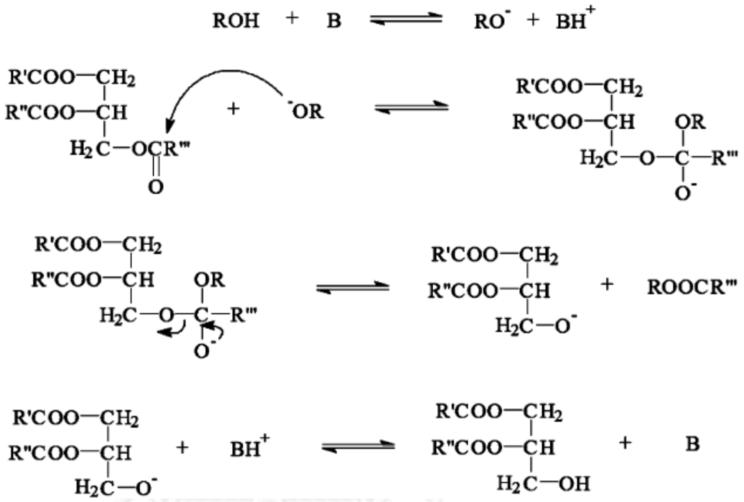


Scheme 2.2 Transesterification reaction.

Scheme 2.1, triglyceride molecules are reacted with alcohol and transformed to monoesters and glycerol. This reaction is a reversible reaction and occurs pass through 3 steps, simultaneously, as shown in Scheme 2.2. Triglycerides reacts 3 moles of methanol to give diglyceride, monoglyceride and 3 moles of fatty acid methyl ester with methanol, commonly used alcohols are methanol, ethanol, propanol and butanol. Methanol is commercially used due to its availability and cost effectiveness. The reaction mechanism of based-catalyzed transesterification is showed in Scheme 2.3.

The 1st step is the generation of an alkoxide ion (RO^-) through proton abstraction from alcohol by base catalyst (B). 2nd step the alkoxide ion attacks a carbonyl carbon of triglyceride molecule and forms a tetrahedral intermediate ion. In

3rd step, it rearranged to generate a diglyceride ion and alkyl ester molecule. Finally, 4th step the diglyceride ion reacts with the protonated base catalyst, which generates a diglyceride molecule and turns the base catalyst into the initial form. The resulting diglyceride is ready to react with another alcohol molecule, thereby starting the next catalytic cycle.



Scheme 2.3 The reaction mechanism of based-catalyzed transesterification.

Usually, the raw material for homogeneous process with base catalyst is refining oil, where the amount of impurities is reduced. An amount of free fatty acids (FFAs) is lower than 0.1-0.5 wt.%, while humidity should be lower than 0.1 wt.% [8, 9], the amount of phosphorus has a maximum in 20-50 ppm and the un-saponificable material should be below 1 wt.% [69].

The commonly used homogeneous catalysts are NaOH, KOH, and their methoxides ion (CH_3ONa, CH_3OK) [71]. The advantages process using homogeneous base catalyst are attained high conversion in a short time of operating condition [7]. There are use a small amount of 1-2 wt.%, to attained high yield of product in a few hours (<30 minutes). The result showed that reactions attain high yield of product in short time, nearly 100% yield [71, 72]. However, it have been reported if oil contains water, free fatty acid, the activity will be reducing. A large amount of FFA content in the oil leads to the formation of unwanted soap in the product and difficultly in the separation of the biodiesel fuel from the glycerol formed during processing, which results in a decrease yield. Water reacts with alkyl ester to produce carboxylic acids, which rapidly react with alkaline metals to form soaps such as $RCOO\text{-}Na^+$. This soap formation makes the process inefficient by reducing alkyl ester yield and interrupting glycerol recovery [73]. In order to solve this problem will be continued to develop, acid catalyst were used instead of alkaline catalysts.

Homogeneous acid

The common raw material used for biodiesel production using homogeneous is refining oil. The major disadvantage is its high price due to the refining process. One way to lower the cost of production process is by reducing the cost of raw material, used oil and waste oil is candidate for the motivation of cheap oil. Homogeneous acid catalysts can be both catalyzed transesterification and esterification reaction goes together.

Acid-catalyzed transesterification process is suitable for high FFA feedstock, there can be esterified high FFA feedstock, reaction yield are methyl ester and water [74, 75]. The process is usually progressed by a Bronsted acid. If the oil source has high FFA content such as waste oil, FFA is also converting to biodiesel. Acid catalysts give very high yields in the transesterification process, request high yield operation under hard condition, such as high reaction temperature and high methanol/oil molar ratio. These suitable for low quality oil such as waste cooking oil, or high FFA oil. Two major disadvantages with transesterification with acid catalyst are the reaction time is 4 times higher than when NaOH is used. The molar ratio of alcohol/oil of transesterification with acid is around 5 times higher than NaOH [76-78]. Many researchers have been working on the transesterification using sulfuric acid under different operational conditions as well as with different raw materials. The most standard case uses methanol, with a molar ratio of 32:1 related to the oil and 1-2 wt.% of H_2SO_4, reaction temperature of 60 °C, reaction time that could be over 30 hours [79]. Goff et al. [80] have studied acid-catalyzed transesterification. H_2SO_4 was selected and there required more than 50 hours to reach 100% of conversion of soybean oil with methanol/oil molar ratio around 30:1, at temperature 65 °C.

However, acid-catalyzed transesterification is still sensitive to water concentration. In previous study, when a small amount of water thus as a little of water in the reaction mixture was able to affect ester yields in transesterification of vegetable oil with methanol, with the reaction almost completely inhibited at 5 wt.% water concentration in feed stock [71, 81]. Water content in oil was less than 0.5 wt.% in order to achieve conversion higher than 90% of ester yield under reaction conditions.

Acid-catalyzed esterification processes is a chemical reaction between carboxylic acid reacts with an alcohol in the presence of acid catalyst (commonly concentrated H_2SO_4) to form an ester. Esterification of fatty acid in excess alcohol in the presence of concentrated H_2SO_4 as a catalyst results in an ester and water. Esterification process is suitable for low-quality of oils and fats because of high levels of fatty acid and high water content contain such as cooking oil, and waste oil. Acid-catalyzed transesterification reaction required higher temperature and methanol/oil ratio than alkali catalyst, the catalytic activity is lower than the alkaline catalyst, but it is not sensitive to moisture. There are reactivity and stability, even though feedstock are low quality oil and contains a small amount of FFA and moisture.

2.2.2 Supercritical Technology

Supercritical technology is an alternative method for non-catalyst reaction for transesterification and esterification process [11]. The reaction completes in a short time, but advantage for it required high temperatures and pressures. In the supercritical state, the oil and methanol are in a single phase, and the reaction occurs spontaneously and rapidly. This process can tolerate water in the feedstock, free fatty acids are converted to methyl esters instead of soap, so a wide variety of feedstock are applied. This operating condition is cause to high energy cost of final product.

The supercritical process consists on reaching a certain operational conditions that will allow one of the fluids to be in supercritical state. When reaching a certain pressure and temperature, both, liquid and gas phase becomes one and there is not possible distinction among them, therefore have reached the supercritical pressure and temperature. This condition is suitable for biodiesel produced in short reaction time and can be varied with any raw material. This technology not required a catalyst but the reaction operate in high temperature and pressure cause to high energy cost of final product [82-84] . Supercritical technology can be accelerated both esterification and transesterification process in the same time.

Esterification of FFA by supercritical process was first described by Saka et al. [85]. Rapeseed oil was hydrolyzed to FFA in a subcritical reaction and then supercritical esterification of FFA with methanol, yield to methyl ester. They tested in several process variables for the hydrolysis reaction in order to improve its conversion to fatty acid. For the best condition, the produced fatty acids were esterifies into biodiesel under high pressure (20 MPa) and high temperature (300 °C) in order to reach high conversion in a short time. They also proposed kinetics for the conversion of triglyceride into FFAs, they have proposed a simple first order kinetics related only to the triglycerides. They have found good agreement between the experimental data and the proposed model.

The transesterification reaction of vegetable oils in the presence of alcohols in a supercritical state does not require a catalyst. The common used alcohol is methanol. Hawash et al. [83] have carried on the transesterification reaction using Jatropha oil and supercritical methanol. They were found that reaction time was less than 4 minutes in order to achieve a yield of 100% with the reaction temperature 320 °C, an operation pressure is around 80 bar. The molar ratio of alcohol/oil was 43:1. Similar work was done by Saka and Kusdiana [85] have studied the reaction of rapeseed oil with methanol. The experiments with a reaction time of 4 minutes, a molar ratio of 42:1 and a pressure over 80 bar and a temperature higher than 240 °C. The final yield was higher than 98% and the FFAs were also esterified in the same time. Tan et al. [86] studied the same reaction but using palm oil as raw materials. They were found that 70% conversion was achieved after 20 minutes of reaction at a temperature of 360 °C and a molar ratio of 30:1.

Besides methanol, several works also studied ethanol as an alternative alcohol from renewable sources. Tan et al. [86] have compared both alcohols (methanol, ethanol) in the same operational conditions. They have found that work with ethanol achieved was almost 3% conversion lower than methanol. A similar work was performed by Gui et al. [87] have studied supercritical transesterification reaction of palm oil using ethanol. They have found that a yield of 79.2% was obtained at temperature of 349 °C, 30 minutes of reaction time, a molar ratio of 33:1 and a pressure over 63.8 bar were used. Mardras et al. [84] compared both types of alcohol, the results showed contrast with previous work, ethanol shows a slightly higher final conversion compared to methanol, reaching almost 100% for ethanol and over 96% for methanol.

2.2.3 Enzymatic Catalysis

The transesterification reaction can be catalyzed with enzymes (biocatalysts), particularly lipases were the most applied [12, 88, 89]. Enzymatic has attracted many attentions in recent years since enzymes can tolerance FFAs and water content in oil to avoid soap formation, thus purification of biodiesel and glycerol is easier than the other methods. Enzymes can be reused and regenerated in several times. For enzymatic catalyst, various type of enzymes which are isolated from microorganisms (Rizhomucor miehei, Pseudomonas cepacia, Caida antarctica). The reaction takes place at low temperature around 25–35°C, but it takes a long time to attain high conversion. However, the main problems of usage of lipases in an industrial scale are their price, particular loss of activity in methanol and long duration of the reaction [90, 91]. Different of raw materials and operational conditions have been tested by several researchers with the aim of studying the optimums operational conditions to produce the biofuel. Enzymatic process could be catalyzed both esterification and transesterification process.

Tan et al. and Bajaj et al. [92, 93] have completed reviews on the transesterification reaction using enzymes. They have compared several authors and discussed on different raw materials and different enzymes and the operational conditions where each of them has given the best results on the biodiesel yield. The result is shown that of them have yields over 90% for each study. A similar work was done by Ranganatham et al. [94] they reviewed of several works about biodiesel produced by enzymatic catalysis. They have compared several works of biodiesel production, they considering not only the vegetable oil and the enzyme used but also the possible cost of production. Antczak et al. [95] have also reviewed of enzymatic ways of producing biodiesel. They have summarized the lipase-catalyst tranesterification for several alcohols and several fats and different enzymes. They have found that, for example, for methanol, the best yield (94.8%) was obtained after 8 hours of reaction. However, the enzyme catalysts are still complex process, cause pollution and environmental problem. Because of enzyme price is high, the reaction time is too long and the reaction yield is low, need more research to develop. Nowadays, to improve the enzyme activity and to prevent the enzyme poisoning is being study [81, 88, 96].

2.2.4 Hydrotreating

Another way to the production of biodiesel from fats and vegetable oils is through hydrotreating (HDT) of the triglyceride containing feed stocks. The hydrocarbons are produced by two reaction pathways: (i) hydrodeoxygenation (HDO) and (ii) hydrodecarbonylation (HDC). n-alkanes originating from HDO have the same carbon number as the original fatty acid chain, i.e. even carbon number, typically 16 or 18. The main reaction by-products of this route are water and propane. On the other hand, HDC yields hydrocarbons with an odd carbon number, they have one carbon atom less in the molecule than the original fatty chain.

Hydrotreating is early used in the petroleum refinery to remove S, N and metals from petroleum-derived feedstocks including heavy gas-oil or vacuum gas-oil. Hydrotreating has been used to produce straight chain alkanes ranging from n-C15 to n-C18, from a fatty acid fraction of oil. The normal alkanes have a high cetane number (above 98) whereas typical diesel fuel has a cetane number around 45. The advantages of hydrotreating over transesterification are that is compatible with the current infrastructure, the process leads to a deoxygenated and thus stable product that is fully compatible with petroleum-derived diesel fuels, the product exhibits high cetane number and low sulfur content [97, 98].

2.3 Heterogeneous Technology

2.3.1 Heterogeneous catalyst at low temperature

Heterogeneous catalysts are currently developed instead homogenous catalyst. There are advantage for separation easily, reusable, longer catalyst lifetime and good for environmental. Many different types of heterogeneous catalyst have been developed. Various basic heterogeneous catalysts have been tested and most reported in the literature for biodiesel production. Firstly, the development of solid catalyst starts from single metal development. Alkaline and alkaline-earth compound were the most studied for transesterification reaction.

Calcium oxide is one of the heterogeneous catalysts that are in common use [34, 44, 99]. Kouzu et al. [100] examined transesterification of soybean oil under reflux methanol in the presence of CaO, $Ca(OH)_2$ and $CaCO_3$. They reported the yield of methyl ester products was 93% for CaO, 12% for $Ca(OH)_2$, and 0% for $CaCO_3$ after 1 hour of operating time. Then CaO was further tested in transesterification of waste cooking oil with acid value of 5.1 mg KOH/g. The yield of FAME was above 99% at 2 hours of reaction time. However, the catalyst changed into calcium soap by reacting with FFAs in waste cooking oil at initial stage of transesterification. Kawashima [44] used CaO as a solid base catalyst for transesterification of rapeseed oil which methanol. They found that after 170 minutes of reaction time, the methyl esters yields of 93% were obtained. Liu et al. [101] also studied transesterification of soybean oil using CaO as a solid base catalyst. Biodiesel yield exceeded 95% in 3 hours using 12:1 molar ratio of methanol to oil and 8 wt.% of catalyst at 65 °C.

Zabeti et al. [36] have done a review several solid catalysts for biodiesel production, in their work they did a recompilation of several works where different substrates as well as different raw materials are used to produce biodiesel in the presence of an alcohol. The authors have summarized work performed with soybean, sunflower, palm kernel, colza and cottonseed oil (among other) and in the presence of metal oxides such as CaO, SrO, $Al_2O_3/TiO_2/ZnO$, among several other. The yield obtained is in all cases higher than 80% showing that all the alternatives presented there are suitable for biodiesel production.

S.T. Jiang et al. [26] used sodium phosphate (Na_3PO_4) for biodiesel preparation from rapeseed oil. They were found that the reaction conditions are affected to the formation of product. For a mass ratio of catalyst to oil of 3 wt.%, molar ratio of methanol/oil of 9:1, reaction temperature 70 °C and rotation speed of 600 rpm, the transesterification was nearly completed with 20 minutes. They summarized that Na_3PO_4 has a similar activity to homogeneous catalyst and could be used repeatedly for 8 runs without any activation treatment and no obvious activity loss was observed. This reaction also compares Na_3PO_4 with $Na_3PO_4.10H_2O$. Since $Na_3PO_4.10H_2O$ is cheaper, but the final yield was only 71.3%, much lower than that of Na_3PO_4 at 99.7%. Paolo de Fillippes et al. [25] also studied about Na_3PO_4 catalyzed transesterification of rapeseed oil. The research shows that the transesterification of rapeseed oil could be catalyzed by both anhydrous and hydrated Na_3PO_4, while polytrisodium phosphate has only a negligible catalytic activity. Na_3PO_4 catalysts are less active than NaOH due to the lower ability to form sodium methoxide. The experimental data are interpreted by using a kinetic model showing that a first order reaction with respect to glycerides concentration is adequate to describe the reaction. This paper also indicates that under the selected experimental conditions, the chemical reaction is the main factor affecting the rate-determining step.

Similarly work have been studied by different metal compound of phosphate [27]. Transesterification of waste cooking oil with methanol by using K_3PO_4 as a solid catalyst show high catalyst properties for transesterification reaction compared to CaO and K_3PO_4. The FAME yield reached 97.3% when used catalyst concentration 4 wt.% at 60 °C for 120 minutes. They introduced K_3PO_4 could be continue hydrolyzed in the presence of water, and HPO_4^{2-}, $H_2PO_4^{-}$ ions and OH^{-} ions could be form in the reaction solution [27]. The catalyst activities of K_2HPO_4 and KH_2PO_4 were also studied and found that they were not catalyzing the transesterification reaction due to weak acidity. Di Serio et al. [102] examined application of vanadyl phosphate (VOP) as catalyst in the transesterification of soybean oil and yielded 80% methyl ester after 1 h reaction time even though the specific surface area of catalyst was low (2-4 m^2/g).

Wan et al. [103] examined the production of biodiesel from soybean oil by transesterification over sodium aluminate ($NaAlO_2$) as a heterogeneous catalyst. The solid base showed high activity for the alcoholysis of soybean oil. The reaction was carried out at a reflux temperature with a 12:1 molar ratio of methanol/oil and 1.5 wt.% of catalyst for a reaction time varying from 50 minutes, in which the methyl ester yield reached 93.9 wt.%. The catalytic durability tests showed slight decrease in activity by repeating the transesterification for three times. They summarized the reaction contained homogeneous and heterogeneous in the same time.

Chinmoy B. et al. [24] used potassium carbonate (K_3PO_4) for transesterification of jatropha curcas oil and methanol. This study was found the reaction complete within 15 minutes when 5 wt.% K_2CO_3, and the methanol/oil molar ratio of 6:1, or 4 wt.% K_3PO_4, the methanol/oil molar ratio of 9:1, at the reaction temperature of 60 °C. Table 2.5 showed the list of previous work studied about transesterification using heterogeneous base catalyst at conventional reaction temperature.

Table 2. 5 Previous researches on transesterification with solid catalysts.

Oil	Alcohol	Molar ratio	Catalyst	Temp. (°C)	Conversion %	Reaction time (h)	Ref.
Canola	Methanol	6 : 1	$CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, $CaCeO_3$	60	79 – 92	10	[54]
Sunflower	Methanol	6 : 1	1%CaO	60 - 120	91	1.5 - 5.5	[43]
Soybean	Methanol	6 : 1	1 - 3 % $CaCO_3$	65	<15	2	[29]
Rapeseed	Methanol	6 : 1	4%Na_3PO_4 $Na_3PO_4 12H_2O$ $Na_5P_3O_{10}$ NaOH	60	82.4 65.3 7.0 98.4	2	[25]

2.3.2 Transesterification coupling with catalyst at high temperature

Conventional transesterification is performed at reflux temperatures (65–70 °C). Normally, accelerating the rate of reaction of a heterogeneous system can be achieved with increase in the amount of alcohol and catalyst use. Besides, increase the reaction rate can be performed by increasing the reaction temperature. When the supercritical method was applied, feeds stock can be either triglyceride or fatty acid. The use a small amount of solid catalyst added into the supercritical process can access to complete conversion within short time. Catalyst applied in supercritical process can be reduced pressure, temperature and operating cost. Many researches worked about the effect of temperature increase with increasing temperature. A similar effect was also detected when the amount of catalyst was increased, higher amount of catalyst will increase reaction rate and then shorter reaction times.

A CaO catalyst showed slow reaction rates at low temperatures [43], but when the reaction temperature was increased to 250°C, complete conversion was obtained in 6 minutes [51]. Similarly, a $CaCO_3$ catalyst exhibited low conversion at low temperature, but complete conversion was obtained in 23 minutes at 200°C [52]. Lukic et al.[41] studied reaction temperatures between 80-200°C and concluded that increasing the reaction temperature resulted in a concomitant increase in product content. The catalytic ability of MgO [53] is quite weak at lower temperatures, but increasing the reaction temperature favorably influenced the methyl ester yield, resulting in high conversions within a few minutes. Transesterification at high temperatures can reduce the amount of catalyst required to achieve a particular degree of conversion within a specified time [17, 54-57].

Demirbas [51] used sunflower oil in a supercritical condition of methanol. When add amount of CaO was found that high an amount of catalyst was necessary to obtained high yield of biodiesel, while using 1 wt.% reaches very low results. Full conversion was achieved at 252°C, 41:1 of molar ratio, a concentration of catalyst 3 wt.% and a pressure of 240 bars. However, the presence of a catalyst will produce a different and possible more complicated down streaming separation and purification.

Melero et al. [48] investigated transesterification of refined and crude vegetable oils with a sulfonic acid-modified meso-structured catalyst. This catalyst yielded fatty acid methyl esters over 95 wt.% for oil conversion close to 100% under the best reaction conditions (180°C, methanol/oil molar ratio 10, and catalyst loading 6 wt.%). In the presence of FFAs in the oils, the sulfonic acid-modified meso-structured catalyst showed high activity toward simultaneous esterification and transesterification. These sulfonated meso-structured materials are promising catalysts for preparation of biodiesel.

Yin J-Z. et al. [60] improved the method from supercritical condition to mild condition with a small amount of sodium silicate (Na_2SiO_3). They concluded Na_2SiO_3 can improve the transesterification reaction of soybean in supercritical methanol. The variables affecting the FAME yield during the transesterification reaction, such as the reaction temperature, catalyst content, and the molar ration of methanol/oil. The experiments were compared with those of non-catalyst experiments. The test results shows that a FAME yield of 95.6% was achieved when the reaction was performed with a catalyst content of 0.5 wt.% at 220°C for 30 minutes.

Yin et al. [61] synthesized biodiesel from soybean oil and methanol under supercritical and subcritical condition. They summarized that under the supercritical, the maximum methyl ester yield exceed 98%, at the molar ratio of methanol to oil was 42:1, and the reaction temperature ranged from 260°C to 350°C. In order to decrease the operational temperature and pressure, with only a little of KOH as the catalyst (KOH/oil = 0.1 wt.%), a 98% yield of methyl ester was obtained in 10 minutes at reaction temperature of 160°C and the molar ration of methanol/oil of 24:1, while only 6% yield of methyl ester was obtained at 260 °C without the catalyst. The result demonstrated that by coupling the catalysis and operates at subcritical operation, a few amount of catalyst could be largely reduced and methanol utilization could be significantly enhanced.

Guan et al. [27] used tri-potassium phosphate (K_3PO_4) accelerated the transesterification of soybean oil under subcritical methanol. Under the optimal conditions, the temperature of 220°C, the methanol/oil molar ratio of 24:1, obtained 95.6% of yield in 30 minutes with only 1 wt.% K_3PO_4.

Calcium carbonate ($CaCO_3$) catalysts can be used to biodiesel production process, it operate at high temperature greater than 200°C to obtained high product yield (>95 %) [52]. Free fatty acids were esterified by the $CaCO_3$ and did not appear to inhibit the catalyst at high temperature. Reaction time of 18 minutes provided essentially complete conversion. No decrease in the activity of $CaCO_3$ was observed after a week of utilization.

Wan et al. [62] prepared $MnCO_3$/ZnO catalyst with different Mn/Zn molar ratio using co-precipitation method. The triglyceride conversion of the transesterification reaction catalyzed by $MnCO_3$/ZnO catalyst achieved 98.3% under the optimized catalyst preparation and transesterification condition, at Mn/Zn molar ration of 1:1, calcination temperature 400 °C, calcination time 0.5 hours, and 4 wt.%

catalyst, 18:1 methanol/oil molar ratio, transesterification temperature of 175 °C and 60 minutes of reaction time. The catalyst was reused 17 times and has shown that the catalyst could maintained maintain a high catalyst activity. The deactivation of the catalyst after 18th cycles of its reuse was caused by the transformation of small granule ZnO to lamellate zinc glycerolate. Table 2.6 showed the previous research used the heterogeneous catalyst operated at high reaction temperature.

Table 2. 6 Previous researches operated at high reaction temperature

Oil	Alcohol	Molar Ratio	Catalyst	Temp. (°C)	Conversion (%)	Time (min)	Ref.
Soybean	Methanol	0.93:1	5% of CHT, MgO, MgO(I), MgO(II), MgO(III)	180-200	70-98		
Soybean	Methanol		$MnCO_3$/ZnO	subcritical	98.3		[62]
			MgO, SrO	subcritical			[18]
Sunflower	Methanol	41:1	CaO	250			[51]
Soybean	Methanol		mano-MgO	sub			[53]
Rapeseed	Methanol	40:1	SrO, CaO, ZnO,TiO_2, ZrO_2	220	100	10	[17]
Soybean	Methanol	40 :1	1-3% $CaCO_3$	200	100	23	[52]
Soybean	Methanol	30:1	1% K_3PO_4	220	95.6		[61]
Soybean	Methanol	24:1	PbO, MgO, MnO_2, BaO, CaO	215	78-85		[49]

2.3.3 Supported alkaline metal/metal ion catalyst

The main disadvantage of solid catalysts operating at conventional reaction temperature is the reaction rate is less than that of the homogeneous system due to the diffusion limitation of the three phases. In addition, the most of the solid catalysts currently used are in powdered form, which is mixed with the products, thus leading to difficultly in separation. Moreover, it has also been found that active species can leach into the reaction products after the reaction, resulting in simultaneous homogeneous and heterogeneous behavior, and complex separation is still required. Hence, heterogeneous catalysts are continuously under development to solve these problems

Normally, small metal particles are unstable at temperature typical of catalytic reactions. One way to overcome this problem is to use structure promoters or catalyst supports, which can provide more specific area and pores for active species, anchor and react with the large triglyceride molecule. Various supports have been investigated to provide shape stability, to reduce mass transfer resistance and to prevent catalyst dissolution into the reaction mixture. Therefore, heterogeneous catalysts used in industry consist of relatively small particles stabilized in some way against sintering. This can be achieved by adding a structural promoter, or by applying particles inside the pores of an inert support. All kinds of materials that are thermally stable and chemically relatively inert can be used as supports, but alumina, silica and carbon are the most common used [104].

En-Chin Su et al. [33] studied the influence of the support structure on the activity and adsorption behavior of Na and Ca-based catalysts for transesterification. Na, K, Li, Ba, and Mg are frequently used in the metallic form or as various ionic forms of halide, carbonate, hydroxide and nitrate. The metal ion-supported catalysts are usually calcined at 400-600 °C before reaction to get rid of the adsorbed atmospheric chemicals. The catalysts generally exhibit the preferential dependence of activity on the surface basicity, rather than on the other properties such as specific surface area and pore volume. In terms of basicity and catalytic activity, the supported halide catalysts show the best results as usual. Zu et al. [34] prepared a series of carbon-supported CaO materials, and Noiroj et al. [35] showed that the support strongly affects catalytic activity.

Boz et al. [39] synthesized solid base catalysts of different potassium compounds such as KI, KF, K_2CO_3 and KNO_3 with the loading amount of 35 wt.%. The synthesized KI/Al_2O_3 solid base catalyst showed the high activity in the transesterification of canola oil with methanol and gave much stable methyl ester content during the reaction with the highest yield of 99.6% at the end of 8 hours of reaction time at 60 °C, with the methanol/oil ratio 15:1.

Liu et al. [105] used a cinder from coal burning industry, with 0.9-2.0 mm diameter, served as the support for CaO/KF to prepare base catalyst particle. The results showed that a maximum triglyceride conversion of 99.9% catalyzed by 2.1 wt.% catalyst (based on the weight of soybean oil) in 20 minutes was obtained with methanol/oil molar ratio of 12:1. Triglycerides conversions were from 99.9 to 96.6% from the first to the fourth time use of the catalyst particle. The formed $KCaF_3$ and K_2O were the main active components for the catalyst activity. The leakage of K and Ca to the water and methanol and the occupation of the active sites by oleic acid were the main reasons for the decrease of triglyceride conversion during repeated use of the catalyst. Fluoride leached into soybean oil, oleic acid, water, and biodiesel were negligible. However, about 1.5 and 3.0 mg F were dissolved into methanol and glycerol.

Owing to its thermal and mechanical stability and its rich chemistry, alumina is the most widely used as a support in biodiesel production process. Alumina is in various structures, As a support, γ-Al_2O_3 offers high surface areas (50-300 m^2/g), mesopores of between 5 and 15 nm, pore volume about 0.6 cm^3/g, high thermal stability and the ability to be shaped into mechanically stable extrudates and pellets [104].

I. Lukic et al. [106] synthesized a new type of catalyst for FAME with K_2CO_3 as active component on alumina/silica support using sol-gel method. The activity of synthesis catalyst was compared with the pure K_2CO_3. The effects of reaction variables, such as reaction time, temperature and methanol to oil ratio, on yield of FAME were investigated. The result found that the temperature of 120 °C and methanol to oil molar ratio 15:1, are optimal conditions for FAME synthesis. However, they also characterized catalyst by XRD analysis, FTIR spectroscopy and N_2 physisorption at 77 K, and tested in the methanolysis of sun flower oil. Similarity works have done by Xie et al. [42] used alumina loaded with potassium as a solid base catalyst in a heterogeneous manner was developed. The catalyst loaded KNO_3 of 35 wt.% on Al_2O_3, after calcined at 773 K for 5 hours, it was found to be the optimum catalyst, which can give the highest basicity and the best catalytic activity reaction. The reaction was carried out at reflux of methanol, with a molar ratio of methanol to soybean oil of 15:1, a reaction 7 hours, and a catalyst amount 6.5%, the highest conversion reached 87%.

Various Al_2O_3-supported alkali and alkali earth metal oxides were synthesized by Benjapornkulapong S. et al. [37], $LiNO_3$, $NaNO_3$, KNO_3/Al_2O_3 with an active metal oxides formed at calcinations temperature of 450–550 °C showed very high methyl ester attained to 93%. For instance, KF/Al_2O_3 and KI/Al_2O_3 catalysts generally showed higher transesterification activities than K_2CO_3/Al_2O_3, KOH/Al_2O_3, and KNO_3/Al_2O_3 [12, 76]. On the other side, results have varied regarding the best performance among nitrates, hydroxide and carbonates [12, 76, 77]. When comparing the results from two different studies [12, 76] examining KF, K_2CO_3, and KNO_3 supported Al_2O_3 catalysts, the different activity orders between the studies were mainly attributed to the difference in impregnated potassium amount. The different of Hammett basicity and oil conversion for K salt-supported Al_2O_3 catalysts with different potassium amount shows in Table 2.7. The other work have been researched on Al_2O_3 used supported active component in transesterification showed in Table 2.8.

Table 2. 7 Different of Hammett basicity and oil conversion for K salt-supported Al_2O_3 catalysts with different potassium amount.

Catalyst	0.35 g K-salt/g Al_2O_3 [12]			2.1 mmol K-salt/g Al_2O_3 [76]		
	K amount (wt.%)	Hammett basicity (H_)	Oil Conversion	K amount (wt.%)	Hammett basicity (H_)	Oil Conversion
KF/Al_2O_3	23.5	15.0 - 18.4	98	8.2	15.0-18.4	86
K_2CO_3/Al_2O_3	19.8	15.0 - 18.4	97	16.4	9.3-15.0	48
KNO_3/Al_2O_3	13.5	9.8 - 15.0	63	8.2	15.0-18.4	67

*The calcinations condition for the catalyst was 500 °C and 3 hours in both studies.

Table 2. 8 Examples uses of alumina supports in transesterification process.

Oil	Alcohol	Molar Ratio	Catalyst	Temp. (°C)	Conversion (%)	Time (h)	Ref.
Soybean	Methanol	55:1	MgO,ZnO/Al_2O_3	70-130	82	7	[35]
Rape oil	Methanol	6:1	10% load KNO_3/CaO	65	98	3	[23]
Soybean	Methanol	15:1	35% KI/Al_2O_3	60	96	8	[42]
Soybean	Methanol	9:1	0.5-1.5% Na/NaOH/Al_2O_3	60	80-95	2	[50]
sunflower	methanol		NaOH/Al_2O_3	60			[38]
canola	methanol	12:1	3 wt.%KF/nano γ-Al_2O_3	60	97.7	8	[39]
canola	methanol	6:1-15:1	KI/Al_2O_3 KF/Al_2O_3 K_2CO_3/Al_2O_3 KNO_3/Al_2O_3	25-60	70-99.6	8	[39]

2. 4 Catalyst leaching

Catalysts leaching under reaction conditions have been reported by many researchers. Lukic et al. [41] showed that K_2CO_3/Al-Si support are very active in the methanolysis of sunflower oil. It was also shown that leaching of some amount of potassium species to the methanol phase during FAME synthesis occurred when the reaction was performed at 120 °C, but when the temperature was below 100 °C, the leaching was negligible. Thus, the catalyst acts as a heterogeneous one under such conditions. The analysis of different working conditions indicated that the temperature of the reaction and methanol/oil molar ratio mainly affected the reaction rate of methanolysis. Although at 120 °C with a methanol/oil molar ratio of 15:1, a yield of over 92% was achieved after 15 minutes, the performed investigation of the catalytic activity of K_2CO_3/Al-Si support showed that at lower temperatures, a heterogeneously catalyzed methanolysis. Claire S. et al. [49] showed that $LiNO_3$/CaO, $NaNO_3$/CaO, KNO_3/CaO and $LiNO_3$/MgO exhibited >90% conversion in a standard 3 hours test. However, the metal leaching from the catalyst was detected, and this resulted in some homogeneous activity. Table 2.9 showed the literature summary of heterogeneous catalyst leaching under reaction condition.

Table 2. 9 The literature summary of heterogeneous catalyst leaching under reaction condition

Catalyst/ Support	**Amount of active species (wt.%)**	**Temp. (°C)**	**Molar ratio**	**Amount of catalyst (wt.%)**	**Yield %conv.**	**Reuse and leaching**	**Ref.**
K_2CO_3/Al_2O_3	-	70	6:1	8	81.1	1st run 81.1% 2nd run 77.1% 3rd run 51.3%	[20]
KOH/Al_2O_3 KOH/NaY	25	60	15:1	3	91	51.3% of K was leached	[35]
KNO_3/Al_2O_3	-	60	65:1	10	94.7	45 wt. % was leached	[37]
KF/Al_2O_3	15	65	15:1	3	97.7	1st run 99.7% 2nd run 61.2 3rd run 60.1	[39]
KNO_3/Al_2O_3	35	70	12:1	6	84	1st run 84% 2nd run 75% 3rd run 72%	[107]
KNO_3/Al_2O_3	35	65	15:1	6.5	87	Not report	[42]
KF/Al_2O_3 LiF/Al_2O_3 CsF/Al_2O_3	20	75	4:1	1.18	96	1st run 96% 4th run 94% 6th run 53%	[108]
K_2CO_3/Al_2O_3	8.7(K)	60	25:1	5.55	99	1st run 99% 2nd run 33% 3rd run 6.5%	[50]

2.5 Continuous production process

The currently production processes to produce fatty acid methyl esters form vegetable oils consume basic catalyst such as NaOH, KOH or $NaOCH_3$, $KOCH_3$, which forms un-recycle waste products. Heterogeneous catalysts are promising and advantages for biodiesel production in continuous processes, could give high quality of product. However, there have a few researches on biodiesel production with heterogeneous catalyst process. Nowadays, only one industrial for continuous production have been developed by the French Institute of Petroleum (IFP) [14, 15] uses heterogeneous base catalysts for the methanolysis of vegetable oils to produce biodiesel. The IFP has announced the construction of more similar industrial plants in Europe based on the use of a heterogeneous catalyst consisted of a mixed oxide of zinc and aluminum with a spinel structure.

G. Hillion et al. [109] studied a new continuous process, where the transesterification reaction is promoted by a completely heterogeneous catalyst. These catalysts consist of a mixed oxide of zinc and aluminum which promotes the transesterification reaction without catalyst loss. The reaction is performed at high temperature than homogeneous catalyst processes. The catalyst section includes two fixed bed reactors that are fed by oil and methanol. In this heterogeneous process, the catalyst is very stable with no metal leaching. There is no formation of either glycerates salts or metal soaps which affords the following advantages: no neutralization step is required, there is no introduction of water, and there is no salt formation; this account for exceptional glycerol purity. In addition, there is no waste production. The purity of methyl esters exceeds 99% with yields close to 100% of the theoretical. The glycerol produced is neutral.

Bournary et al. [110] invented a new commercial continuous biodiesel production process, where a solid catalyst consist of zinc oxide and alumina was used as a results showed that the process does not required post treatment to remove the catalyst from biodiesel and methyl esters yields, close to theoretical value, were achieved at high pressure and temperature. Moreover, glycerol obtained through this process had purity approximately 98%.

Robert S. et al. [14, 15] studied the production of linear monocarboxylic acid esters with 6-26 carbon vegetable oils or animal oils, in the presence of a catalyst that is selected from among zinc oxide, mixture of zinc oxide and aluminum oxide, and zinc aluminates. The summary of the invention by using zinc oxide which corresponds to the formula $ZnAl_2O_4$, xZnO, yAl_2O_3 as catalyst, either continuously or discontinuously. All these catalysts are in many form of a powder, of balls, extrudates, or pellets. In a continuous process in a fixed bed reactor, it is work at temperatures of 210–250 °C, at pressure 30-50 bar, VVH between 0.3 and 3 and the alcohol to oil weight ratio 2/1 to 0.1/1.

2.6 Kinetics of transesterification

Many researches have been reported about transesterification of various vegetable oil and alcohol. Freedman et al. [111] earliest studied the kinetics of the acid- and base-catalyzed transesterification of soybean oil with 1-butanol, and methanol at the molar ratio of alcohol to oil 30:1 and 6:1. Noureddi and Zhu [112] studied kinetics of base-catalyzed transesterification of soybean oil with methanol at

6:1 molar ratio of alcohol to oil. Significantly, they found that a pseudo-first-order kinetics provides a satisfactory mechanism with experimental results at large molar excess of alcohol and second-order kinetics provided a satisfactory mechanism with experimental results at 6:1 molar ratio of alcohol to oil. The reported both catalytic and non-catalytic of transesterification. Many researchers have been reported for the kinetic of the transesterification reaction using solid catalyst. The mechanism is related to the reaction as elementary step from triglyceride to diglyceride without intermediate step.

Zanette et al. [31] performed a kinetic study by used a semi-empirical model was built to represent the experimental data. This work investigates the production of FAME from jatropha curcas oil using the variety of heterogeneous catalyst resins, zeolites, clays, hydrotalcites, aluninas and niobium oxide. In an attempt to represent the experimental kinetic data, a semi-empirical model based on balance equations adopted. Modeling was then carried out by the estimation of rate constants for some possible reactions. The overall transesterification reaction is given by Equation 2.9

$$\mathrm{TG+3MeOH} \leftrightarrow \mathrm{3FAME + GLY} \qquad (2.9)$$

The overall reaction is assumed to occur in three consecutive steps: in the first step (2.10), the transfer of fatty acid (FA) from triglycerides (TG) to methanol (MeOH) gives diglycerides (DG) and fatty acid ethyl esters (FAME). In the second step (2.11), monoglycerides (MG) and FAME are formed by transfer of a FA from DG to methanol. Finally, in the third step (2.12), FAME and glycerol (GLY) are formed by transfer of a FA to methanol.

$$\mathrm{TG + MeOH} \overset{\mathrm{k1,k2}}{\Longleftrightarrow} \mathrm{DG + FAME} \qquad (2.10)$$

$$\text{DG + MeOH} \overset{\text{k3,k4}}{\Longleftrightarrow} \text{MG + FAME} \quad (2.11)$$

$$\text{MG + MeOH} \overset{\text{k5,k6}}{\Longleftrightarrow} \text{FAME + GLY} \quad (2.12)$$

Assuming that Equation 2.10 to 2.12 are reversible, parameter $k_{1\text{-}6}$ represents the rate constants for each step. In addition, it was assumed that the available acyl groups are randomly distributed amoung the TG, DG and MG. The reaction step described in Equation 2.10–2.12 and the following set of equations can be written:

$$\frac{1}{m_{CAT}}\frac{dC_{TC}}{dt} = -r_1 \quad (2.13)$$

$$\frac{1}{m_{CAT}}\frac{dC_{TG}}{dt} = r_1 - r_2 \quad (2.14)$$

$$\frac{1}{m_{CAT}}\frac{d_{MG}}{dt} = r_2 - r_3 \quad (2.15)$$

$$\frac{1}{m_{CAT}}\frac{dC_{FAME}}{dt} = r_1 - r_2 - r_3 \quad (2.16)$$

$$\frac{1}{m_{CAT}}\frac{dC_{MetOH}}{dt} = -r_1 - r_2 - r_3 \quad (2.17)$$

Where

$$r_1 = k_1 C_{TG} C_{MetOH} - k_2 D_{DG} C_{FAME} \quad (2.18)$$

$$r_2 = k_3 C_{DG} C_{MetOH} - k_4 C_{MG} C_{FAME} \quad (2.19)$$

$$r_3 = k_5 C_{MG} C_{MetOH} - k_6 C_{FAME} C_{GLy} \quad (2.20)$$

Which m_{CAT} represents the mass of catalyst used.

Guan et al. [27] used K_3PO_4 as a solid catalyst and the derivative of kinetic model is introducing heterogeneous reaction mechanism step are described as below.

a. Mass transfer of methanol (A) from methanol phase to oil phase through methanol-oil interface.

b. Mass transfer of methanol from oil phase to catalyst surface

c. Mass transfer of triglyceride (B) from oil phase to catalyst surface

d. Chemical reaction of methanol and triglyceride at catalyst surface.

And the rate of each step express as:

$\mathrm{r_1 = k_L a_c (C_{Ab} - C_A)}$, from methanol phase to oil phase

$\mathrm{r_2 = k_{Ac} a_c (C_A - C_{As})}$, from oil phase to catalyst surface

$\mathrm{r_3 = k_{Bc} a_c (C_B - C_{Bs})}$, from oil phase to catalyst surface

$\mathrm{(-r_A) = (-r_B) = k_R C_{As} C_{Bs}}$, chemical reaction

If $\mathrm{r_1 = r_2 = r_3 = -r_A = -r_B}$, then the equation of overall rate in the batch reactor is shown in equation 2.21.

$$\mathrm{(-r_B) = -\frac{dC_A}{dt} = \frac{C_{Ab} C_B}{\frac{C_{Ab}}{k_{Bc} a_c} + \alpha C_B + \frac{1}{k_R}}}, \text{ With } \alpha = \frac{1}{\mathrm{k_L a_c}} + \frac{1}{\mathrm{k_{Ac} a_c}} \qquad (2.21)$$

More researchers studied for reaction mechanism of solid catalysts. Paolo D.F. et al. [25] examined the activity of Na_3PO_4 to produce methyl ester from rapeseed oil. The experimental data are interpreted by using a kinetic model showing that first order reaction with respect to glycerides concentration is adequate to describe the reaction. The literature data involves the active participation of methoxide ions. As a consequence, the efficiency of Na_3PO_4 as a catalyst should be related with the production rate of sodium methoxide. As indicate by the experimental data, a possible scheme involving the phosphate is as follows in Equation 2.22–2.24.

$$\mathrm{Na_3PO_4 + CH_3OH \longrightarrow Na_2HPO_4 + CH_3ONa} \qquad (2.22)$$

$$\mathrm{TG + CH_3ONa + H_2O \longrightarrow ME + CH3OH + NaOH + DG} \qquad (2.23)$$

$$\mathrm{NaOH + Na_2HPO_4 \longrightarrow Na_3PO_4 + H_2O} \qquad (2.24)$$

Where, the step 2 (2.23) represents the transesterification reaction. This equation show Na_3PO_4 collected at the end of the reaction is still active if reused in other transesterification reaction.

Dossin et al. [113] studied transesterification of ethyl acetate with methanol over magnesium oxide. A kinetic model was developed base on a three step 'Eley-Redial' type of mechanism applied in liquid phase, describing the experimental data over the investigated range of experimental conditions. Transesterification reaction occurs between methanol adsorbed on a MgO free basic site and ethyl acetate from the liquid phase. Methanol adsorption assumed to be rate-determining. Table 2.10 summarized of the kinetic study in previous work.

Table 2. 10 Kinetic study in previous work with catalyst and non-catalytic reaction

Oil	Alcohol	Molar ratio	Kinetic Model	Ref.
Palm	Methanol	6:1	2nd order	[114]
Soybean	Methanol	6:1	2nd order	[112]
Soybean	1-butanol	30:1	1st order	[111]
	Methanol	6:1	2nd order	
Palm	Methanol	6:1	Pseudo 2nd order	[115]
Ethyl acetate	Methanol	0.1:10	Eley-Ridel	[113]

CHAPTER III

EXPERIMENTAL

3.1 Materials and chemicals

3.1.1 Materials

The refined palm olein used in this research was purchased from the local market (Olean Brand) and industrial-grade methanol (purity: 99.84 wt.%), were used as the reactant in this work. Palm olein was analyzed for its physical properties and fatty acid compositions, before used as a raw material in this research.

3.1.2 Chemicals

- Tri-sodium phosphate do-decahydrate ($Na_3PO_4.12H_2O$) from Ajax Chemical used as a catalyst.

- ¼ Extrudates alumina (γ-Al_2O_3) from Alfa Aesar used as a supported catalyst (surface area of 166.33 m^2/g).

- Standard HCl 0.1 molar used for titration.

- Methyl orange used as an indicator.

- Phenolphthalein used as an indicator.

- Heptane (C_7H_{16}) purity 99.99 wt.% used as an analytical solvent.

- Methyl Decanoated ($C_9H_{19}CO_2CH_3$) with purity of 99.5 wt.% from Supelco used as an internal standard for gas chromatograph technique.

- Standard FAME mixed (RCO_2CH_3, R= C8:0, C10:0, C12:0, C14:0, C16:0, C18:0, C18:1, C18:2, C18:3, C20:0, C22:0, C22:1, C24:0) from Supelco with purity of 99.5 wt.% used as a standard to identify the peaks at different relations.

3.2 Methodology and apparatus

3.2.1 Transesterification reaction

The activity test of Na_3PO_4 catalyzed transesterification reaction of palm olein and methanol was performed in bath reactor. The experiments were conducted in a 2 litres stainless-steel autoclave equipped with a variable speed agitator (5–1500 rpm). The reactor could be heated while the temperature was controlled by a jacketed heating element. The reactor pressure was maintained at 800 psi with nitrogen gas. The catalyst was first put in a stainless steel basket that was placed in the middle of the reactor vessel. Palm olein was put into the reactor in predetermined amounts, and the feed bomb was filled with methanol. The system was then purged with nitrogen. Next, the reactor was heated to the desired temperature while the liquid was stirred at a constant speed. When the reactor reached the reaction temperature, methanol was fed into the reactor. Samples were taken at specific times, dipped into cold water to stop the reaction, and then separated in a centrifugal separator. The product was separated and purified with warm water. The samples were analyzed for FAME content using gas chromatography. A schematic diagram of the experimental set up is shown in Figure 3.1.

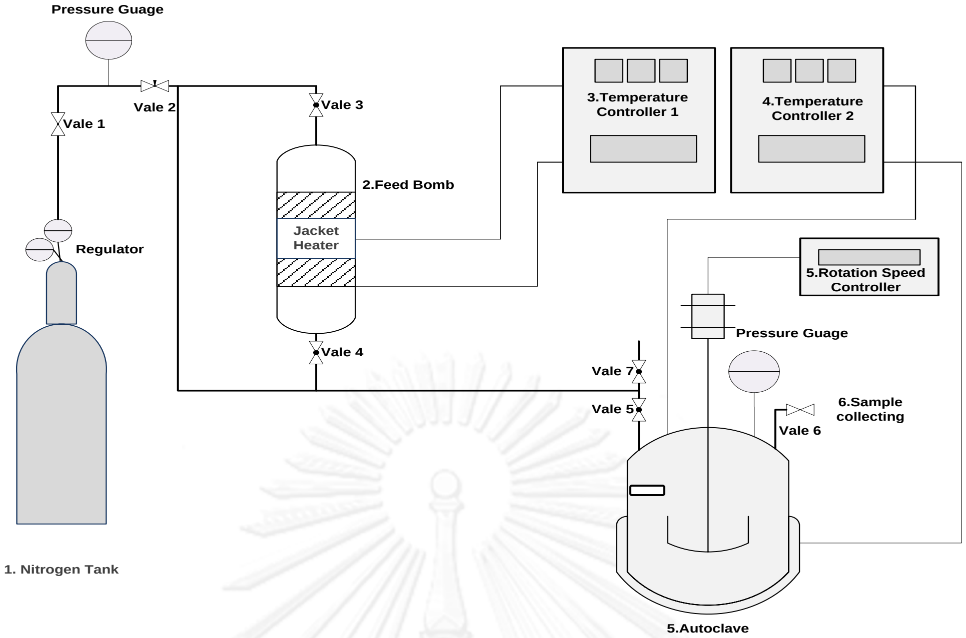


Figure 3. 1 Schematic diagram of the experimental setup for the transesterification process.

Effect of reaction variables on the methyl ester product were tested in bath reactor. The experimental operating condition of transesterification of palm olein and methanol is showed in Table 3.1.

Table 3. 1 The experimental operating conditions

Experimental Variables	Reactions Conditions
Catalysts	Na_3PO_4
Raw materials	Palm Olein, Methanol
Agitation Speed	100-1200 rpm
Methanol/oil molar ratio	1:3-1:30
Temperature	150 – 250°C
Catalyst amount	0–1 wt.%

3.3 Catalyst preparation

The catalysts used in this research were prepared prior to transesterification reaction. Two form of catalyst have tested in its activity on this work, the powdered form of Na_3PO_4 and the modified surface area of Na_3PO_4 by impregnated onto a big shape form of alumina supported catalyst.

3.3.1 The preparation of Na_3PO_4 in powdered form

Sodium phosphate used in this research is formulated of $Na_3PO_4.12H_2O$. This form is cheap price and stable, the most application as fertilizer in agricultural. Transesterification using $Na_3PO_4.12H_2O$ have been studied by S.T. Jiang et al. [26] and showed low of product yield caused from water in molecule is interfered with the reaction system. Prior to transesterification reaction, $Na_3PO_4.12H_2O$ was eliminated water from molecule. The catalyst was dried in oven at 110 °C for 24 hours, and then calcined in a muffle furnace at 500°C for 5 hours before the transesterification reaction.

3.3.2 The preparation of Na_3PO_4 on alumina

The Na_3PO_4 loaded on γ- Al_2O_3 catalyst is prepared by the incipient –wetness impregnation of aqueous solution on an alumina supports [38, 39, 116].The incipient –wetness impregnation utilizes a volume of water that is less than or equal to the amount required to fill the pores of the support material. On the basis of the characterized water absorbance of 1/4” γ-Al_2O_3 extrudates, the sample was first dried at 120 °C in oven and then placed into a 2-neck 1000 ml flask. Remove air and moisture under vacuum. Active metal precursor (Na_3PO_4) is dissolved in de-ionized water at the value of solubility of Na_3PO_4 in water (8.8 g./100 g water). The preparation procedure of Na_3PO_4/Al_2O_3 is showed in Figure 3.2.

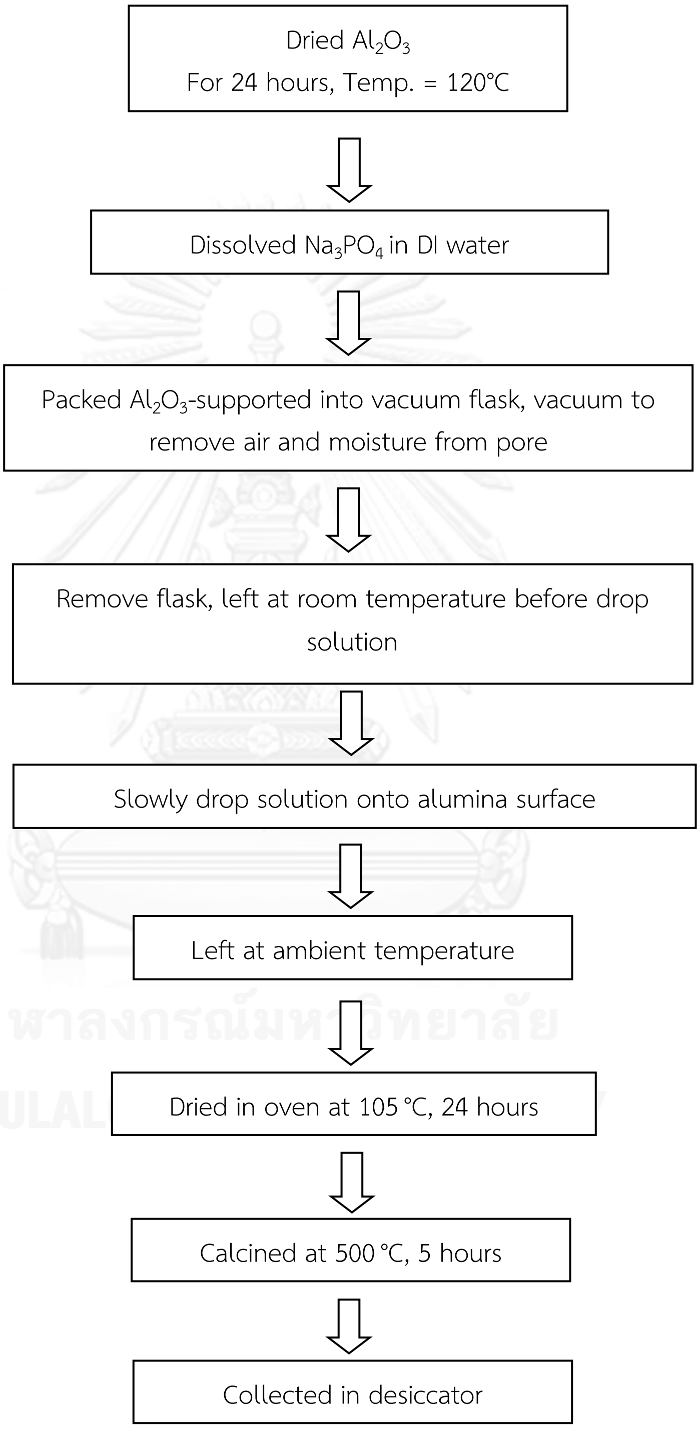


Figure 3. 2 The preparation procedure of Na_3PO_4/Al_2O_3 by incipient-wetness impregnation method.

Then the sodium phosphate containing solution is added to the catalyst support containing the same pore volume as the volume of the solution added. Slowly drop DI water on alumina surface until it can be observed some water out of pore. Excess water on top of the alumina was removed and weighed. Water absorbance of alumina was determined from the difference of weights of wet and dry alumina. The pore volume calculated from this work was 0.87 cm^3/g. of Al_2O_3. The preparation procedure of Na_3PO_4/Al_2O_3 is shown in Figure 3.2.

The Al_2O_3-support was first dried overnight in an oven, and then subjected to vacuum to remove air and moisture from the catalyst pores. Next, sodium phosphate solution was added slowly into the support. The impregnated catalyst was left overnight at room temperature, and then dried at 105 °C for 24 hours. Then, the catalyst was calcined at 500 °C for 5 hours in air. The prepared catalyst was further analyzed by ICP–OES and the actual loading of Na_3PO_4 on Al_2O_3 was calculated to be 6.5 wt.% of Na_3PO_4.

3.4 Analytical method

3.4.1 FAME content by gas chromatograph technique

The FAME products were analyzed by gas chromatography (Variance 3800). A polar capillary column (Agilent, HP-Innowax 20M) which had an internal diameter of 0.32 meter, a length of 30 meter and a film thickness of 0.25 μm, and a Flam Ionization Detector (FID), were used. Helium was used as the carrier gas at a pressure of 10 psig. The injector and detector temperature were set at 260°C and 230°C, respectively. The programmed temperature was set for an initial temperature of 80°C for 5 minutes, and then the rate was increased with the heating rate set at 20°C/min up to a final temperature of 230°C where it was held for 5 minutes. Methyl decanoate, which was used as an internal standard, was mixed with heptane to prepare a stock solution. After a sample was accurately weighted, an internal standard stock solution was added to the sample. The FAME content was defined as the ratio of the weight of FAME determined by the GC to the weight of oil used, as shown in Equation 3.1.

$$\text{Yield of FAME} = \frac{\sum \mathbf{Wt.of\ FAME\ (g)}}{\mathbf{Wt.\ of\ Palm\ Oil\ Used\ (g)}} \times 100\% \qquad (3.1)$$

The FAME content was calculated using the compensated normalization method with internal standardization. A standard FAME mix (C8-C24) from Supelco was used to identify the peaks at retention times and to correct the peak area using the response factors of the compound. Experimental and analytical errors were checked by repeating the process three times. The analytical error was less than 1.5% on average. The operating conditions to analysis methyl ester shows as below in Table 3.2 and Table 3.3.

3.4.2 Glycerin analysis by gas chromatograph technique

The operating conditions to analysis of acryl content of mono-glycerides, di-glycerides, free glycerine and triglycerides) shows in Table 3.3.

Table 3. 2 Operating condition of gas chromatograph to analysis FAME yield.

Variables	Condition
Column	Non-polar capillary (Carbowax)
Detector	Flam Ionization (FID)
Carrier gas	Helium
Flow rate of carrier gas	2 ml/min
Pressure of carrier gas	10 psig
Detector Temp	250 °C
Injector Temperature	230 °C
Initial Column Temperature	80 °C
Final Column Temperature	230 °C
Heating rate	20 °C/min

Table 3. 3 Operating condition of gas chromatograph to analysis mono-glycerides, di-glycerides, triglycerides (EN 14105).

Variables	Condition
Column	DB1 length 10 m , ID 0.32 mm, film thickness 0.1 um
Detector	Flam Ionization Detector (FID)
Carrier gas	Hydrogen
Pressure of carrier gas	80 kPa
Detector Temperature	380 °C
Initial Column Temperature	50 °C
Final Column Temperature	370 °C

3.4.3 BET surface area and adsorption isotherm

The BET surface areas and pore size distribution of the catalyst were measured by using the multipoint N_2 adsorption–desorption method BELSORP-max of BEL at liquid-nitrogen boiling point temperature at the PTT Research Center. All samples were de-gass at 120 °C for 12 hours under reduced pressure (< 1 torr) prior to the sorption measurements. The specific surface area (S_{BET}) of each sample was calculated using the Brunauer, Emett, Teller (BET) method.

3.4.4 Scanning electron microscope and energy dispersive spectrometry (SEM/EDS)

The catalyst distribution on alumina and the morphology of the prepared catalysts were observed by using Scanning Electron Microscope (SEM), JFM-7600F (JEOL). The element chemical analysis of the synthesized catalyst surfaces was carried out using the energy dispersion X-Ray Spectroscopy Model (EDS) At the PTT Research Center. An accelerating voltage of 20 kV was used for sample morphology determination and electron probe micro analyzer (EPMA) images of the catalyst were obtained on a Shimadzu EPMA–1720 with optical image magnifications of 40–400,000X.

3.4.5 Inductively Couple Plasma (ICP - OES)

This technique consists of a high-temperature plasma generated from ionized gas. The Inductively Coupled Plasma (ICP) is the analytical technique used for the detection of a trace amount of metals in the product samples. This research used ICP method to analysis the solubility of heterogeneous catalyst in oil phase. Sodium and phosphorus content of the prepared catalyst, the used catalyst and the leaching of catalyst into reaction product, were analyzed using Inductive Couple Plasma Perkin Elmer Optima 3000.

The prepared catalyst and the used catalyst were digested into solution before analysis by ICP. Each sample about 0.1 gram of catalyst were digested in a solution containing solution of 20 ml of HCl (conc.), 10 ml of HNO_3 (conc.), and 10 ml of H_2O. The sample mixture was heated until the color of Al_2O_3 support changed to white color. During the heating step, H_2O was added to the mixture to maintain the volume. Then, about 5 drops of HF were added into the mixture in order to digest the support to solution. Next, the heating step was repeated until the solution turned to clear. Then, the volume of solution was made up to 50 ml by adding de-ionized water. The concentration of sodium and phosphorus in the prepared solution was analyzed by ICP. The obtained concentration was converted to convenient wt.% of sodium per weight of Al_2O_3.

3.4.6 FT-IR Analysis

FT-IR Spectra of the samples were measured using the KBr pellet technique. Spectra were recorded on a Perkin Elmer Spectrum One. Spectra were recorded on a Shimadzu IR-Prestige-21 spectrometer with 4 cm^{-1} resolution. The scanning range was from 400 to 4600 cm^{-1} under the atmosphere conditions (5 mg of sample with 100 mg of KBr).

3.4.7 X-Ray Diffraction

The XRD measurement of the synthesized catalysts were performed on Bruker AXS D8 Discover using Cu-K_α radiation over a 2θ Bragg angle range of 5° to 75° with a step size of 0.02 degree/step of 0.5 sec/step. The Cu - K_α radiation from a Cu X-ray tube running at 40 kV/40 mA, was used in sample. The data were analyzed with DiffracPlus software, and phases were identified according to Power Diffraction Database (JCPDS, International Centre for Diffraction Data).

3.4.8 Thermal Gravimetric Analysis (TGA)

Thermalgravimetric is commonly used to determine mass loss due to decomposition, oxidation, or loss of volatiles (such as moisture). To analysis amount of Na_3PO_4 prepared on alumina support, the sample was carried out on an AETARAM SETSYS 16 TG/DTA/DSC apparatus operating under a flow of air at 10 K/min heating rate up to 800°C.

3.4.9 Particle size analyzer

The most important physical property of solid catalyst is particle size. The particle size distribution has a direct influence on catalyst properties. Measurement of particle size distribution of dried–Na_3PO_4 and calcined–Na_3PO_4 were analyzed by Mastersizer-S (Malvern). Range Lens: 300 RF mm He-Ne laser source Beam lenght λ: 633 nm. The dispersing medium was ethanol.

3.4.10 Base strength with Hammett titration method

The basic strength of the catalyst (H_) was determined following Hammett indicator method to qualitatively measure the base amount [17]. The Hammett indicators were used: neutral red (H_= 6.8), bromothymol blue (H_= 7.2), Phenolphthalein (H_= 9.3), 2, 4-dinitroaniline (H_= 15.0), 4-nitroaniline (H_= 18.4). Approximately 100 mg of the catalysts was shaken with Hammett indicator and methanol, then left to equilibrate until no further color changes were observed. The base strength of the catalyst was defined as being stronger than the Hammett indicator if it showed a color change, but weaker if it showed no color change. (As shown in Appendix B-3).

3.5 Glycerine purity

The glycerol product obtained from the reaction is continued to titrate in order to find glycerol purity. The determination of glycerol content is determine follow the BS 5711: Part 3c1979.

3.6 Catalyst deterioration

The main problem of heterogeneous catalyst is the dissolution of active component into the reaction mixture. The deterioration of the catalyst have caused by several factors such as the dissolving of the catalyst in polar substances, methanol, water and free fatty acid. The leaching of active components from Al_2O_3-supported catalyst into product after the reaction effect on the efficiency of the catalyst reuse and it also affects the quality of the final FAME product. Hence, the catalyst dissolves in methanol, the leaching of catalyst under reaction condition and the catalyst reuse, were studied in this work.

3.6.1 Catalyst dissolves in methanol

The catalyst leaching in methanol was studied by contact the amount of pure Na_3PO_4 (calcined at 500 $^{\circ}$C for 5 hours) with methanol under reaction condition. After finish, the solid Na_3PO_4 was filtered with filter paper, and then dried in oven overnight. The solution of methanol was filled with filter paper, and then was titrated with standard HCl solution 0.1 M. Compared the amount of Na_3PO_4 collected from the experiment with the original weight of Na_3PO_4 before the reaction.

3.6.2 Catalyst leaching under reaction condition

The catalysts leaching to the reaction product were studied at the end of reaction. After the reaction finished, the liquid samples were collected and the determined catalyst content by Inductive Couple Adsorption (ICP) method. Both of Na, P leached from the prepared Na_3PO_4 on Al_2O_3-supported was compared with standard.

3.6.3 Catalyst reusability

The reusability of catalyst also study in this research. At the end of reaction, the spent catalyst was recovery by separated from reaction mixture. The catalyst was further used in subsequent runs without regeneration. Five consecutive reactions were performed using the same catalyst and reaction conditions. After finished the last recycle batch, the spent catalyst was washed with dehydrated methanol for 3 times in order to remove glycerine and impurities from catalyst. After treat, the catalyst dried in oven at 12°C for 24 hours, and then collected in the desiccator for use in the next experiment.

3.7 Errors checking

The errors checking in this work were separated by, the experimental error and the analytical error. The experimental checking is calculated by repeating the experimental for 3 times. The experimental were plotted in error bar as shown in equation 3.2.

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

$$\text{Range} = X_{max} - X_{min} \qquad (3.3)$$

The analytical error studied by repeating the sample pretreatment for 7 times, and analysis by injected to GC for 7 times. The analytical errors were calculated at 95% confidence error (2SD) was found to be less than 1.5% on average.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, the experimental results of transesterification reaction between palm olein and methanol using sodium phosphate as a heterogeneous catalyst were reported. Sodium phosphate used as a catalyst in this work was prepared in two forms;, powdered form, and prepared on alumina support. The prepared catalysts were characterized using XRD, FT-IR, TGA, SEM-EDX, BET, and ICP-OES. The catalytic activity test were conducted in a batch reactor in order to study the effect of various parameters on the formation of methyl ester product such as agitation speeds, methanol/oil molar ratio, reaction temperature, catalyst amount and impurities contenting in raw materials. The experimental results were reported with the use of sodium phosphate in powdered form, the use of sodium phosphate prepared on alumina support, and comparison of catalyst in two forms. The results and discussion were presented in this chapter.

4.1 Characterization of palm olein

Palm olein used as a raw material in this research was analyzed its physical properties and fatty acid composition. Acid value of palm olein was determined following the AOCS Official Method Cd-3a-63 procedure (Appendix A-2). Moisture content was calculated by Karl Fisher method. Sponification value and molecular weight of palm olein were calculated following the AOCS Recommended Cd-3a 94. The results are summarized in Table 4.1. Fatty acid composition of palm olein was analyzed by Gas Chromatograph technique (Appendix B). The results are showed in Table 4.2.

Table 4. 1 Physical properties of palm olein.

Properties	Value
Acid value (mg $_{KOH}$/g)	0.358
Moisture content (wt. %)	0.104
Sponification value (mg $_{KOH}$/g)	197.07
*Molecular weight (g/mol)	852.58

*The average molecular weight of palm olein in this work was calculated from the saponification value (S.V. =197.07) as 850.76 g/mole, according to AOCS Recommended Practice Cd -3a-94.

Table 4.2 showed that palm olein contains high concentration of palmitic acid and oleic acid. Compared with jatropa oil, soybean oil and palm kenel, there are difference in fatty acid composition. Jatropa oil shows high concentration of palmitoleic acid and oleic acid, while palm kernel shows of lauric acid is the predominant compound in palm kenel oil. The degree of unsaturated and saturated fatty acids in each type of oil effect directly when used as a fuel in car. High amount of saturated fatty acid increased in cetane number and oxidation stability value, but affect higher cloud point [2]. Fuel properties of products derived from the experiments were also analyzed.

Table 4. 2 Fatty acid composition of palm olein in this research compared with previous work.

Properties	Palm olein (This work)	Jatropa oil [24]	Soybean oil[117]	Palm kernel [118]
Caproic (C6:0)	-	-	-	0.24
Capryic (C8:0)	-	-	-	5.14
Capric (C10:0)	-	-	-	4.82
Lauric (12:0)	0.53	-	-	59.83
Myristic (C14:0)	1.04	15.0	-	14.92
Palmitic(C16:0)	38.67	4.80	12.3	5.38
Stearic (C18:0)	4.10	-	5.8	1.52
Arachidic (C20:0)	0.35	-	-	-
Behenic (C22:0)	0.80	-	-	-
Total saturated fatty acid (wt.%)	**45.49**	**19.8**	**18.1**	**91.85**
Palmitoleic (C16:1)	0.23	27.22	-	6.87
Oleic (C18:1)	42.90	32.48	-	1.28
Linoleic (C18:2)	10.92	3.41	26.5	-
Lionenic (C18:3)	0.24	0.78	49.9	-
Arachidic (C20:0)	-	-	5.9	-
Erucic (C22:1)	-	13.18	-	-
Lignoceric (C24:0)	-	0.48	-	-
Nervonic (24:1)	-	-	-	-
Total unsaturated fatty acid	**54.51**	**77.55**	**82.3**	**8.15**

4.2 Characterization of sodium phosphate

Sodium phosphate have a general formulated as $Na_3PO_4.12H_2O$, this form is very cheap and most available. However, previous work have reported that the transesterification reaction with catalyst in this formulate is showed low of product yield, caused from water in molecule of sodium phosphate interferes the reaction [26]. Hence, the catalyst has to calcine under suitable temperature prior to the transesterification reaction. Then, the catalyst was characterized using several techniques of the Thermogravimetric Analysis (TGA), Hammett indicator, X-ray diffraction (XRD), surface area with BET technique, scanning electron microscopy (SEM), and particle size analyzer.

4.2.1 Thermalgravimetric Analysis (TGA)

Prior to analyze its thermal properties, $Na_3PO_4.12H_2O$ was dried in oven at 110°C for 24 hours. The catalyst after dried was first analyzed by TGA technique in order to find the suitable temperature to dehydrate sodium phosphate molecule. The thermal behavior of the Na_3PO_4 sample is showed in Figure. 4.1.

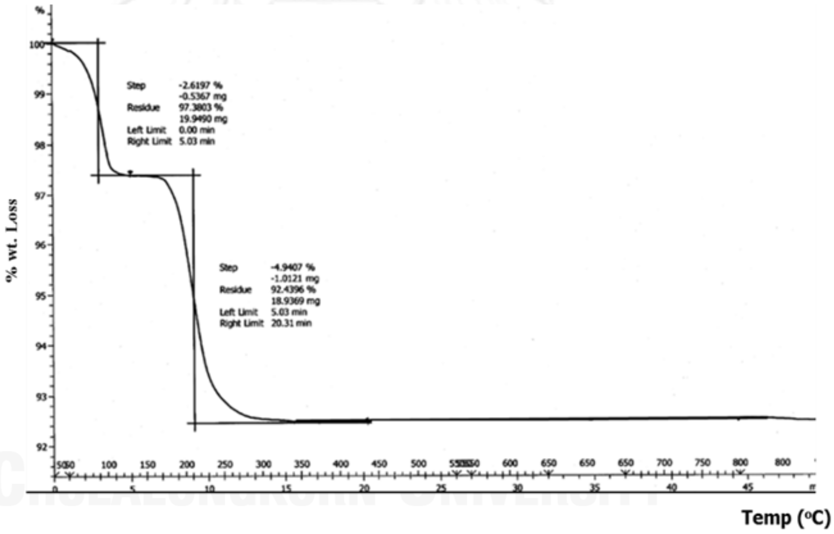


Figure 4. 1 Thermalgravimetric Analysis of Na_3PO_4

It can be seen in Figure 4.1, the results exhibited two main weight losses at identified that the weight loss of Na_3PO_4 occurs at the temperature range of 60-150°C and 150–450°C, significantly. The results showed that after temperature of 450°C, the weight of sodium phosphate is not changed. The total weight loss amounted to

7.55% and could be attributed to the elimination of carbon dioxide and water from the sample [103]. From the result of TGA, the catalyst was then calcined at 500°C before the transesterification reaction to dehydrate the catalyst.

4.2.2 FT-IR Analysis

To further study the structure of Na_3PO_4 before and after calcined, the samples were analyzed by FT-IR. The results are presented in Figure 4.2. The FT-IR spectra showed a very intense broad band at approximately 3456 cm^{-1}, that could be ascribed to the δ_{OH} stretching vibration of the hydroxyl groups due to the adsorbed water molecule and bending at 1635 cm^{-1} [119]. However, this position became weak after calcination due to the dehydration of water from sodium phosphate molecule. Besides, the minor absorption peak at about 1635 cm^{-1} may be assigned to the δ_{OH} bending vibration mode of H_2O molecules absorbed from air.

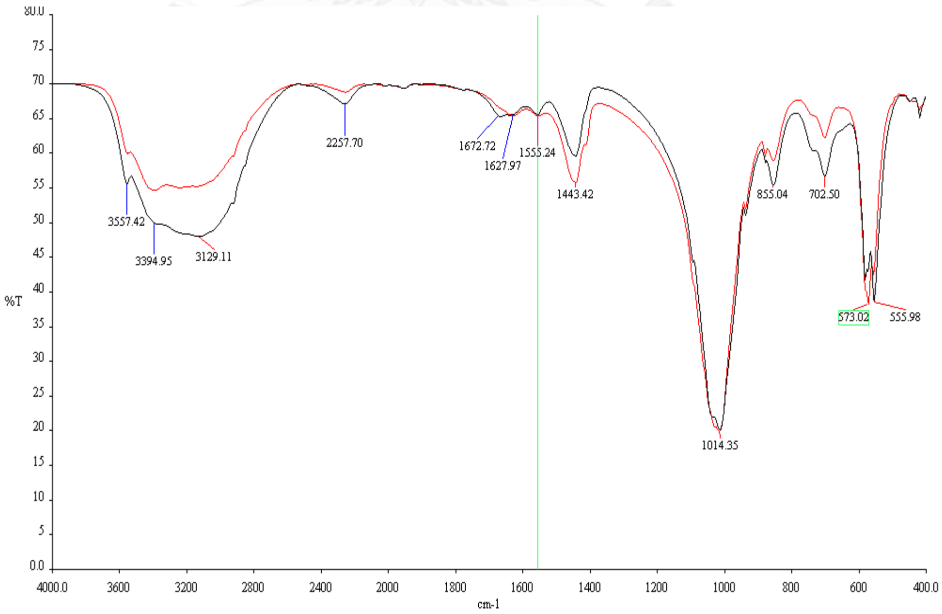


Figure 4. 2 FT-IR Spectra of dried-Na_3PO_4 (black line) and calcined-Na_3PO_4.

4.2.3 X - Ray Diffraction

The powdered form of catalysts, $Na_3PO_4.12H_2O$, dried-Na_3PO_4, and calcined - Na_3PO_4 were analyzed using XRD technique. The results are shown in Figure 4.3-4.8. Figure 4.3 showed the XRD patterns of $Na_3PO_4.12H_2O$, and Figure 4.4 showed structures identified of $Na_3PO_4.12H_2O$. It can be seen that the catalyst in this form showed only hexagonal structure.

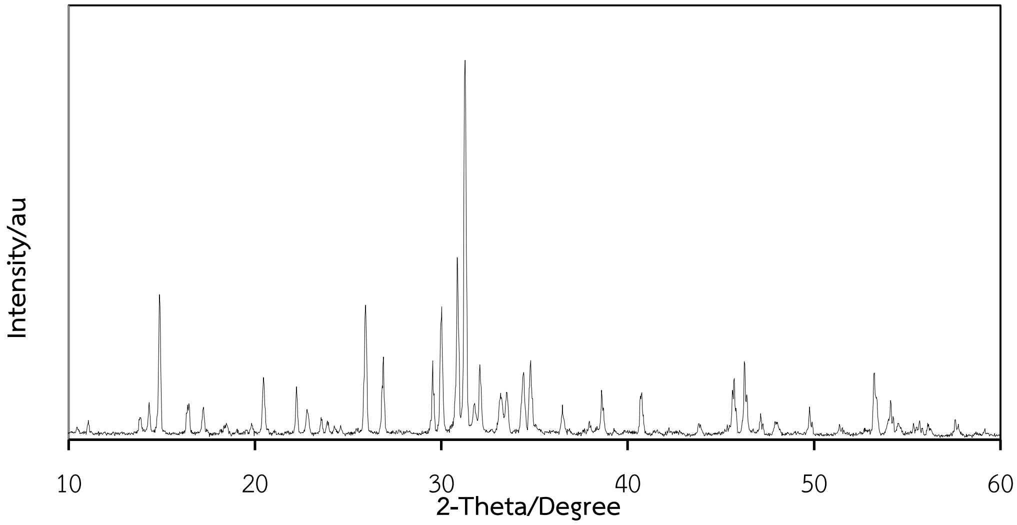


Figure 4. 3 XRD patterns of $Na_3PO_4.12H_2O$.

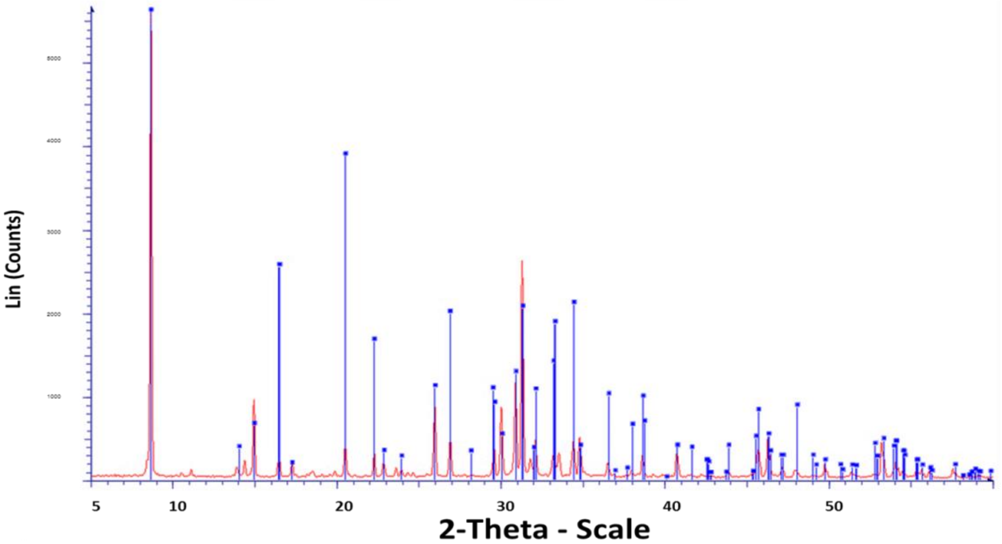


Figure 4. 4 XRD patterns of $Na_3PO_4.12\ H_2O$. (■) Hexagonal.

Figure 4.5 showed the XRD patterns of dried-Na_3PO_4, and Figure 4.6 showed the structure of dried-Na_3PO_4. This pattern can be identified that after dried in an oven for 24 hours, the pattern hexagonal of $Na_3PO_4.12H_2O$ is changed to monoclinic, and orthorhombic. The patterns of dried-Na_3PO_4 showed the most phase of monoclinic, and the orthorhombic is presented slightly.

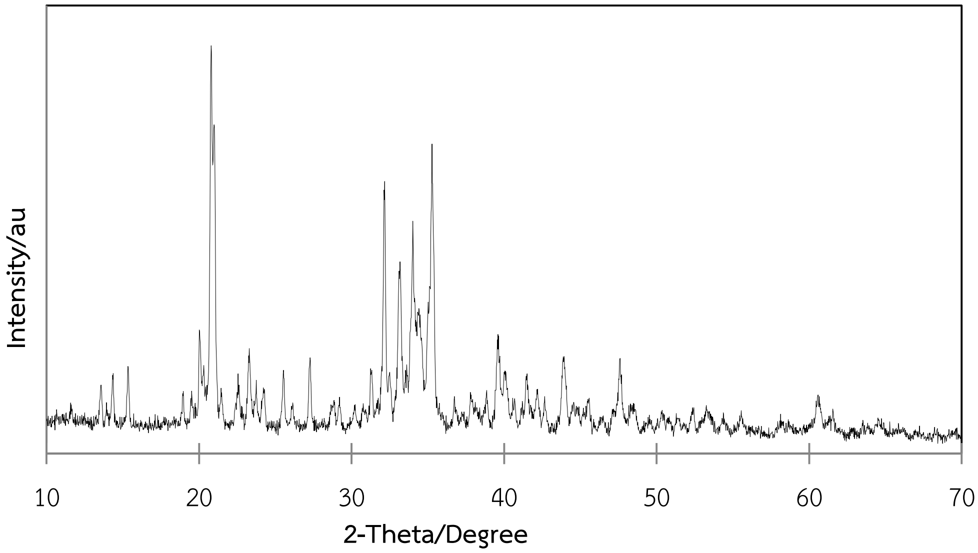


Figure 4. 5 XRD pattern of dried-Na_3PO_4.

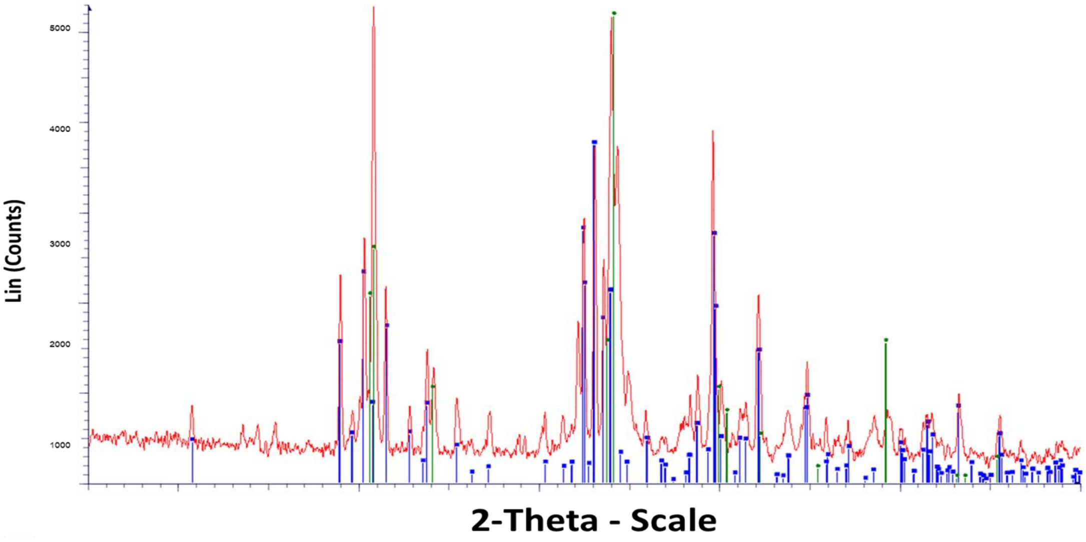


Figure 4. 6 XRD pattern of dried-Na_3PO_4. Monoclinic Na_3PO_4 (blue), Orthorhombic Na_3PO_4 (green).

Figure 4.7 showed the XRD patterns of calcined-Na_3PO_4 and Figure 4.8 showed phase identified of Na_3PO_4. This pattern can be identified that after calcined for 5 hours in an oven, the XRD patterns of Na_3PO_4 is presented the tetragonal, β-orthorhombic, and γ-orthorhombic.

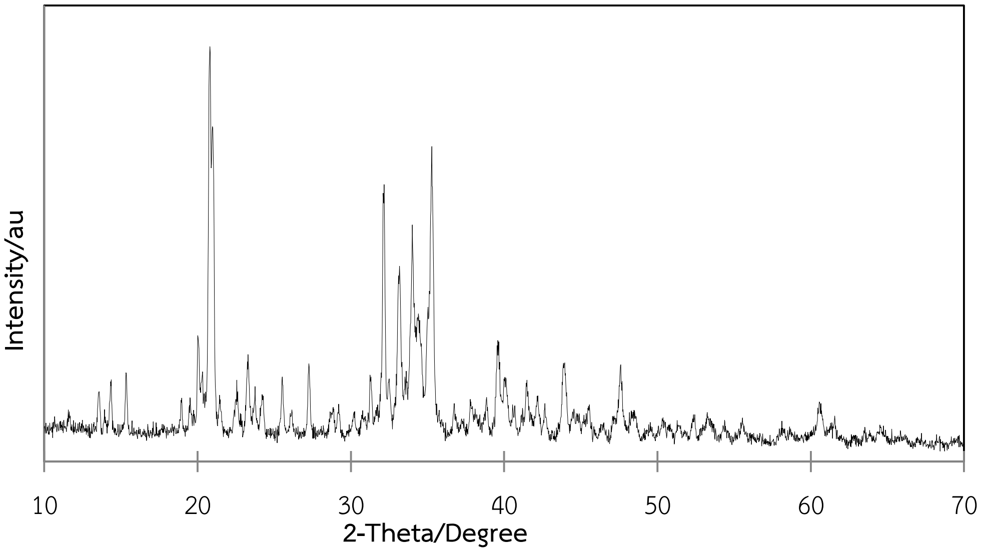


Figure 4. 7 XRD patterns of calcined-Na_3PO_4.

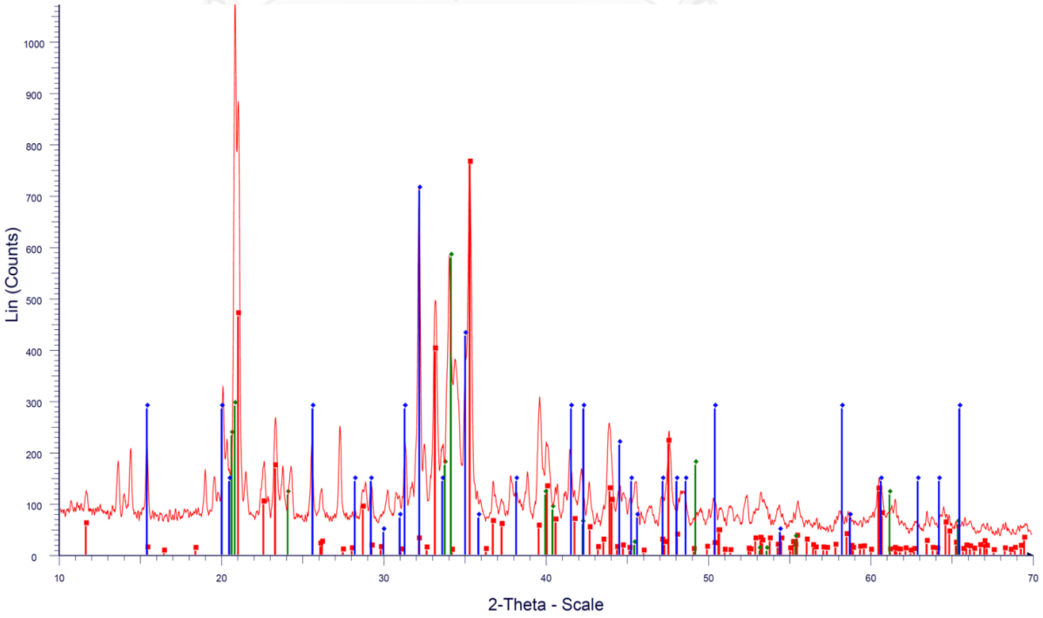


Figure 4. 8 XRD patterns of calcined–Na_3PO_4. Tetragonal Na_3PO_4 (red), Orthorhombic **β**-Na_3PO_4 (blue), Orthorhombic γ-Na_3PO_4 (green).

The orthorhombic phases have presented in dried-Na_3PO_4 is changed to tetragonal, and orthorhombic is changed to β-orthorhombic, and γ-orthorhombic, this phase is very intense.

4.2.4 BET surface area and basic strength

Dried-Na_3PO_4, and calcined-Na_3PO_4 were analyzed for their surface area and compared with the literature works. The basic strength (H_) of catalysts was determined using the Hammett indicator method (Appendix C). The both of dried -, and calcined Na_3PO_4 showed the basic strength in range of $15<H\_<18.4$. The basic strength and BET surface area are summarized in Table 4.3. However, it have been reported that the activity of solid catalysts is strongly dependent on their basicity not only for surface area [17, 120]. Although low surface of Na_3PO_4, but also showed high catalytic activity. The analysis of textural properties indicated that the calcined Na_3PO_4 at 500 °C had the BET surface area of 1.76 m^2/g. However, it was found that the BET surface area of dried-Na_3PO_4 showed very low of surface area and cannot detect using BET technique after repeated for 3 times.

Figure 4.9 shows the BET adsorption/desorption isotherm of calcined-Na_3PO_4. The result showed that no desorption line, it can be identified that Na_3PO_4 is a non-porous catalyst.

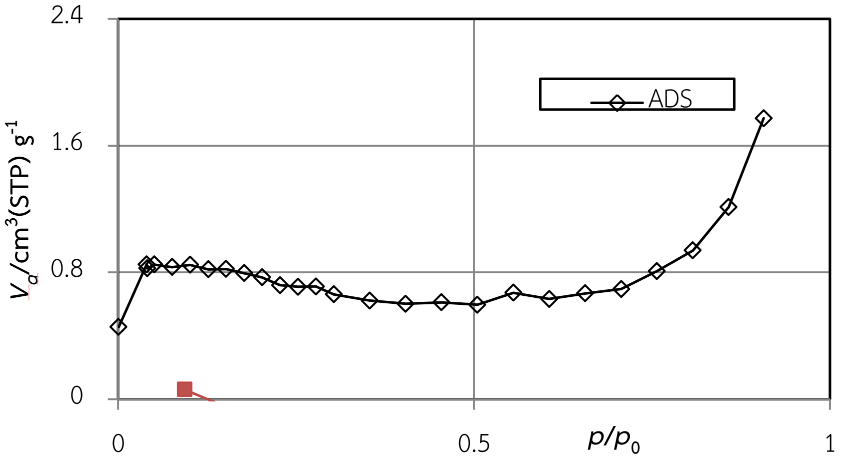


Figure 4. 9 Adsorption/desorption isotherm of calcined-Na_3PO_4

Table 4. 3 Comparison of basic strengths and surface area as determined by Hammett indicator and BET method of difference catalyst.

Catalyst	Basic strength (H_)	Surface area (m^2/g)	Ref.
Dried Na_3PO_4	15<H_<18.4	-	This research
Calcined Na_3PO_4	15<H_<18.4	1.76	This research
$VOPO_4$	-	2.4	[121]
ZrO2	H_<6.8	4.3	[17]
TiO2	6.8<H_<7.2	10.9	[17]
$NaAlO_2$	15<H_<18.4	-	[103]
SrO	15<H_<18.4	8.0	[17]
CaO	9.3<H_<15.0	2.8	[17]
ZnO	7.2<H_<9.3	1.4	[17]

Bancquart et al. [122] studied the other solid base catalysts such as MgO, ZnO, CeO_2 and La_2O_3. They confirmed that stronger basicity of the catalysts resulted in their higher activity for transesterification.

4.2.5 Particle size distribution (PSD)

The particle size distribution has advert influence on the catalyst properties. In this work, dried-, and calcined-Na_3PO_4 in powdered form, were determined its particle size distribution. The results showed in Figure 4.10-4.11, the catalyst size rather disperses in wide ranges of analysis from 250-350 µm. The calcined catalyst is a slightly smaller than dried-Na_3PO_4 and the curve of distribution became narrow after calcined.

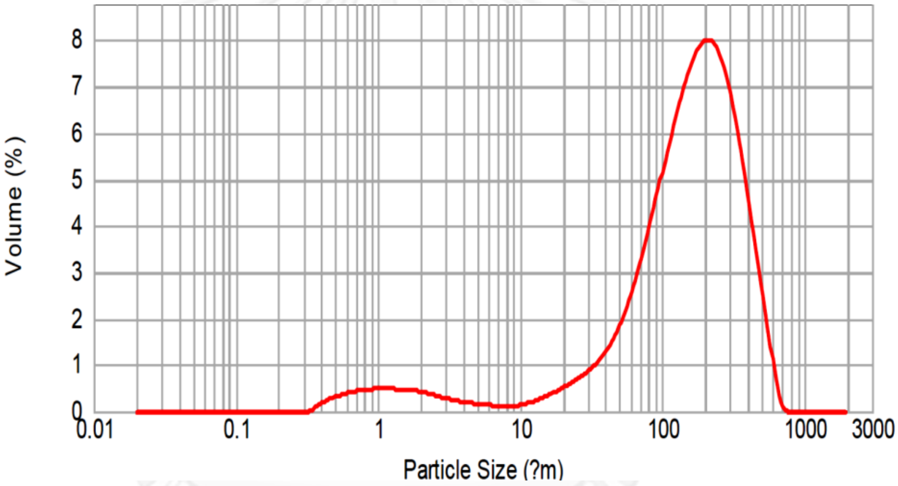


Figure 4. 10 Particle size distributions of the dried-Na_3PO_4.

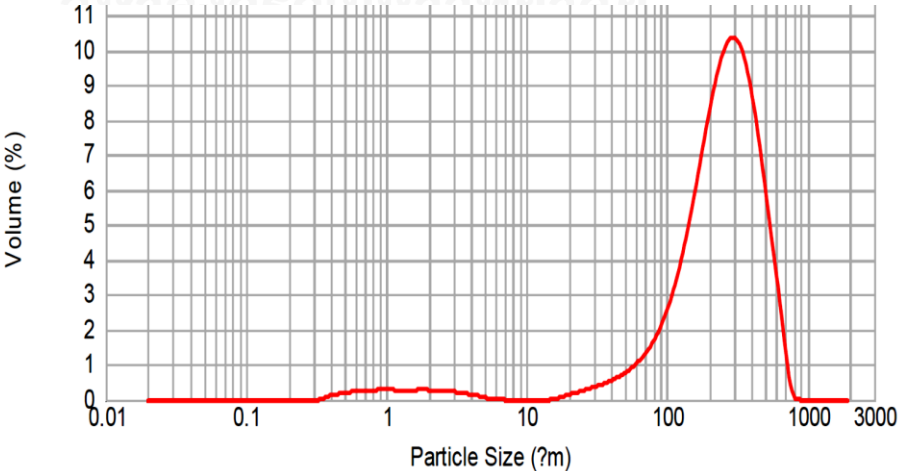
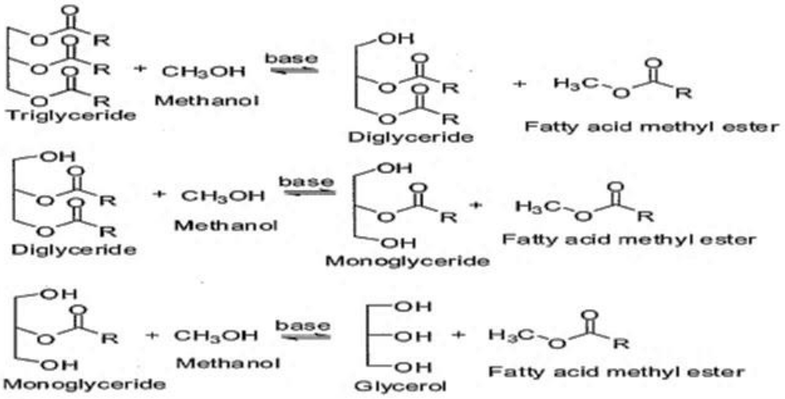


Figure 4. 11 Particle size distribution of the calcined-Na_3PO_4.

4.3 Transesterification using Na_3PO_4 as a heterogeneous catalyst

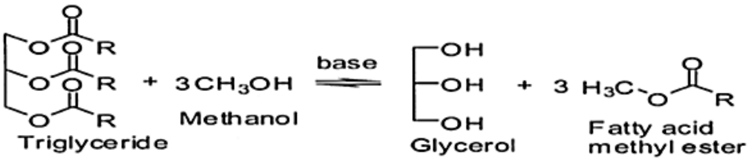
Transesterification reaction of triglycerides using Na_3PO_4 a heterogeneous catalyst have been studied at conventional temperature (65–80 °C) by Fillippes et al. [25] and S.T. Jiang et al. [26]. This reaction is reversible reaction and involves three steps that take place simultaneously. Diasakou et al. [123] proposed that triglycerides react with methanol to produce diglycerides, and then diglycerides react to produce monoglycerides. Finally, monoglycerides react with methanol to yield glycerin as a by-product. At each reaction step, one molecule of the methyl ester is produced for each molecule of methanol consumed. Transesterification involves three steps as shown in Scheme 4.1.



Scheme 4.1 Transesterification reaction involves three steps.

Product analysis in our work is analyzed by ignoring product intermedias (mono-, di-, and triglycerides). The reaction proceeds from triglyceride reaction with 3 moles of methanol, give 3 moles of methyl ester, and 1 mole of glycerine, the overall reaction is shown is Scheme 4.2.

FAME products were analyzed by gas chromatograph technique and compared with standard FAME mixed from Supelco to calculate FAME yield. The calculation of FAME by using response factors of the compound to correct theirs peak area and calculate amount of analysis. The calculation is shown in Appendix A and B.



Scheme 4.2 The overall reaction of transesterification of triglyceride and methanol.

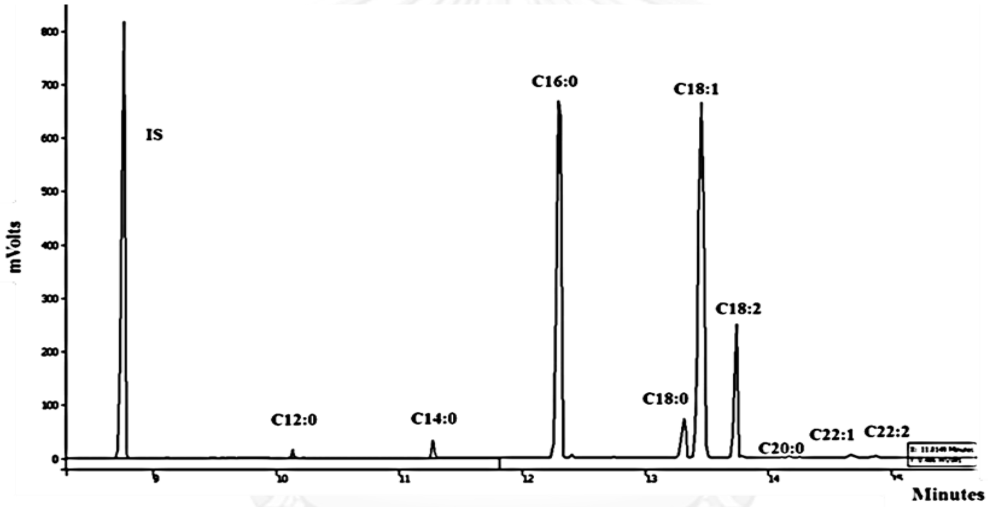


Figure 4. 12 Gas chromatogram of fatty acid methyl ester in a product sample.

The analytical results detected the reaction products, glycerine, the product intermediates (mono-, di-, and tri-glycerides), and FAME, as shown in Figure 4.12, and 4.13. Nevertheless, our research focused on the formation of FAME products only. The samples collected from the reaction appeared to be clean and transparent. Figure 4.12 shows a gas chromatogram of the FAMEs in the product sample, methyl laurate (C12:0), methyl myristate (14:0), methyl palmitate (16:0), methyl palmitoleate (C16:1), methyl stearate (18:0), methyl oleate (18:1), methyl linoleate (C18:2), methyl linolenate (C18:3), methyl arachidate (C20:0), methyl behenate (C22:0), and methyl erucate (C22:1), sequentially. The results show that the amount of product corresponds to the proportion of fatty acid content in the palm olein raw material, as can be seen in Table 4.2.

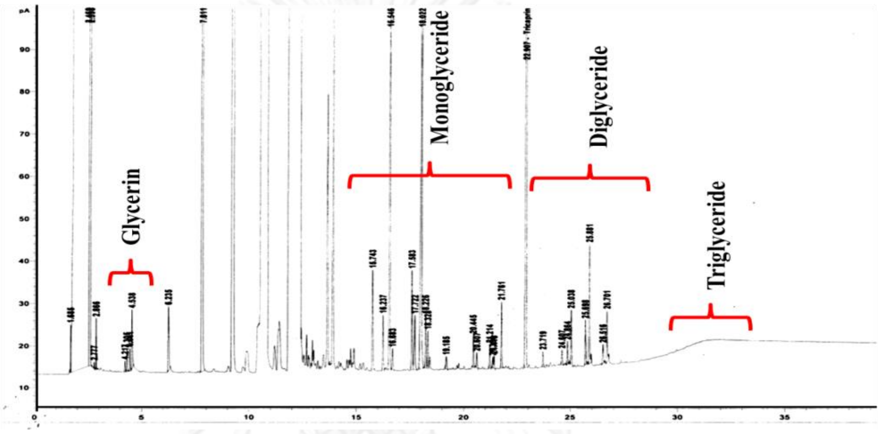


Figure 4. 13 Gas chromatogram of glycerol analysis in the product sample.

4.4 Errors Checking

The errors checking in this work were separated by, the experimental errors and the analytical error. The experimental errors are calculated by repeating the experiment for 3 times and then error bars were plotted (the experimental are shown in Appendix D). The analytical errors are studied by repeating the sample preparation for 7 times, and analysis by injected to GC for 7 times. Then, it can calculate the standard deviation value (SD) of the results was found less than 1.47 % (95 % confidence error).

4.5 Data interpreting

In this work, the effects of reaction parameters on the formation of FAME product were studied in period time from 0-240 minutes, before the system approach to equilibrium conversion. The samples were analyzed by Gas Chromatography method. The yield of FAME products was calculated according equation 4.1.

$$\text{Yield of FAME Products} = \frac{\text{Wt.of FAME (g)}}{\text{Wt.of Sample}} \text{ X } 100\% \qquad (4.1)$$

Then, the data collected from the experiment was taken to plot a graph showing the relationship between the percentages of FAME product (wt. %) on time of 0-240 minutes. The FAME products showed that the whole reaction in our experiment can be divided into three main stages: in the first stage, FAME yield increased greatly within around 60 minutes; in the second stage, FAME yield increased slowly over the next 60 minutes; in the third stage, the reaction almost achieved equilibrium yield and the FAME yield changed a little after 80 minutes. However, the time of each stage depended on the reaction condition. The amounts of FAME product on time were converted to un-methyl ester concentration (mon-, di-, tri-glycerides). Then, plot a graph to show the rate of reaction at the initial time of reaction from 0-60 minutes before the system approach to equilibrium stage. Since the initial stage of the reaction, the reaction products remain low. Hence, it can be assumed that the rate of reaction depends on the concentration of triglyceride only. To assume the simple mechanism for use in the calculation [Agra et al., Cotes and Wenze] [115], the assumption of reaction as shown by the following.

1. The FAME products were calculated at the initial time of reaction from 0-60 minutes.

2. The concentration of product has no effect on the reaction rate at initial stage.

3. Non-reversible reaction, hence, the reaction occurs forward only.

4. The concentration of methanol during the reaction is constant.

Thus, pesudo-1st order irreversible reaction was applied, the rate of reaction as shown below:

$$-r_{TG} = \frac{1}{3} r_{ME} = -\frac{dC_{TG}}{dt} = k' C_{TG} \quad (4.2)$$

$$k' = kC_{MeOH}, \ k = \text{ Rate constant} \quad (4.3)$$

$$-\ln \frac{C_{TG}}{C_{ME,O}} = k't \quad (4.4)$$

$$C_{TG} = C_{TG,0}(1 - X_{TG}) \quad (4.5)$$

$$X_{TG} = \frac{1}{3} X_{ME}, \ C_{ME} = C_{TG,o} X_{ME} \quad (4.6)$$

$$ln \frac{C_{TG,O}}{C_{TG}} = ln \frac{C_{TG,O}}{C_{TG,O} - \frac{C_{ME}}{3}} \quad (4.7)$$

From the relationship, plot of $ln \frac{C_{TG,O}}{C_{TG,O} - \frac{C_{ME}}{3}}$ versus time to calculate the rate constant.

4.6 Transesterification reaction using Na_3PO_4 as a catalyst

In this part, the powder form of Na_3PO_4 after calcined was tested its catalytic activity in the transesterification reaction. Effect of reaction variables on the formation of FAME product are studied in this research, the degree of mixing, methanol/oil molar ratio, reaction temperature, catalyst amount and effect of water and FFAs contents in raw materials, also study in the case of applied catalysis using sodium phosphate with low quality oil as raw materials.

4.6.1 Transesterification of Na_3PO_4 compared to NaOH

In order to study the transesterification reaction of palm olein and methanol catalyzed by Na_3PO_4, the experiment was compared its activity to NaOH conventional homogeneous catalysts, that were the most applied currently. The activity test was performed at the temperature of 65 °C, the amount of catalyst 0.5 wt. % of oil, and the agitation speed of 600 rpm. The results are shown in Figure 4.14.

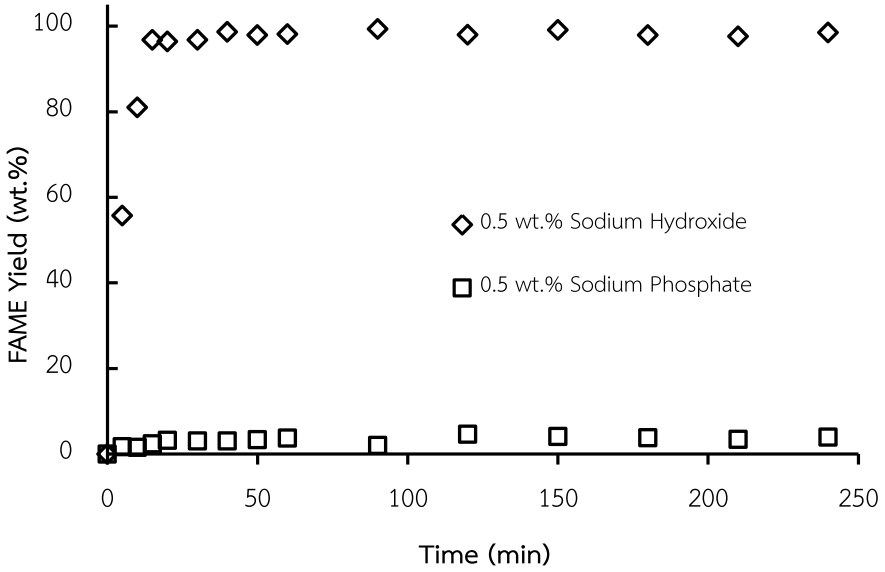


Figure 4. 14 Transesterification reaction using Na_3PO_4, compared to NaOH. Agitation speed: 600 rpm. Temperature: 65°C. Molar ratio of methanol/oil: 6:1. Amount of Na_3PO_4: 0.5 wt.%.

The experimental results show that NaOH showed very good catalytic activity in transesterification reaction of palm olein and methanol, the formation of product occurs rapidly within 15 minutes, whereas Na_3PO_4 showed a slightly of FAME products using the same amount of catalyst (0.5 wt.%). This is cause from NaOH homogeneous catalyst can be dissolved in the reactants and act as homogeneous pathway. When compare with Na_3PO_4, large of mass transfer resistance of 3 phases occurring (oil, methanol, catalyst), results in slow reaction rate. It can be seen that the system used Na_3PO_4 as a heterogeneous catalyst showed only 3 wt.% yield, while the system used NaOH as a homogeneous catalyst showed up to 96 wt.% of FAME product in a few minutes.

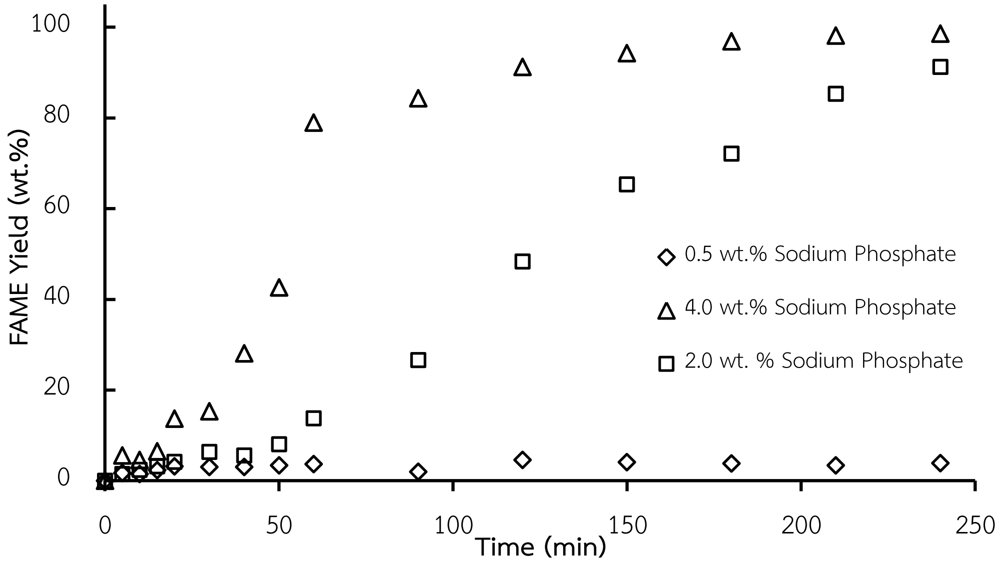


Figure 4. 15 Transesterification reaction using Na_3PO_4. Amount of catalyst: 0.5-4.0 wt.%. Agitation speed: 600 rpm. Temperature: 65°C. Molar ratio of methanol/oil: 6:1

However, the reaction rate of homogeneous system can be increased by 2 ways, increasing the reaction temperature and the amount of catalyst. The next experiment was by increasing the amount of Na_3PO_4 operated at 65°C. The results are shown in Figure 4.15. The results showed when increasing the amount of catalyst from 0.5 to 4 wt.%, high amount of FAME product is increased, dramatically. When increasing the amount of catalyst increases the amount of surface area in the reaction makes the reaction faster when the catalyst increased. Compare with the literature have been worked by S.T. Jiang [26] and Fillippes et al. [25], they had summarized the amount of 4 wt.% Na_3PO_4 is the suitable ratio to attain high product yield. They described that Na_3PO_4 are less active than NaOH due to the lower ability to form sodium methoxides.

In the next section, increasing of the reaction rate by increasing reaction temperature was studied and effect of reaction variables on the FAME products were investigated.

4.6.2 Effect of agitation speed

One of the main problems of heterogeneous catalyst associated with the formation of tree phases (oil, methanol, and heterogeneous catalyst). In order to reduce the phase barrier can be achieved by increasing the degree of mixing. In this part of our research, the agitation speeds were varied by adjusting the mixing control from 100-800 rpm. The experiments were studied at methanol/oil molar ratio of 6:1, reaction temperature of 190°C, and catalyst amount was fixed at value of 0.5 wt.% Na_3PO_4. The formation of FAME products versus time are shown in Figure 4.16, and the plot of un-methyl ester concentration (C_A) versus time are shown in Figure 4.17 (a). At the agitation speed of 100 rpm and 200 rpm, the reaction rate changed slowly due to the large term of mass transfer resistance. When continue increase the agitation speed from 200-400 rpm, the FAME products increase with the speed increased. However, when increase the agitation speeds higher than 400 rpm, the reaction rate changed insignificantly. In Figure 4.17 (a), plot of un-methyl ester concentration versus time shows correspondence trend to Figure 4.16. The concentrations of un-methyl ester are decreased when increasing agitation speeds from 100-400 rpm. Accordingly, the concentrations of un-methyl ester are not changed with increasing an agitation speeds higher than 400 rpm. Figure 4.17 (b), plot the rate of reaction at the initial time of reaction from 0-60 minutes. It can be seen that at the agitation speeds increase with increasing agitation and when the agitation speed higher than 400 rpm, the rate of reaction are identical. Therefore, agitation speed of 600 rpm was chosen to the next experiment in order to minimized mass transfer resistances.

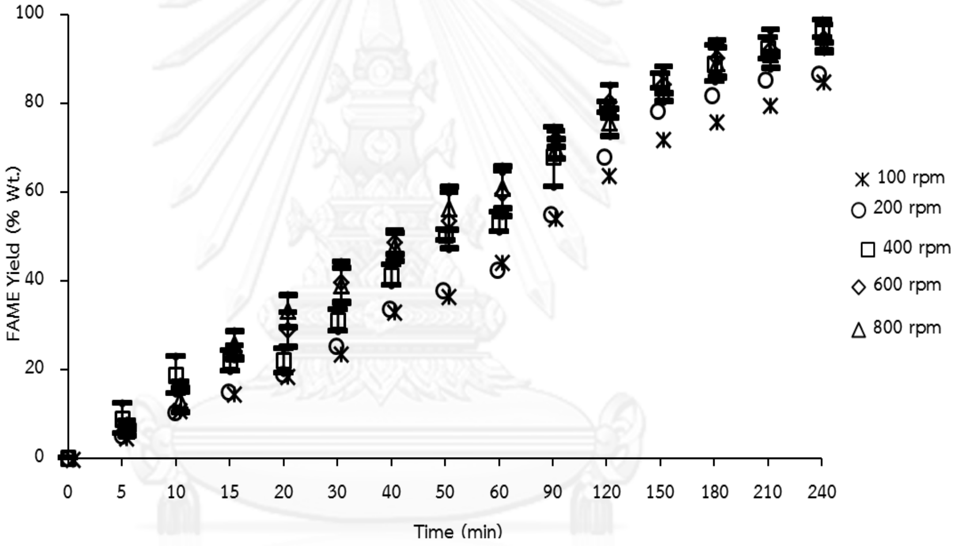
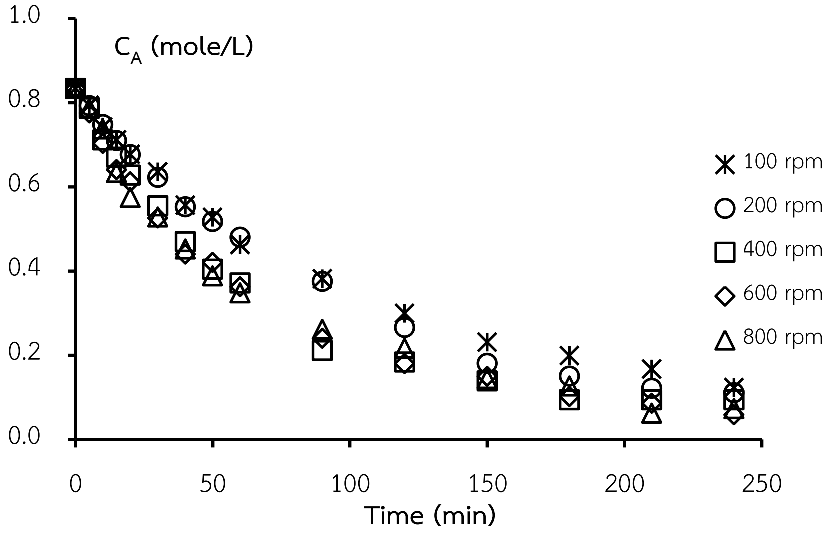


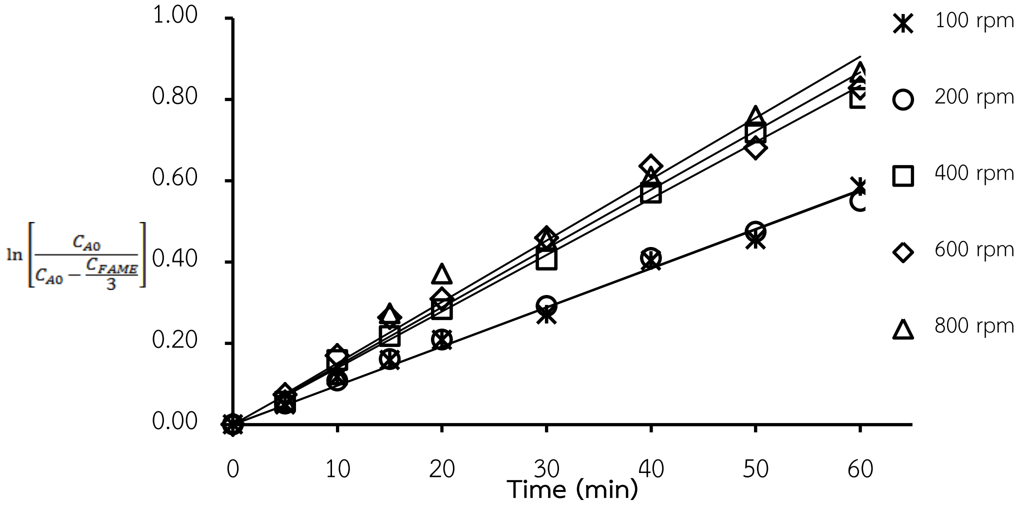
Figure 4. 16 Effect of agitation speeds on the FAME yield. Agitation speed: 100–800 rpm. Molar ratio of methanol to oil: 6:1. Reaction temperature: 190 °C. Amount of Na_3PO_4: 0.5 wt.%.

In the heterogeneous system, methanol, oil and catalyst are not soluble in each other, methanol lie on the top of oil without stirring. At the agitation speed of 100-200 rpm, the results showed slightly change in FAME contents versus time. This is cause from the large term of mass transfer resistance in the heterogeneous system.

However, increasing in agitation speed can be promoted the mass transfer of 3 phases, thus increasing the rate of reaction.



(a) Plot of un-methyl ester concentration versus time.



(b) Initial rate of reaction.

Figure 4. 17 Effect of agitation speed. Agitation speed: 100-800 rpm. Molar ratio of methanol/oil: 6:1. Temperature: 190°C. Amount of catalyst: 0.5 wt.% Na_3PO_4. (a) Un-methyl concentration (mono-, di-, tri-glycerides) versus time. (b) Initial rate of reaction from 0-60 minutes.

As faster agitation speeds as higher molecule collision frequency and more reaction are occurred, then the higher oil conversion achieved. Slower mixing speed needs longer time to reach equilibrium oil conversion. The speed must reach a certain value in order to minimize the term mass transfer resistance. In this work, we increase the speed of agitation until the mass transfer is not affect to the reaction anymore and the agitation speed of 600 rpm is enough to minimize the mass transfer resistance.

The effects of mixing speed have been reported by many researchers, however there were reported in different value from 400-800 rpm for the the heterogeneous system [25]. The study found that the speed does not affect much in higher temperature the reaction, as the reaction temperature is low. At low temperatures (50-80 °C), and without stirring, the reactants methanol and oil layers are separated by methanol is above the reaction prevented. However, it have been reported that high temperature the speed is less effective, because of the solubility of the alcohol in the oil is increased when the temperature rises [31]. Many researchers have been studied on effect of agitation speed and reported that the heterogeneous reaction operated at low temperature used the agitation speeds is around 300-600 rpm are enough to minimize mass transfer of 3 phases. In homogenous system, the agitation speed is not affect too much and the speed was around 300 rpm.

4.6.3 Effect of methanol/oil molar ratio

The molar ratio of alcohol/oil is one of the most important variable affecting transesterification reactions. The stoichiometric molar ratio of methanol/oil is theoretically 3:1. An excess stoichiometric amount shifts the reaction equilibrium to right hand side. In this research, investigation of the effect of molar ratio of methanol on FAME yield was conducted using the molar ratio from 3:1 to 30:1. The experiments were conducted at reaction temperature of 190°C with 0.5 wt.% Na_3PO_4. The formation of FAME products with different ratios of methanol as shown in Figure 4.18, the change of un-methyl ester concentration versus time is shown in Figure 4.19 (a), and plot of the rate of reaction with different molar ratio of methanol/oil at initial time from 0-60 minutes is shown in Figure 4.19 (b).

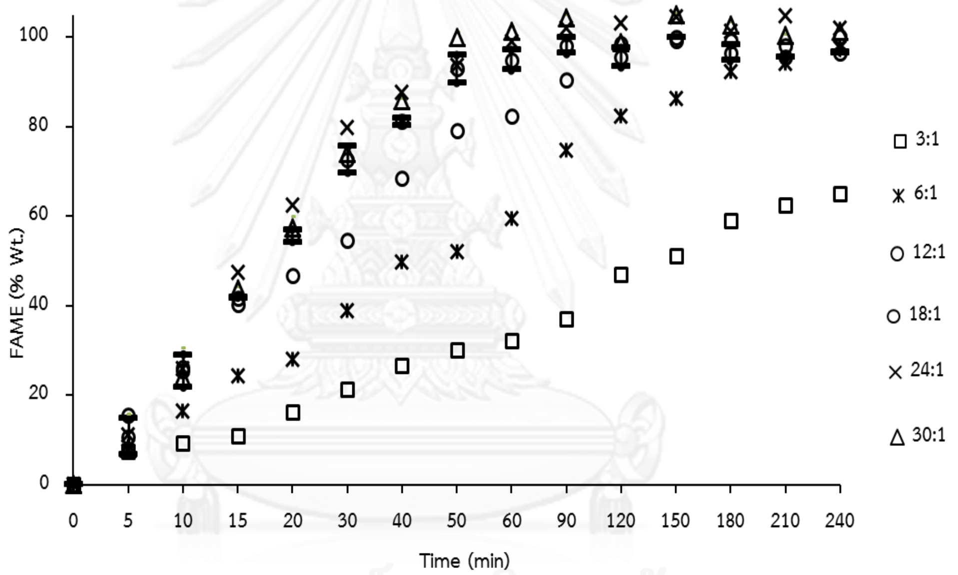
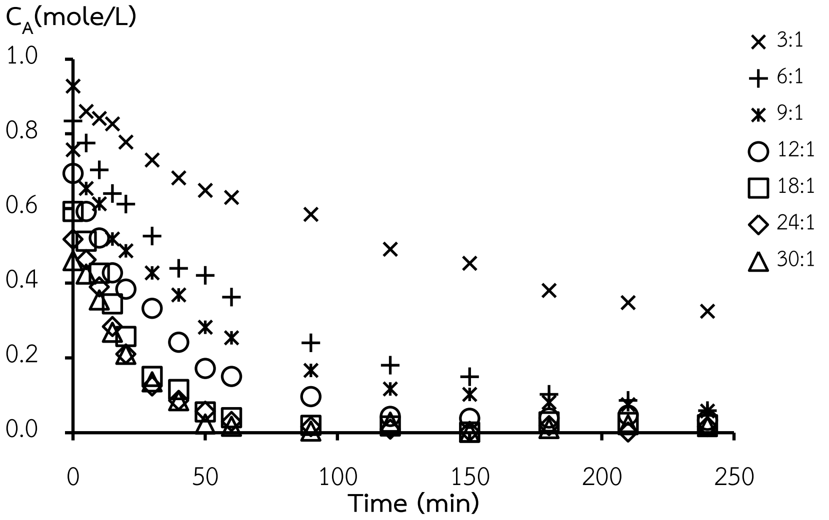
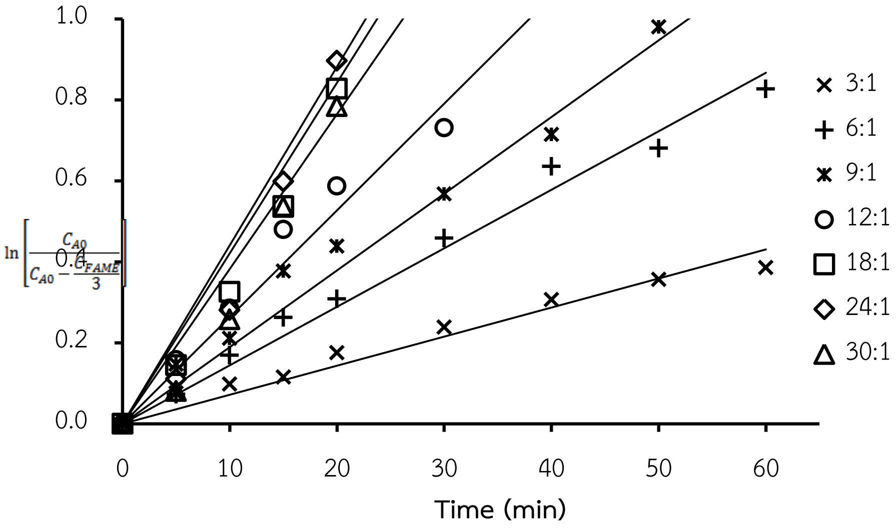


Figure 4. 18 Effect of molar ratio of methanol/oil. Agitation speed: 600 rpm. Methanol/oil molar ratio: 3:1–30:1. Temperature: 190°C. Amount of Na_3PO_4: 0.5 wt.%.

At the stoichiometric methanol/oil molar ratio of 3:1, the FAME products showed slowly increase as time and the reaction is achieved to equilibrium yield with only 60 % of FAME product. However, when double increase the molar ratio of methanol to oil, from 3:1 to 6:1, drastically improve the rate of reaction. It can be seen that the reaction proceeds rapidly with an increase in the molar ratio of methanol/oil from 3:1 to 18:1. Higher molar ratios drastically increased the FAME content over time.



(a) Plot of un-methyl ester concentration versus time.



(b) Initial rate of reaction.

Figure 4. 19 Effect of molar ratio of methanol/oil. Molar ratio of methanol/oil: 3:1-30:1. Agitation speed: 600 rpm. Temperature: 190°C. Amount of Na_3PO_4: 0.5 wt.%. (a) Un-methyl ester (mono-, di-, tri-glycerides) versus time. (b) Initial rate of reaction versus time from 0-60 minutes.

In the last stage, the transesterification reached a state of equilibrium, but the final yields of FAME are different which increasing from 66.2 to 98.3 wt.% of FAME depending on the molar ratio was used. Eventually, the reaction is limited by the solubility of oil in methanol phase. Under the study condition, at molar ratios higher than 18:1, the FAME contents are almost identical and further increases in methanol do not affect the reaction rate.

In Figure 4.19 (b), it is evidently showed while the molar ratio of methanol/oil was increased higher than 18:1, the rate of reaction does not change. This is limited by the dissolution of oil in methanol phase which increases when increasing the methanol amount into the system, results in the rate of reaction are improved with the amount of methanol. However, the rates of reaction are constant at the methanol amount from 18:1-30:1. The dissolution of oil in methanol is constant after the methanol higher than 18:1, at the specific temperature of 210 °C.

Transesterification is a chemical equilibrium reaction. An excess of methanol compared to oil is generally used to drive the reaction forward, thus producing higher yields of methyl esters. However, eventually the amount of methanol had no effect on the reaction rate [124] . One fact to consider is that methanol and oil are insoluble in each other at molar ratios higher than 3:1. In the case of a solid catalyst, the existence of 3 phases at the initiation of reaction is limits contact between the reactant and the catalyst. It can be concluded that the concentration of the alcohol has to balance between the rate of diffusion by the formation of two phases of fluid, and the shifting of the reaction towards product [23]. This research shows that 18:1 is the appropriate proportion for maximum yield. In contrast, while higher methanol/oil molar ratios is interfere with the separation of glycerol, methanol. Saka et al. have described that polar hydroxyl group can also work as an emulsifier at the same time [125]. Therefore, at molar ratio of methanol to oil 18:1 was chosen for the other experiments in our work.

4.6.4 Effect of reaction temperature

Reaction temperature strongly affects the reaction rate. To study the effect of reaction temperature, the experiments was performed at temperatures from 150 to 250 °C. The molar ratio of methanol to oil was fixed at a value of 18:1 with 0.5 wt.% Na_3PO_4.

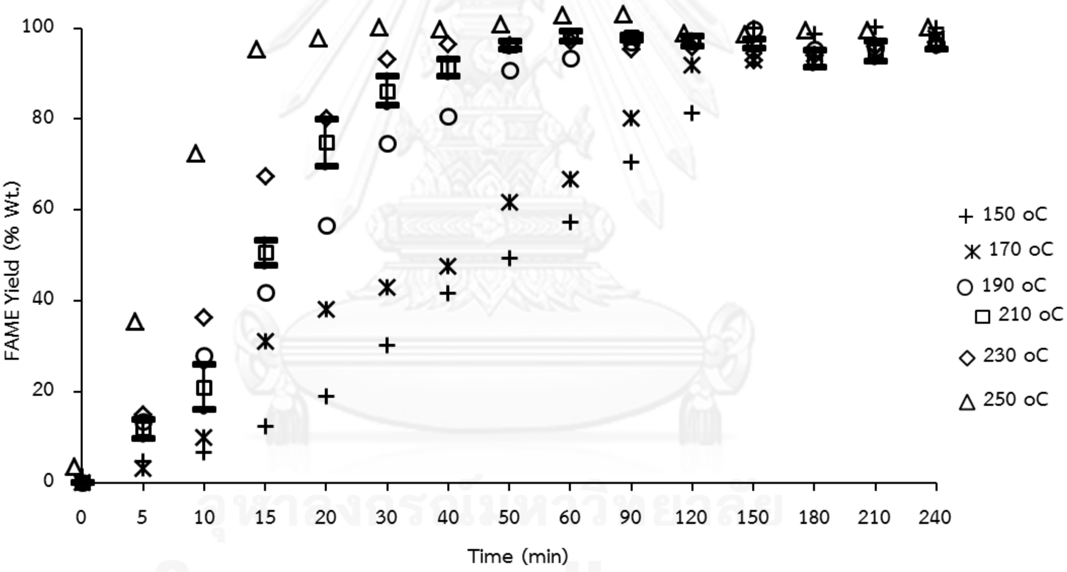
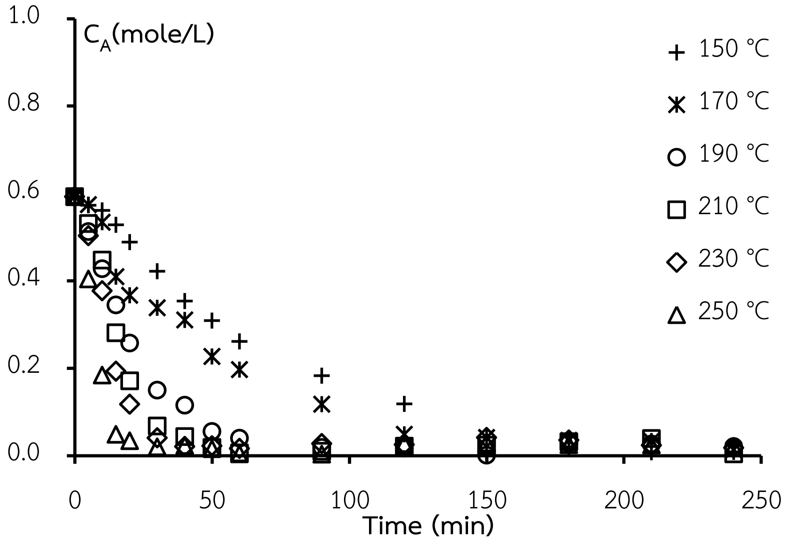


Figure 4. 20 Effect of reaction temperature on FAME yield. Agitation speed 600 rpm. Temperature: 150-210°C. Molar ratio of methanol/oil: 18:1. Amount of Na_3PO_4: 0.5 wt.%.

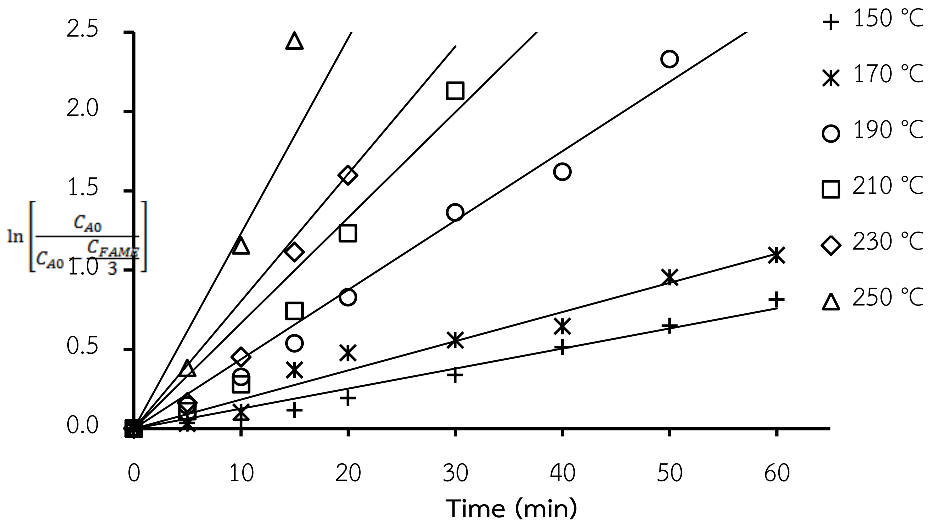
Figure 4.20 shows the formation of FAME products as a function of the reaction time. It was observed that the formation of product increased with increasing reaction temperature from 150-250 °C. Figure 4.21 (a), plot of un-methyl ester concentration versus time showed in accordance with results in Figure 4.20.

The concentrations of triglyceride are decreased on time when higher temperatures were applied to the reaction system.

Figure 4.21 (b) showed the rate of reaction at initial time from 0-60 minutes, it was evidently observed that reaction rate increased with increasing the reaction temperature. At the reaction temperature of 210°C, the FAME content reached equilibrium value within 30 minutes. At the reaction temperature of 250°C, the reaction proceeded very quickly, and complete conversion of oil was observed within 20 minutes period. However, it was observed that the glycerol product under these conditions exhibited a darker color than the samples obtained at lower temperature.



(a) Plot of un-methyl ester concentration versus time.



(b) Initial rate of reaction.

Figure 4. 21 Effect of reaction temperature. Agitation speed: 600 rpm. Molar ratio of methanol/oil: 18:1. Temperature: 150-250°C. Amount of Na_3PO_4: 0.5 wt.%. (a) Un-methyl ester (mono-, di-, tri-glycerides) versus time. (b) Initial rate of reaction: 0-60 minutes.

Transesterification reaction is an endothermic reaction, so increasing the reaction temperature favors higher product yields [10-11]. Saka and Kusdiana reported that at high temperature, non-polar triglycerides can dissolve well in methanol to form a single phase of methanol and oil, resulting in an increase in FAME content [126][9], methanol is a polar solvent and has hydrogen bonding between OH oxygen and OH hydrogen to form methanol clusters. As a result, non-polar triglyceride can be well dissolved with methanol at high temperature to form single phase of methanol and oil resulting in an increase of FAME content.

It have been reported that the effect of mass transfer limitation was minimized when oil and methanol were completely homogeneous [127]. High temperature will promote the reactants mix well, making the reaction was improved with increasing the reaction temperature. Besides, the rate of reaction is depended on the rate constant (k) as a function of temperature which increased with increasing the reaction temperature. To quantify the effects of reaction temperature on FAME content and calculate the activation energy of the transesterification reaction using Na_3PO_4, the experimental results were interpreted in terms of kinetics of converting palm olein to methyl esters. The results are shown in the next section (Determination of activation energy).

4.6.5 Effect of mass ratio of catalyst

The role of the catalyst is very important to promoting the rate of reaction. The effects of the mass ratios of the catalyst to oil were determined based on comparison with a non-catalytic reaction under the same conditions. Although the transesterification reaction can be occurred by itself at temperatures approximately 200°C, the reaction very slow, and the formation of desired esters is not selective due to incomplete alcoholysis of triglyceride derivatives [123, 128]. In this research, the effect of different amounts of catalyst varying from 0.0 to 1.0 wt.% Na_3PO_4 of oil, were examined. The molar ratio of methanol to oil was 18:1 with a reaction temperature of 210°C. The results are shown in Figure 4.22. It is clear that the transesterification reaction between palm olein and methanol must be a catalyzed reaction. Small amounts of FAME product were detected when there was no catalyst in the reactor.

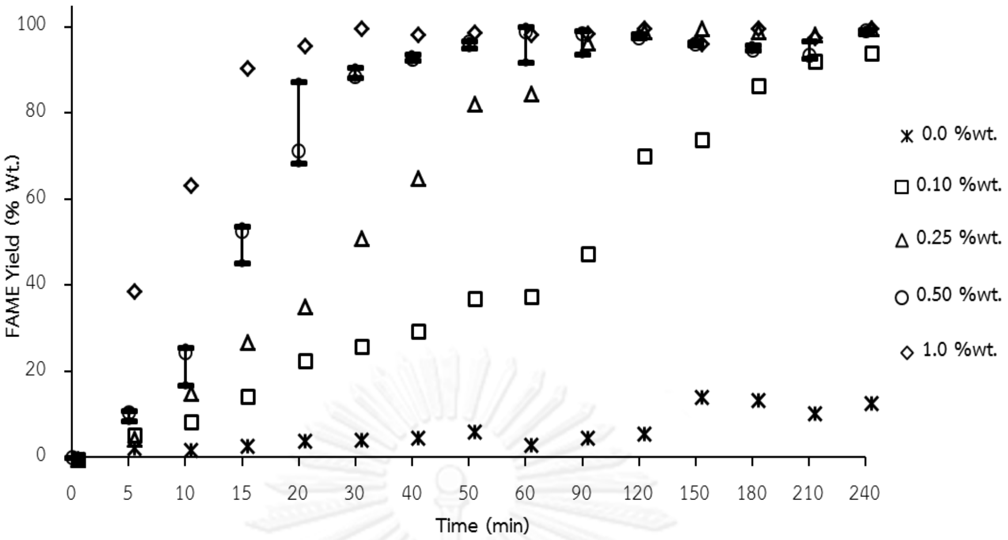
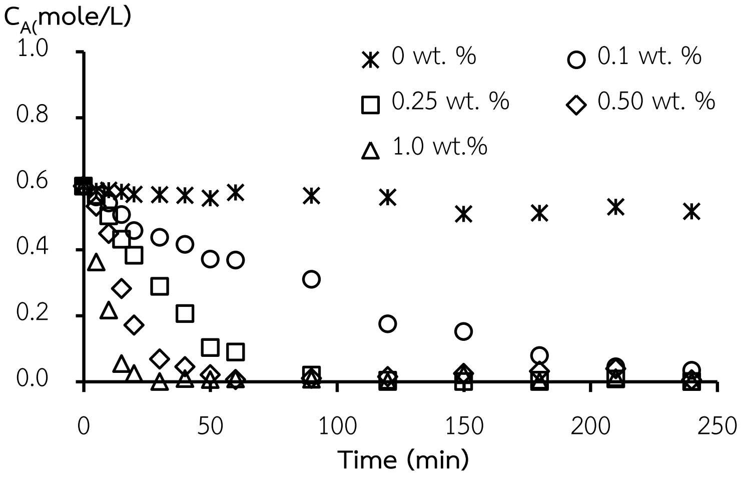
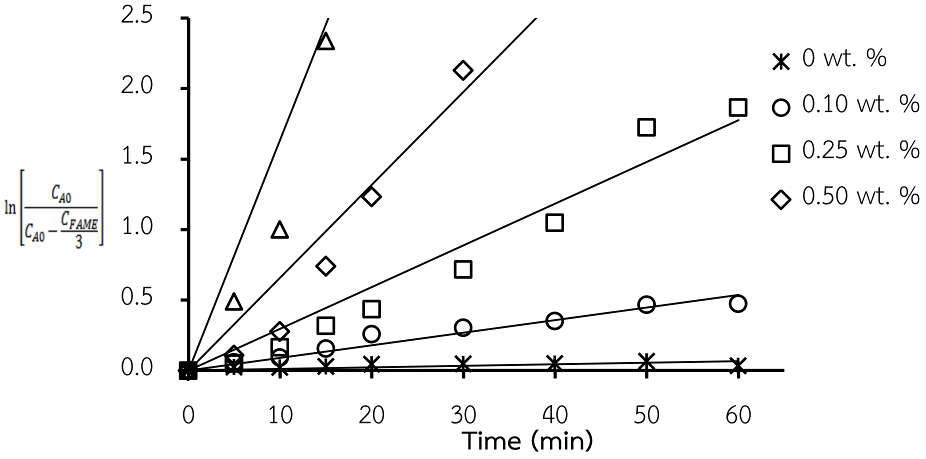


Figure 4. 22 Effect of mass ratio of catalyst/oil on FAME yield. Agitation speed: 600 rpm. Temperature: 210°C. Molar ratio of methanol/oil: 18:1. Amount of Na_3PO_4: 0.0-1.0 wt.%.

When only a small amount of Na_3PO_4 (0.1 wt.%) was added to the reactor, the FAME content was greatly increased, and the reaction rate increased with an increased in the amount of catalyst. Figure 4.23 (a) showed concentration of un-methyl ester versus time, this result showed that the concentration of triglyceride was almost constant when the catalyst not present in the reaction system. At the maximum amount of catalyst (1 wt.%) in the reactor, the oil was completely converted within 30 minutes. This study clearly showed that sodium phosphate can be used effective transesterification catalyst with only 1 wt.% of catalyst sufficient to accelerate the reaction. Catalysts work by reducing the activation energy of the reaction, so the presence of catalyst helps a reaction to reach equilibrium more quickly.



(a) Plot of un-methyl ester concentration versus time.



(b) Initial rate of reaction.

Figure 4. 23 Effect of mass ratio of catalyst/oil: 0-1.0 wt.% Na_3PO_4. Agitation speed: 600 rpm. Methanol/oil molar ratio: 18:1. Temperature: 210°C. (a) Un-methyl ester (mono-, di-, tri-glycerides) versus time. (b) Initial rate of reaction from 0-60 minutes.

Figure 4.23 (b) showed plot of the initial rate of reaction from 0–60 minutes, it evidently showed that the rate of reaction greatly increased with increasing the catalyst amount in the reactor. The result showed at 1 wt.% of Na_3PO_4 added into the reactor showed the highest reaction in a short time (20 minutes).

4.6.6 Effect of water contents in raw materials

In production system using conventional catalysts, the water and FFA content in the feedstock can significantly affect the system. The presence of both component cause soap formation and reduces catalyst effectiveness. Therefore, transesterification with an alkali catalyst is suitable for biodiesel derived from refined oil feedstock. To ensure that high percentage of product is obtained, the amount of water and FFAs in the oil must not exceed 0.06 wt.% and 0.5 wt.%, respectively [124]. Usually, the cost of biodiesel production is dependent on the cost of the raw materials and the cost of processing [129]. The processing cost can be reduced by using a heterogeneous catalyst that can be recycled and eliminating the water treatment step. The use of low-cost feedstock such as waste oil or non-edible type oil can reduce the cost of biodiesel production. However, waste oil contains as much as 6 wt.% water and 10 wt.% free fatty acids [130].

The effects of water and free fatty acid content in oil can be studied by applying Na_3PO_4 as a catalyst to low-quality oil. The effect of water contents in oil was carried out with different amount of water equivalent to 0–10 wt.% of methanol were added to the methanol. The experiments were fixed at a molar ratio of methanol to oil of 18:1, a reaction temperature of 210°C, and 1 wt.% Na_3PO_4. The results of the formation of FAME product versus time at different amount of water contents are shown in Figure 4.24. The results are compared with an experiment where water was not present. It can be seen that FAME contents decrease with time as the amount of water increases. There was a slower rate of reaction when the system had increased amounts of water. However, all experiments are still attained high equilibrium conversion as in the experiment without addition water within 90 minutes.

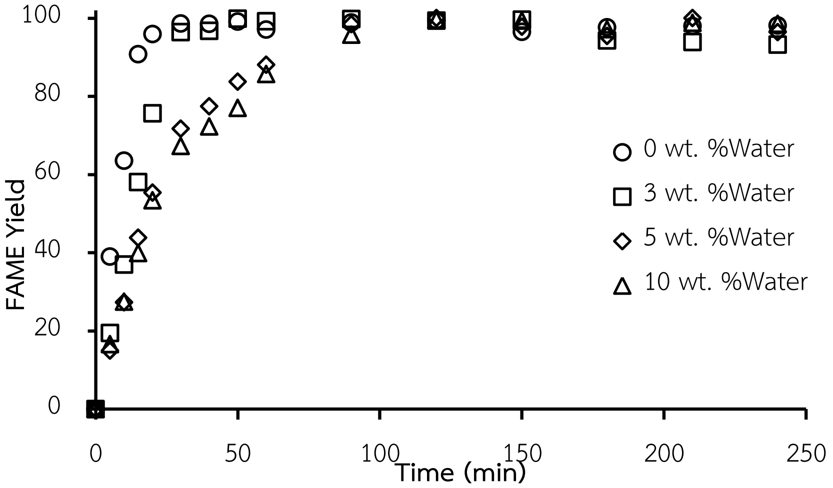
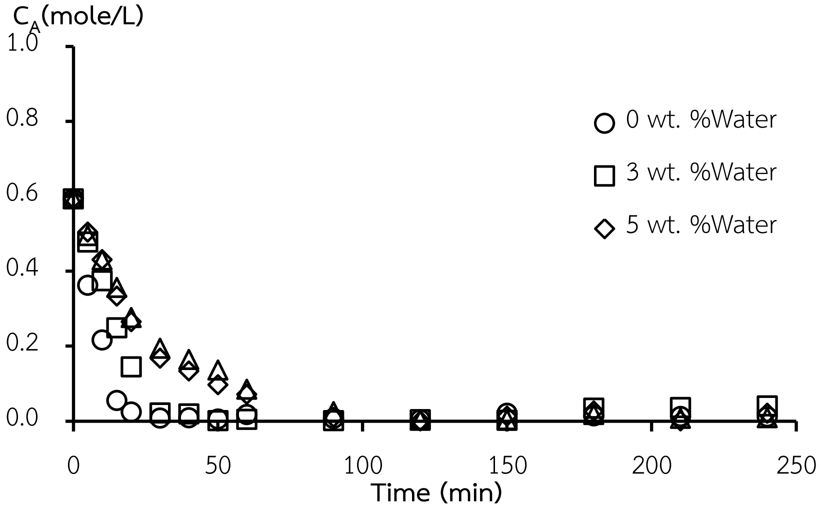
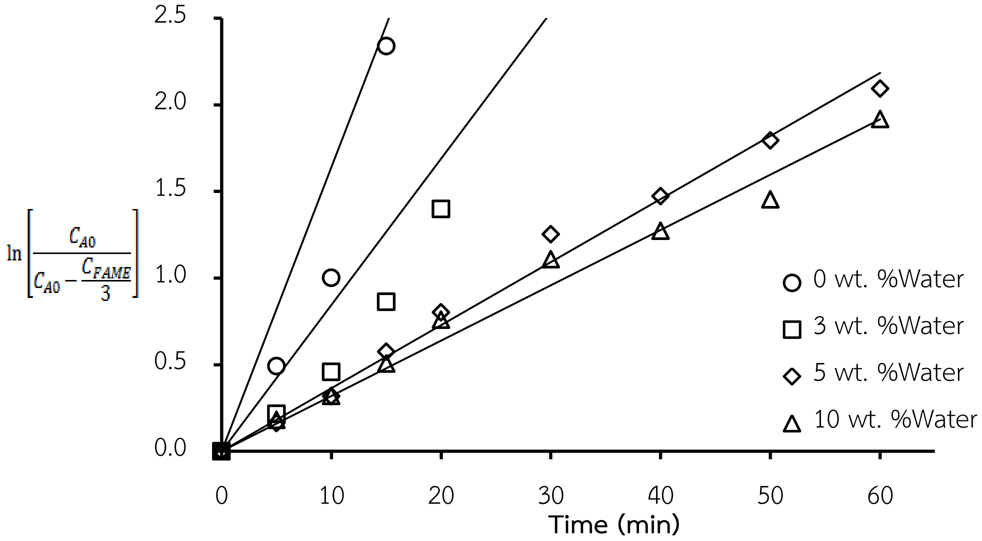


Figure 4. 24 Effect of water contents in raw materials on FAME yield. Agitation speed: 600 rpm. Temperature: 210°C. Molar ratio of methanol/oil: 18:1. Amount of Na_3PO_4: 1.0 wt.%. Water contents in methanol: 0–10 wt.% H_2O in methanol.

Figure 4.25 (a) shows the effect of water contents in oil on the concentration of un-methyl ester versus time, it is shown that the concentration of triglycerides are decreases as the amount of water in the reaction increasing. It can be summarized that water contaminate in the reaction are affected the rate of reaction only the initial time of reaction. Figure 4.25 (b), plot the rate of reaction shows that the reaction rate slows when the water in the system increases.



(a) Plot of un-methyl ester concentration versus time.



(b) Initial rate of reaction from 0-60 minutes.

Figure 4. 25 Effect of water contents in raw materials. Agitation speed: 600 rpm. Molar ratio of methanol/oil: 18:1. Temperature: 210°C. Amount of Na_3PO_4: 0.5 wt.%. (a) Un-methyl ester concentration (mono-, di-, tri-glycerides) versus time. (b) Initial rate of reaction from 0-60 minutes.

It have been reported that the water content in raw materials is not affected the rate of reaction when operating at high temperature. When there is a little water in the system, water acts as a catalyst in hydrolysis reaction, the reaction products are glycerol and fatty acids. Hydrolysis of triglyceride is shown in equation 4.8.

$$\text{Triglycerides} + 3H_2O \rightarrow \text{Glycerol} + 3\text{Fatty acids} \qquad (4.8)$$

Next reaction, free fatty acids reacts with base catalyst dissolved in water, soap formation and water are occurred, and saponification reaction is shown in equation 4.9.

$$\text{Fatty acid} + \text{Base} \rightarrow H_2O + \text{Soap} \qquad (4.9)$$

However, saponification can be occurred direct from triglyceride reaction with base catalyst dissolved in water, given glycerine and soap, as shown in equation 4.10.

$$\text{Triglycerides} + 3\text{Base} \rightarrow \text{Glycerol} + 3\ \text{Soap} \qquad (4.10)$$

In the systems contaminate with water, the complex reaction of transesterification, hydrolysis, esterification and saponification. However, the results showed water contaminate in feedstock not reduced the equilibrium conversion.

4.6.7. Effect of FFAs contents in raw materials

The effects of FFAs contents in oil on the formation of FAME products were studied by varying amount of FFAs from 0–10 wt.%. The different amounts of Palm Fatty Acid Distillate (PFAD) were added into oil in order to study effect of FFAs contents in raw material. The reaction conditions was fixed at a molar ratio of methanol/oil of 18:1, a reaction temperature of 210°C, and 1 wt.% Na_3PO_4. The formation of FAME product versus time at various amount of FFAs are shown in Figure 4.26. The concentration of un-methyl ester versus time are shown in Figure 4.27 (a) and 4.25 (b), it can be seen that FAME products decreased while increasing the FFAs amount in the reaction system. The concentrations of triglycerides are decreased as increasing the amount of FFAs. The plot of rate of reaction at initial time from 0–60 minutes shows that the reaction rate slows when the FFAs in the system increases.

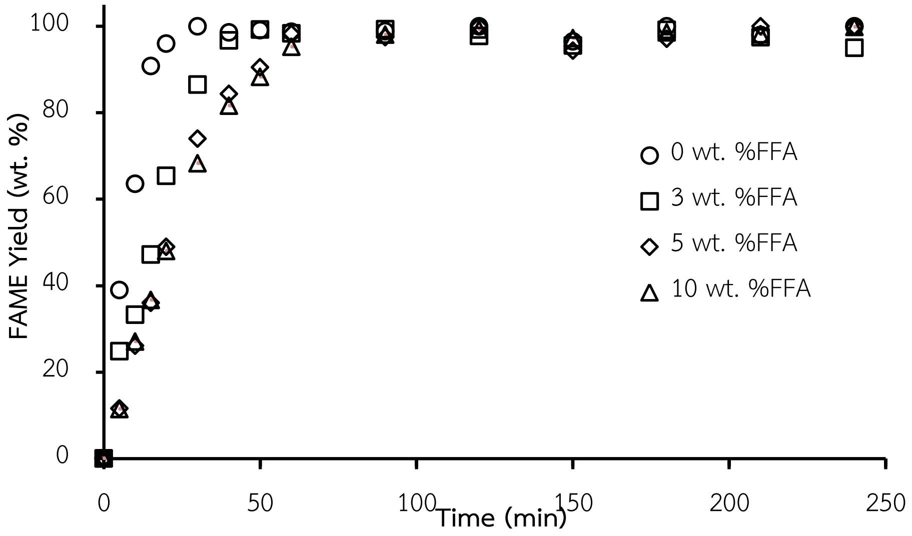
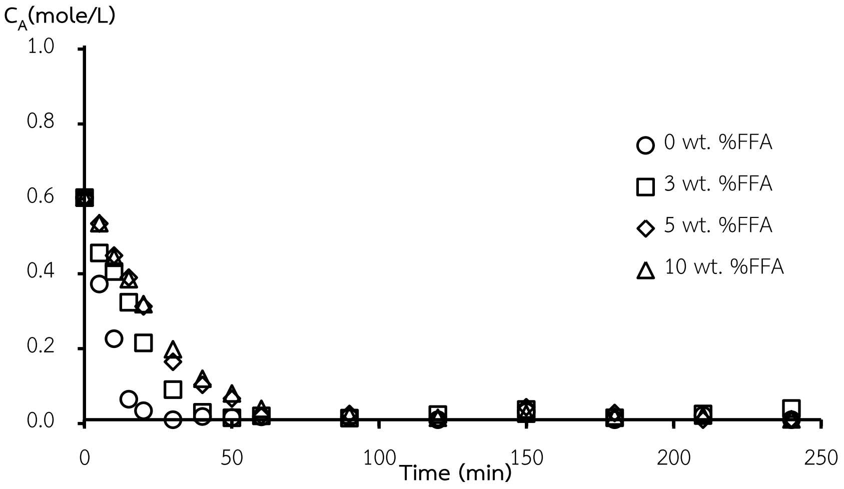
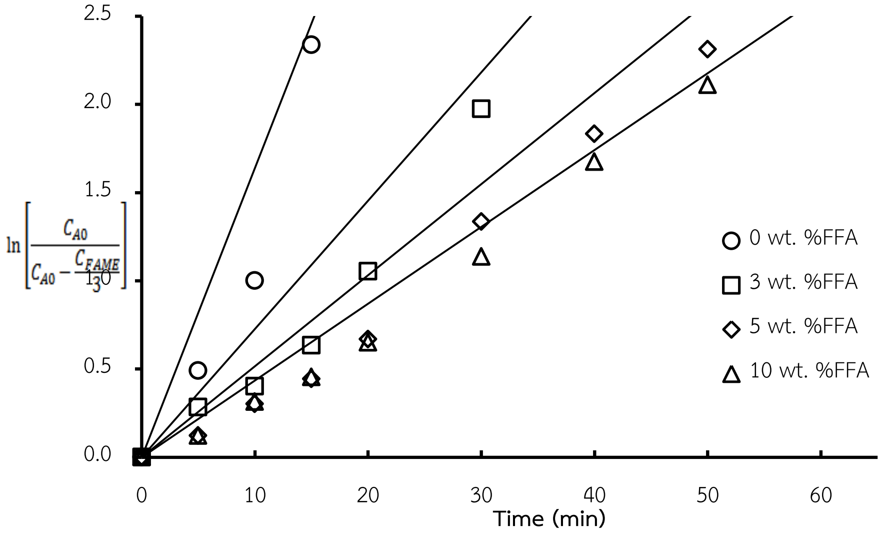


Figure 4. 26 Effect of FFAs contents in raw materials on FAME yield. Agitation speed: 600 rpm. Temperature: 210 °C. Molar ratio of methanol/oil: 18:1. Amount of Na_3PO_4: 1.0 wt.%. FFAs contents in oil: 0-10 wt.%.

The effects of varying amount of FFAs content in oil showed a similar trend to the effects of additional water. The reaction approached equilibrium conversion in only 60 minutes. This finding clearly shows that the presence of either or both component in the reaction feedstock reduces the reaction rate, but it does not have any effect on the equilibrium conversion. The reaction tends to reach its equilibrium slower in the presence of water and/or FFAs than when these components are absent.



(a) Plot of un-methyl ester concentration versus time.



(b) Initial rate of reaction.

Figure 4. 27 Effect of FFAs contents in raw materials. Agitation speed: 600 rpm. Molar ration of methanol/oil: 18:1. Temperature: 190°C. Amount of Na_3PO_4: 0.5 wt.%. FFAs content: 0-10 wt.%. (a) Un-methyl ester concentration (mono, di, triglycerides) versus time. (b) Initial rate of reaction from 0-60 minutes.

Yin et al. [61] reported an upper limit for water and oleic acid tolerance in soybean oil with K_3PO_4 as a catalyst of 5 wt.%, and 3 wt.%, respectively. Similarly, a study by Wang et al. [54], examined the effect of water under reaction conditions of

0.5 wt.% NaOH and a temperature of 250 °C. They found that the water content of the reactants had to be less than 1.5 wt.% to obtain a high yield within 10 minutes. Nair et al. [131] synthesized biodiesel from waste frying oil using CaO and found that when water and FFAs were present in the feed, three types of reactions (transesterification, hydrolysis, and alkyl esterification of fatty acid) occurred simultaneously. Warabi et al. [128] also found that alkyl esterification is faster than transesterification and that all FFAs in the feed, whether present originally or as the products of hydrolysis, are completely transformed into alkyl esters.

According to research worked by Melero et al. [48] that investigated transesterification of refined and crude vegetable oil with sulfonic acid-modified meso-structure catalyst. In the presence of FFAs in the oils, the catalyst showed high activity toward simultaneous esterification and transesterification. Kawashima et al. [44] reported results consistent with this research. FFA was esterified by $CaCO_3$ and does not appear to inhibit the catalyst and no decrease in the activity of the catalyst.

In non-catalytic processes, the amount of water present in the feedstock did not have a significant effect on the biodiesel yield. The conversion tended to increase slightly with increased FFA content in rapeseed oil [132]. However, in a catalytic system, it may be reduce the effectiveness of the catalyst when the system contains both components because the base catalyst dissolves in water and the product esterification of FFA also generates water. This decreases the effectiveness and reusability of the catalyst. The duration of this study was extended until the system approached equilibrium. It can be observed that both components only had an effect at the beginning of the reaction. Transesterification at high temperature has the ability to convert the FFAs in triglycerides to methyl esters, but the reaction time must be extended. However, a catalytic system contaminated with water and FFA operates via a complicated mechanism, so more study is needed to determine the reaction pathway.

4.6.8 The solubility of Na_3PO_4 in methanol

The solubility of the heterogeneous catalyst under reaction conditions is a very important factor that has to be considered. This factor indicates the efficiency of the catalyst. However, few studies have reported the solubility of solid catalysts, which are always assumed to be insoluble. Nevertheless, if the solid catalyst partially dissolves, it requires purification. Normally, leaching of a catalyst is accelerated by the presence of polar substances such as methanol, water, and FFAs [124]. Although Na_3PO_4 is insoluble in methanol, it can be dissolved in H_2O at 8.8 wt.%.

To study catalyst reusability, Na_3PO_4 separated from the reaction was rinsed with methanol and dried at 120 °C in an oven. The used catalyst did not exhibit significantly decreased activity after 3 runs. We further studied the solubility of Na_3PO_4 in methanol under the study conditions. The calcined Na_3PO_4 was agitated with methanol at a mixing speed of 600 rpm, a reaction time of 4 hours, and a temperature of 250 °C. The catalyst was filtered with filter paper and dried in an oven for 24 hours. The methanol was titrated with standard 0.1 molar HCl solution. The results showed only a 0.14 wt.% loss of Na_3PO_4 . It can be concluded that, under the experimental conditions used, the catalyst is insoluble. The catalyst showed potential to be developed for industrial-scale production. However, because the catalyst is in the form of a powder, it is difficult to separate out at the end of the reaction. As a result, some of the catalyst may be loss during separation. Further research in part two, to prepare Na_3PO_4 on a large supported catalyst to make separating the catalyst from the product easier.

4.6.9 Determination of activation energy

The reaction rate constant could be evaluated from oil conversion. Kinetic study under different reaction conditions have been carried out by many researchers [2, 15, 16]. In this research, to quantify the effect of reaction temperature, the experimental results were interpreted in terms of kinetics of converting palm oil to methyl ester under various reaction temperatures. The reaction was assumed to be a 1^{st} order irreversible reaction because access of methanol was always used. It is also assumed that the reaction proceeds from triglyceride to methyl ester ignoring other complex reaction step. Rate of reaction is proposed as in equation 4.2 - 4.7.

$$-r_{TG} = \frac{1}{3} r_{ME} = -\frac{dC_{TG}}{dt} = k'C_{TG} \tag{4.2}$$

$$k' = kC_{MeOH},\ k = \text{rate constant} \tag{4.3}$$

$$-\ln\frac{C_{TG}}{C_{ME,O}} = k't \tag{4.4}$$

$$C_{TG} = C_{TG,0}\,(1-X_{TG}) \tag{4.5}$$

$$X_{TG} = \frac{1}{3} X_{ME}, \quad C_{ME} = C_{TG,O}X_{ME} \tag{4.6}$$

$$ln\frac{C_{TG,O}}{C_{TG}} = ln\frac{C_{TG,O}}{C_{TG,O}-\frac{C_{ME}}{3}} \tag{4.7}$$

From the relationship, plot of $ln\frac{C_{TG,O}}{C_{TG,O}-\frac{C_{ME}}{3}}$ versus time (t) to calculate the rate constant. Using above relationship and the results from experiments conducted at molar ratio of methanol to oil of 18:1, amount of catalyst of 0.5 wt.% and temperatures of 150–250°C. The chemical rate constants (k) were significantly affected by temperature and were showed in table 4.4. The rate constant value increased with increasing reaction temperature.

Table 4. 4 The chemical rate constants (k).

Temperature (^{o}C)	k(s^{-1})
150	0.0127
170	0.0185
190	0.0446
210	0.0738
230	0.0818
250	0.1267

The activation energy can be determined from the plot of the natural logarithm of initial rate against the reciprocal of the reaction temperature (Arrhenius plot) as shown in Figure. 4.28. The activation energy is calculated through the Arrhenius equation, which include activation energy (Ea) and the frequency factor (A) given below.

$$k = Ae^{\frac{-E_a}{RT}} \tag{4.11}$$

Where, R is the universal molar gas constant, and T is the temperature (k). Because the activation energy is dependent on temperature, the rate constant at any temperature can be computed using Equation 4.12.

$$\ln k = \ln A - \frac{-E_a}{RT} \tag{4.12}$$

Equation 11 is a linear equation, and therefore a plot of $\ln_k$ and $\frac{1}{T}$ given in Figure 4.28 validates that it is a first order reaction. The activation energy (E_a) was calculated using Figure 4.28.

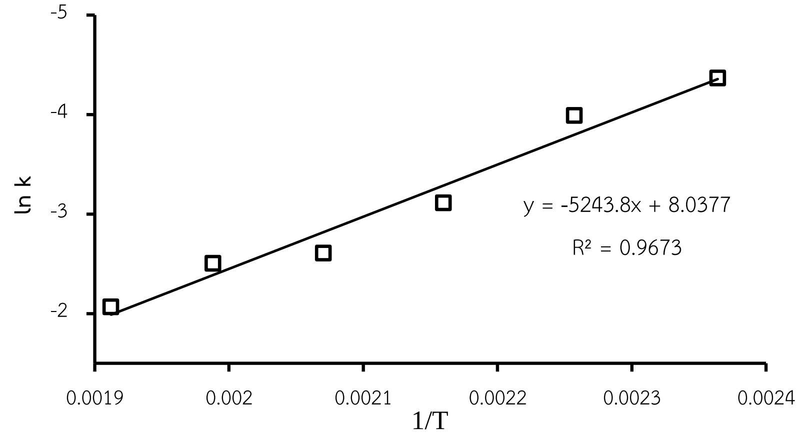


Figure 4. 28 Arrhenius plot of ln k versus 1/T

The activation energy was estimated (150–250°C) by an expression to the Arrhenius equation and its calculated from this model, was 43.6 kJ/mol. Many researchers have been reported the activation energy of transesterification reaction. Anusan P. et al. [127] carried out with palm oil from 150–200°C, they estimated the activation energy was 90.9 kJ/mol (from zero order) and 105 kJ/mol (from 1st order). Wang et al. [18] reported activation energy for non-catalytic transesterification reaction of soybean and methanol of 92 kJ/mol in their experiments which were conducted at temperatures between 200–260°C. They also reported an activation energy of 85.4 kJ/mol of rapeseed oil and methanol in the system with sodium hydroxide catalyst.

Permsuwan A. et al. [19] estimated the activation energy of non-catalytic transesterification reaction between palm oil and methanol at temperatures between 150–200°C to be in the range of 91-105 kJ/mol. The results in this research indicate that in the system using catalyst can reduce the activation energy of the system when compared with non-catalytic system. Compare to non-catalytic reaction of triglyceride, high activation energy of the study may represent high energy barrier from the effect of the mass transfer limitation. When compares to from 150–250°C, the activation energy was 43.60 kJ/mol.

4.7 Catalyst characterization of Na_3PO_4/Al_2O_3

The prepared Na_3PO_4/Al_2O_3 catalysts were characterized by SEM-EDX in order to study the dispersion of catalyst, inner and outer pore of the catalyst. FT-IR used to study the structure of catalyst. Thermal gravity analysis (TGA) is used to study the weight loss of catalyst at temperature.

4.7.1 SEM-EDX Analysis

The scanning electron micrographs of calcined–Al_2O_3 (a) and Na_3PO_4/Al_2O_3 (b) are shown in Figure 4.29. It can be seen that no significantly difference was observed by SEM images between the calcined-Al_2O_3 and calcined-Na_3PO_4/Al_2O_3 samples. Base on the results alumina retains its structure after loading with sodium phosphate, which is important for analysis.

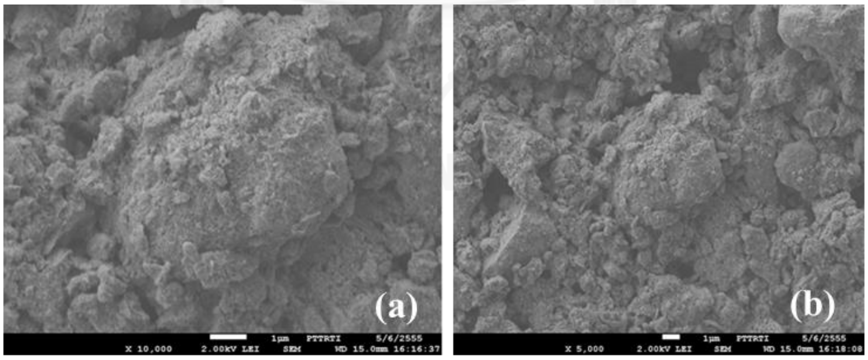


Figure 4. 29 SEM images of (a) calcined-Al_2O_3, (b) calcined-Na_3PO_4/Al_2O_3

The EDX mapping showed in Figure 4.30 (a-c) identified that a good dispersion of sodium (Na) and phosphorus (P) on various position of the Na_3PO_4/Al_2O_3. Figure

4.30 (a) showed the inner, 4.30 (b) showed (inner) and 4.30 (c) showed cross-section. The results identified a good dispersion of Na_3PO_4 onto the surface of Al_2O_3.

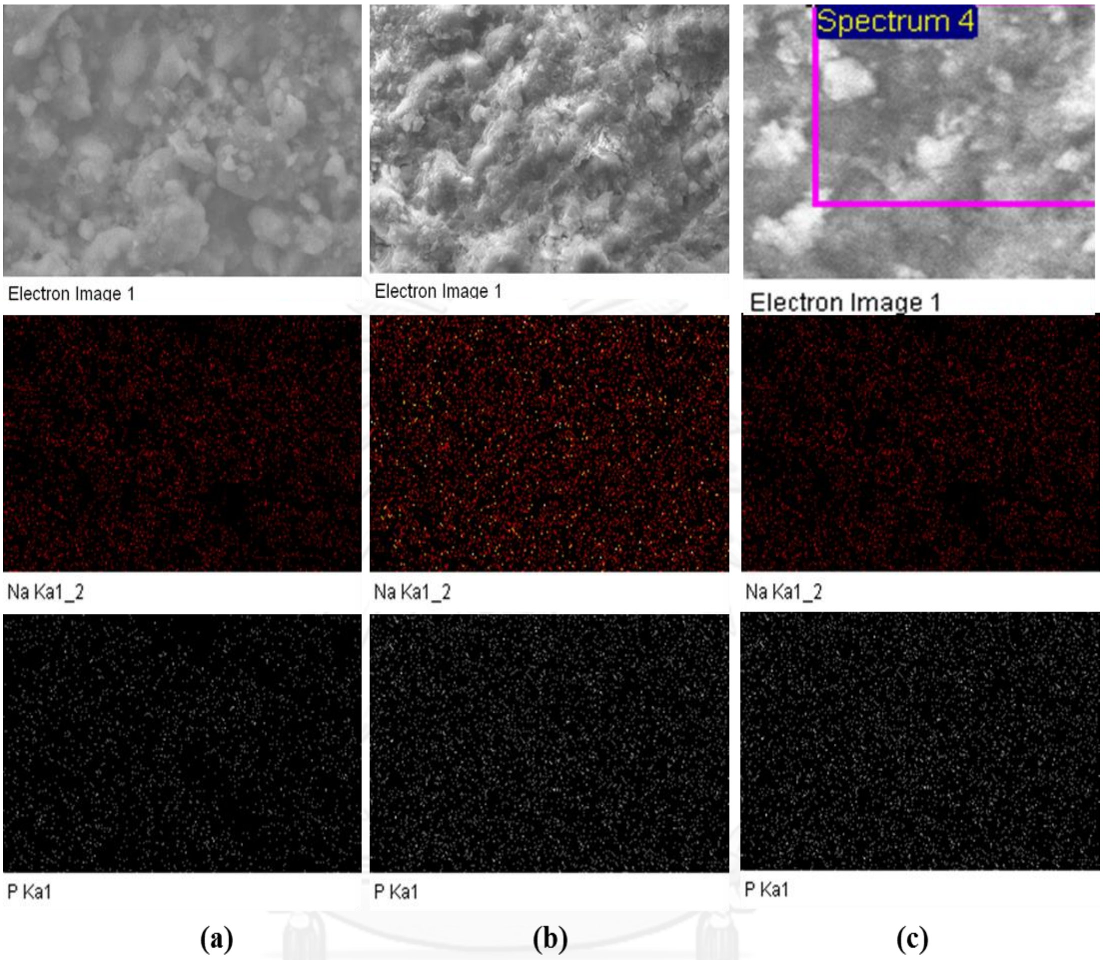


Figure 4. 30 EDX elemental mapping of sodium and phosphorus onto the Na_3PO_4/Al_2O_3 at various positions, inner (a), outer (b) and cross–section (c).

4.7.2 FT-IR analysis

The FT–IR spectroscopy has become one of the most useful tools in the analysis of phosphate species adsorption on solid surface. The FT-IR analyses of catalysts are performed to obtain more information about catalyst structure. The spectra of the samples, Al_2O_3 (dried and calcined), Na_3PO_4 (dried and calcined) and Na_3PO_4/Al_2O_3 (dried and calcined) are showed in Figure 4.31-4.33. All of the samples showed an intense broad band at approximately 3456 cm^{-1} that can be ascribed to γ_{OH} stretching vibrations. In addition, the absorption peak at 1635 cm^{-1} may be assigned to the δ_{OH} bending vibrations of H_2O molecules absorbed from air. The adsorption peaks became weak after calcined.

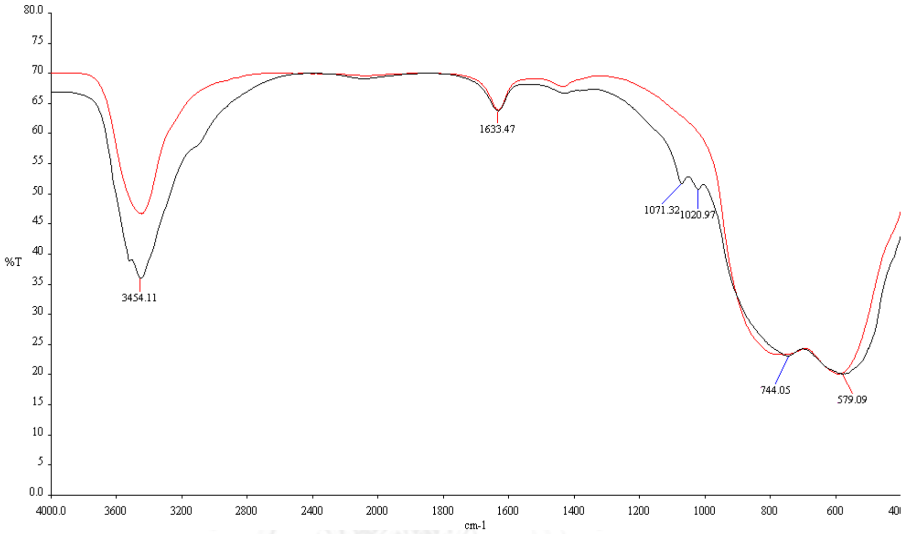


Figure 4. 31 FT-IR spectra of Al_2O_3, before (black line) and after (red line) calcined.

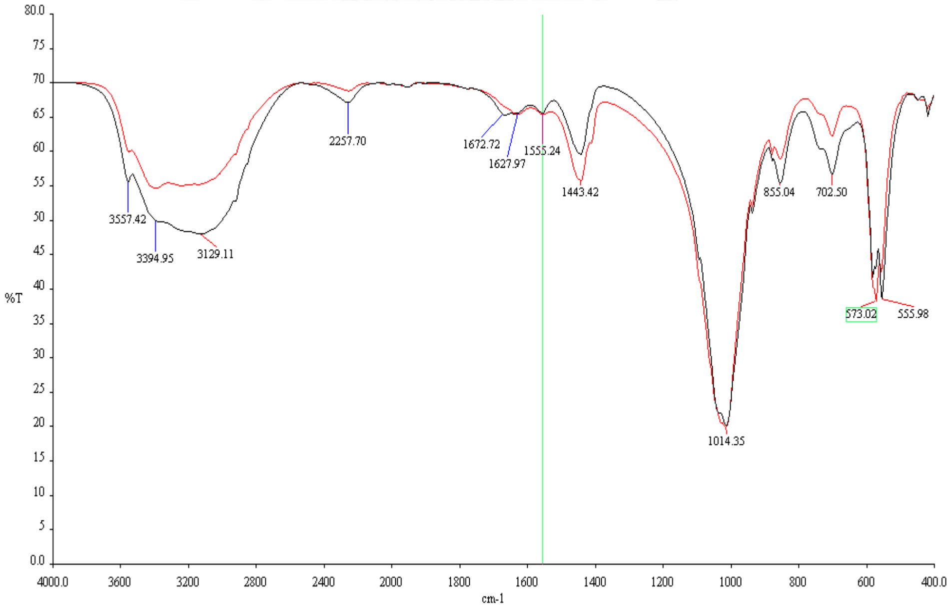


Figure 4. 32 FT-IR spectra of Na_3PO_4 before (black line) and after (red line) calcinations.

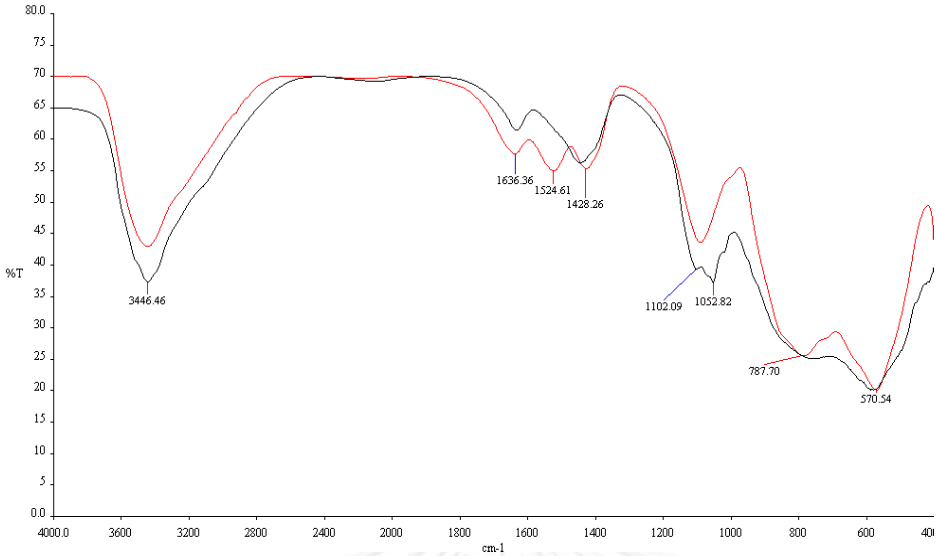


Figure 4. 33 FT-IR spectra of Na_3PO_4/Al_2O_3, before (black line) and after (red line) calcinations.

A comparison of the FT-IR spectra of calcined-Al_2O_3, calcined-Na_3PO_4 and calcined-Na_3PO_4/Al_2O_3 are presented in Figure 4.34. Compared to the spectrum of calcined-Al_2O_3, the spectrum of calcined-Na_3PO_4/Al_2O_3 shows a strong peak at approximately 1080.66 cm^{-1}, which can be attributed to the new structure of phosphate sorbed onto alumina [133]. Zheng T-T. et al [134] studied the sorption of phosphate onto meso-porous γ-Al_2O_3, they summarized according to our work that the band at 1080 cm^{-1} showed the adsorbed species of phosphate onto γ-Al_2O_3.

The bands of Al_2O_3 (a) became weak after impregnation and calcination (c) due to the exchange of Na and P ions with hydrogen groups in the Al_2O_3 support [119]. Lie et al. [105] found that $KCaF_3$ and K_2O were the main active components for the catalyst activity.

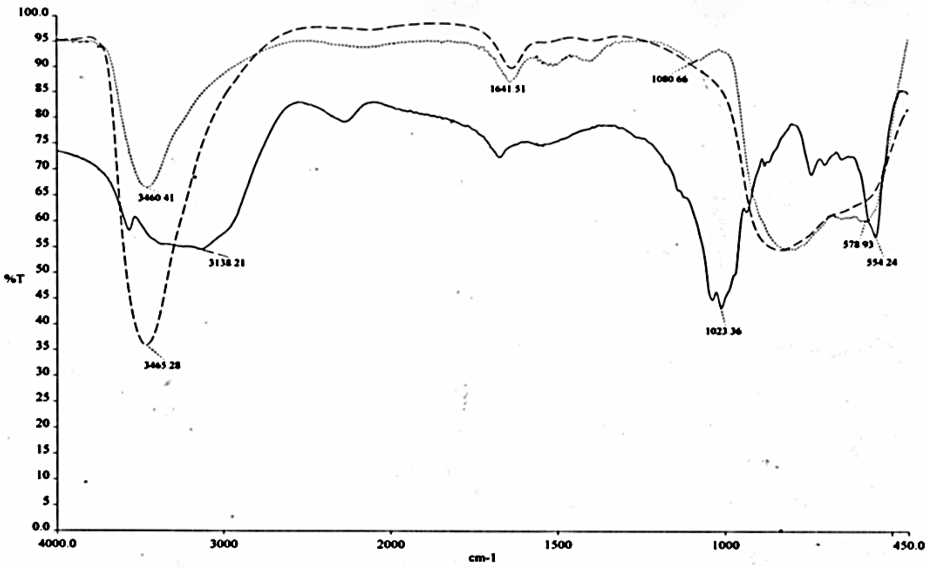


Figure 4. 34 FT-IR Spectra of Calcined-Al_2O_3(— –), Calcined-Na_3PO_4 (—) and Calcined-Na_3PO_4/Al_2O (....).

4.7.3 BET surface area and adsorption isotherm

The nitrogen adsorption isotherms of Al_2O_3, and the synthesized catalysts exhibited the typical Type IV isotherm, to indicate that the Na_3PO_4-impregnated Al_2O_3 catalyst supports are meso-porous. Figure 4.33 is showed the N_2 adsorption-desorption isotherm of the synthesized catalyst.

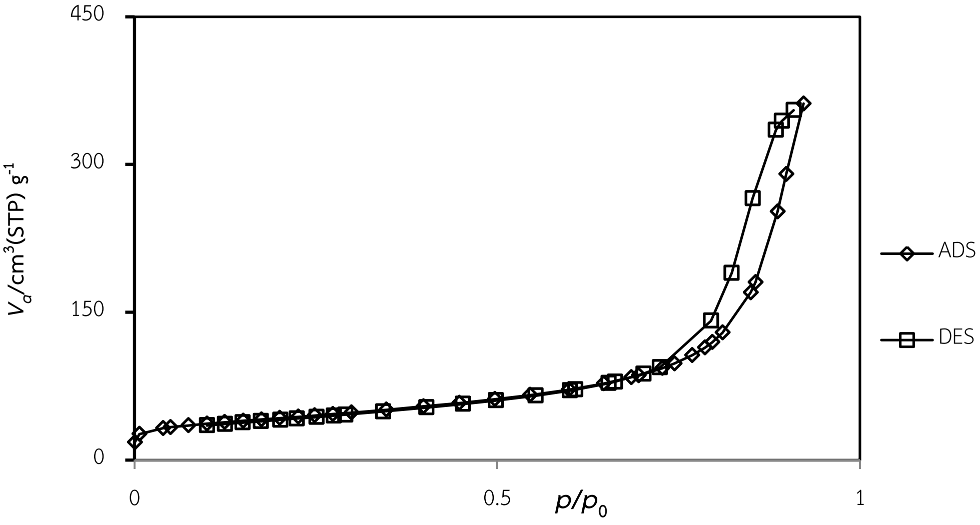


Figure 4. 35 The N_2 adsorption-desorption isotherm of the prepared Na_3PO_4/Al_2O_3.

The BET surface area, total pore volume and average pore size of the catalysts as measured by N_2 adsorption are shown in Table 4.5. The results indicate that the surface area and pores of alumina were not covered by sodium phosphate during the impregnation. It can be observed that γ-Al_2O_3 is loaded with Na_3PO_4, and the surface area and total pore volume are both slightly reduced due to the Na_3PO_4 covering on the porous surface of γ-Al_2O_3. After loading with Na_3PO_4 and calcined at 500 °C for 4 hours, the surface area and total pore volume both increased due to an increase in the number of small regular crystals. The average pore sizes increased as follows: dried γ-Al_2O_3<dried Na_3PO_4/γ-Al_2O_3 and calcined γ-Al_2O_3 <calcined Na_3PO_4/γ-Al_2O_3. A possible explanation for this trend is that thin layers that form on the Al_2O_3 surface reduce the number of small pores but have no effect on the number of larger pores. As a result, catalyst pore sizes become more equal overall, and an increase in average pore size is observed.

Table 4. 5 BET surface area, total pore volume and average pore size of the prepared catalysts.

Type	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Avg. pore size (A^o)
Dried γ-Al_2O_3	166.63	0.5554	133.34
Dried Na_3PO_4/γ-Al_2O_3	145.33	0.5345	147.11
Calcined γ-Al_2O_3	146.26	0.5303	145.03
Calcined Na_3PO_4/γ-Al_2O_3	149.50	0.5297	149.75

Samik et al. impregnated of K_3PO_4 on mesoporous NaZSM-5 with 5, 10, 15 % (w/w). The research showed after impregnated with 5 and 10 wt.% K_3PO_4, the pore remain a mesoporous materials with pore diameter in the range of 3.8-9.6 nm, while impregnation of 15 wt.% K_3PO_4 on NaZSM-5 resulting in the formation of non-porous solids.

Table 4.6 showed that the volume of micro-pore, meso-pore and total pore volume of the catalyst. It can be seen the most of pore size of the prepared Na_3PO_4/Al_2O_3 remains mesopore structure after prepared on alumina.

Table 4. 6 The volume of micro-pore, meso-pore and total volume of the prepared catalysts

Sample	**V (cm^3/g)**			
	V_{micro}	V_{meso}	V_{total}	$\%V_{meso}$
Dried γ-Al_2O_3	0.20	0.554	0.754	73.47
Dried Na_3PO_4/γ-Al_2O_3	0.30	0.531	0.831	63.9
Calcined γ-Al_2O_3	0.20	0.456	0.656	69.51
calcined Na_3PO_4/γ-Al_2O_3	0.36	0.565	0.925	61.08

According to Fernandez et al. [45], the critical diameter, defined as the diameter of the smaller cylinder through which molecule can pass without distortion, of a triglyceride molecule is approximately around 2 nm. Lopez Granados et al. [135] reported that methyl oleate has diameter approximately 2.5 nm, and the diameter of triglycerides is at least two times larger. The preparation of alumina–supported catalyst should be therefore have a pore size greater than the triglyceride molecule’s critical diameter. The study have been reported for a narrow pore catalyst (mean pore diameter ≅ 4 nm), a 50 % decrease of catalyst activity relatively to activity of catalyst with medium (d ≅ 6nm) and wide pore (d ≅ 8 nm) size could be expected (Coenen, 1986)

The use of meso–structure support has been shown to improve catalytic performance compared to micro–structured supported, as the larger pores in the meso–structure supports likely reduce mass transfer resistant [48, 136]. Robert Stern [14] was employed based on alumina balls having starting surface area of 146 m^2 and pore volume of 1.1 cm^3/g. The balls have a diameter 1.6 to 3 mm. The alumina balls are impregnated with zinc nitrate, and then subjected to calcination at 500 ^oC. The catalyst obtained has surface area 65 m^2, pore volume 0.63 cm^3/g.

The capillary condensation of N_2 was observed at the relative pressure range of 0.90 and 0.95. The pore size distributions of the materials that were used in this study are shown in Figure 4.36. The most of the pores are in the 7-40 nm size range and the distributions are relatively narrow.

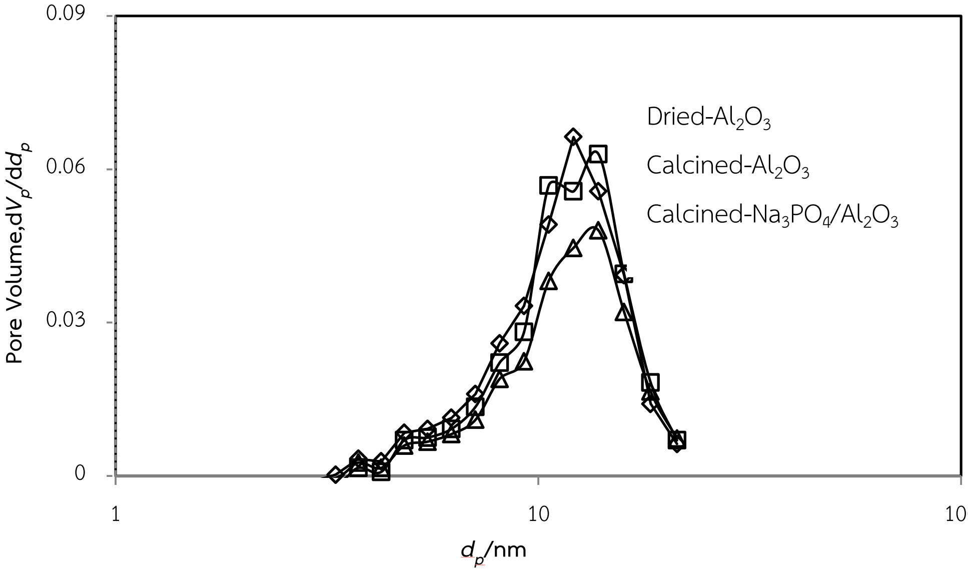


Figure 4. 36 Compares the pore size distribution of the prepared N_3PO_4/Al_2O_3, dried-Al_2O_3 and calcined-Al_2O_3.

4.7.4 X-ray Diffraction

X-ray diffraction patterns of γ-Al_2O_3 and Na_3PO_4/Al_2O_3 before and after calcination is shown in Figure 4.37. Only diffraction peaks (2Θ = 37.0°, 46.0° and 66.7°) corresponding to the amorphous Al_2O_3 support were observed in the XRD patterns, and characteristic peaks of neither Na_3PO_4 nor any new species were observed. These results indicate that Na_3PO_4 is well dispersed on the alumina support, likely as a monolayer due to interactions between Na_3PO_4 and the surface support. According to results summarized by Xi and Li [42], KI loadings on alumina lower than 30 wt. % do not affect the XRD pattern. In this work, because a very small amount of Na_3PO_4 (6.5 wt.%) was applied onto the alumina support, no variation in the XRD patterns was observed. The results showed any diffraction peak, a fact identicating that the samples are not crystalline. [137]. Samik et al. synthesized of meso-porous NaZSM-5 and impregnation of K_3PO_4 with 5, 10 and 15 % w/w. The results characterized using XRD showed that the structure of NaZSM-5 remained unchanged after impregnated with K_3PO_4.

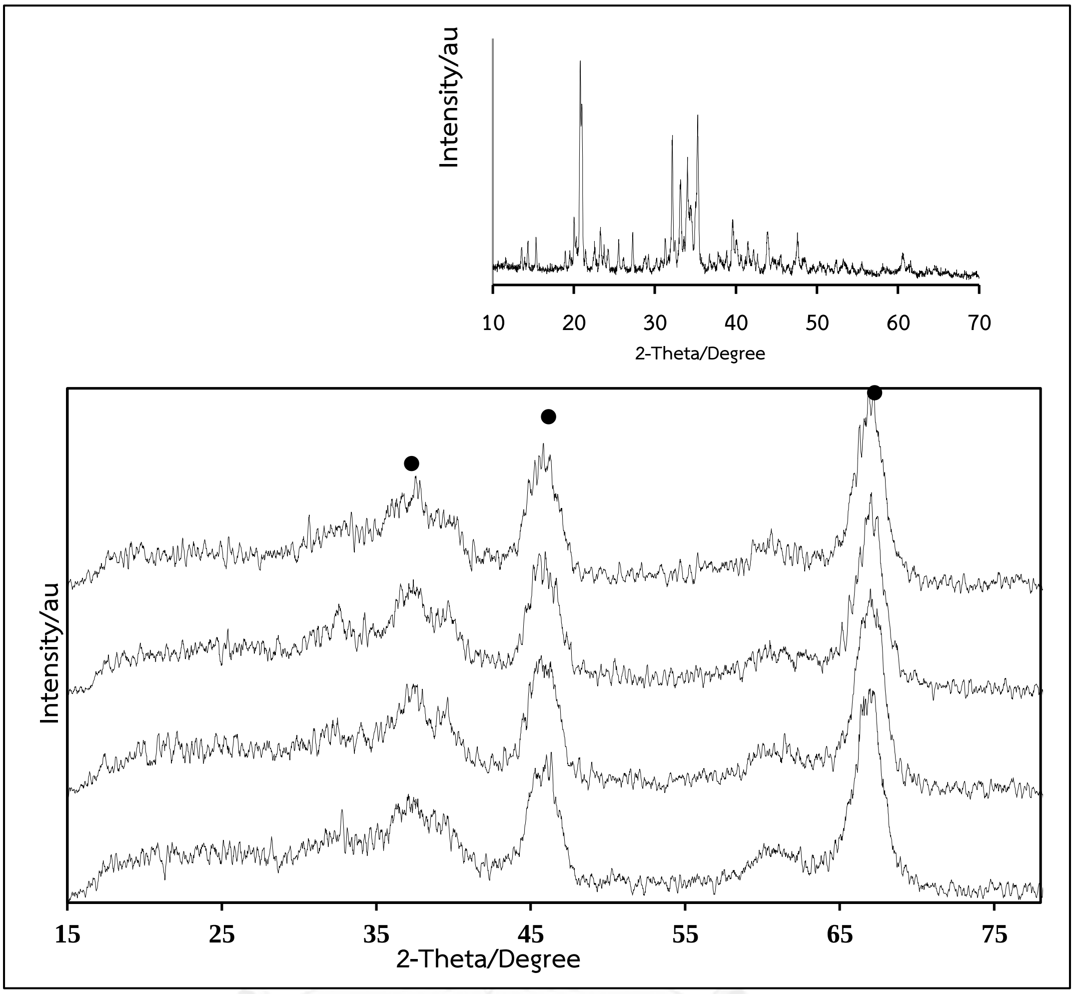


Figure 4. 37 The XRD patterns of (a) dried-Al_2O_3, (b) calcined-$Al_2O_{3,}$ (c) dried -Na_3PO_4/Al_2O_3 and (c) calcined-Na_3PO_4/Al_2O_3. (●) Al_2O_3. (Inset Na_3PO_4).

On the other hand, the FT-IR spectra indicated a phosphate surface complex was formed at 1080 cm^{-1}. The XRD results are not clear regarding the structures between Na3PO4 and γ-Al2O3. The XRD results were not able to indicate a new structure, and more research is needed to clarify this structure.

4.7.5 Inductive couple plasma (ICP-OES)

The prepared Na_3PO_4/Al_2O_3 was taken to analyze the actual loading of catalyst by elemental analysis. The prepared catalyst was digested with acid solution and analyzed by ICP technique. The amount of sodium and phosphorus were compared with standard to calculate the actual loading. The result was found 6.5 wt.% actual loading of Na_3PO_4 prepared on Al_2O_3 surface (Na=3.2 wt.%, P=1.21 wt.%). This value is used to calculate for study the activity of the prepared catalyst.

4.8 Transesterification using Na_3PO_4/Al_2O_3-supported catalyst

The prepared Na_3PO_4/Al_2O_3 used as a catalyst in this part was calculated at equivalent amount of Na_3PO_4 concentration in the previous part without the support. The effect of reaction variables on the methyl ester products, the agitation speed, the methanol/oil molar ratio, the reaction temperature, the catalyst amount and the catalyst reusability, were also investigated in this part.

4.8.1 Effect of agitation speed

In heterogeneous system, the reaction is limited by mass transfer between the three phases present in the system (oil/methanol/solid catalyst), resulting in a slow rate of reaction [138]. One way to reduce mass transfer resistant is by increasing mixing intensity, and optimization of mechanical agitation is essential to oil transesterification for biodiesel production. In this part of research the catalyst was prepared on alumina–supported, to evaluate the influence of the mixing intensity on transesterification reaction; the reaction was studied with agitation speeds between 600 and 1000 rpm. A methanol/oil molar ratio of 6:1, reaction temperature of 190 °C, and an amount of catalyst equivalent 0.5 wt.% of oil was used for this experiment.

The results showed in Figure 4.38, the formation of methyl ester versus time, and Figure 4.39 (a) showed the un-methyl ester concentration versus time. It was showed that increasing the mixing intensity from 600 rpm to 1000 rpm increased methyl ester production. In heterogeneous system is explained by the initial triglycerides mass transfer controlled region, followed by the chemical controlled regions in the latter period [20]. Increasing the agitation speed promotes mass transfer between phases, resulted in improving the reaction rate as well. Figure 4.39 (b) showed the rate of reaction versus time. As faster mixing speed as higher molecule collusion frequency and more reaction are occurred, then the higher oil conversion achieved. As slower mixing speed needs longer time to reach equilibrium oil conversion. The speed must be reach to minimize the term of mass transfer resistance [34, 57, 103]. Acceleration of the agitation speed could be shortening the reaction time.

At 1000 rpm, the reactions run not affected by mass transfer limitations. The mass transfer limitation is effectively minimized at mixing speeds higher than 1000 rpm. At mixing intensity higher than 1000 rpm, the overall reaction rate was not further affected by external mass transfer [139].

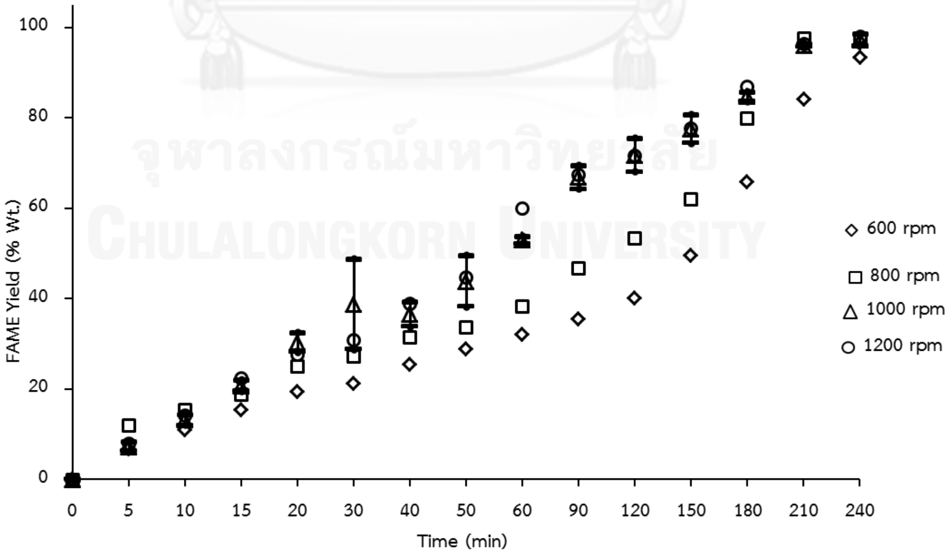
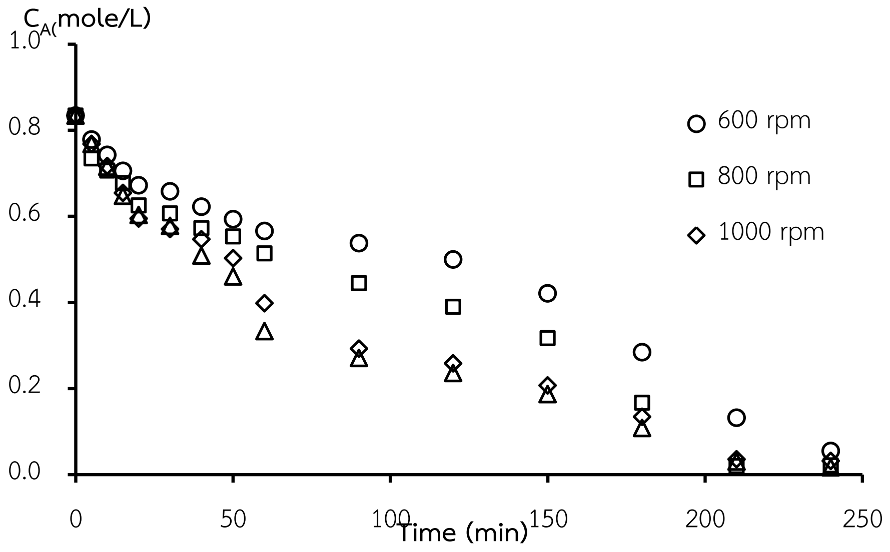
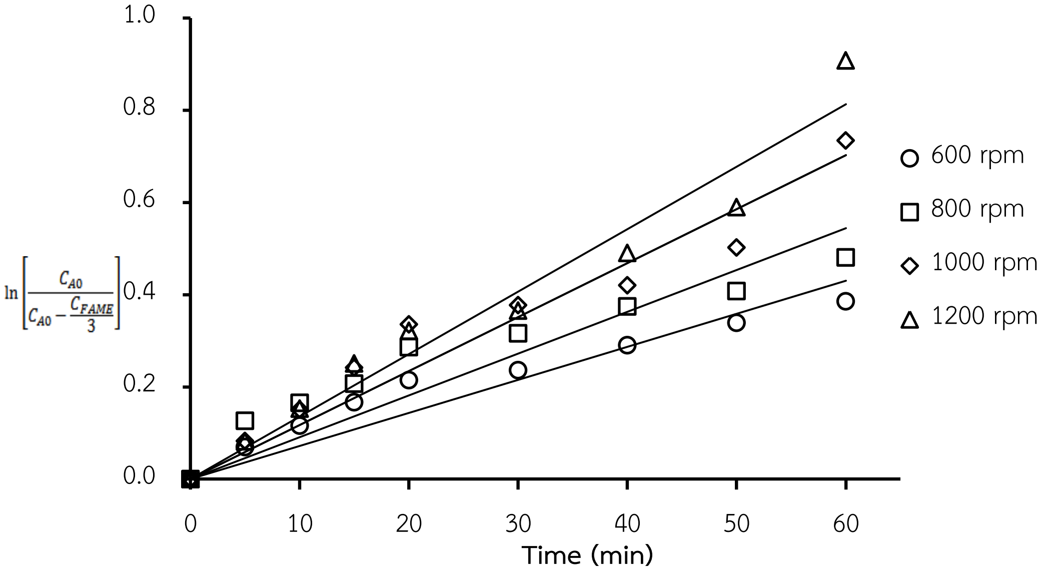


Figure 4. 38 Effect of agitation speed on FAME yield. Temperature: 190 °C. Molar ratio of methanol/oil: 6:1. Amount of Na_3PO_4/Al_2O_3: 0.5 wt.% Na_3PO_4.



(a) Plot of un-methyl ester concentration versus time.



(b) Initial rate of reaction from0-60 minutes.

Figure 4. 39 Effect of agitation speed. Agitation speed: 600-1200 rpm. Molar ratio of methanol/oil: 18:1. Temperature: 190 $^{\circ}$C. Amount of Na_3PO_4: 0.5 wt.%. (a) Un-methyl ester (mono-, di-, tri-glyceride) concentration versus time. (b) Initial rate of reaction from 0-60 minutes.

Moreover, the mass transfer is related to the size of the dispersed (methanol) phase, which reduced rapidly with progress of methanolysis reaction [140]. Increasing mixing reduced drop size and the reaction take place well. FAME yield increases with increasing agitation speed because the mass transfer rates of methanol to oil phase through the oil-methanol interface are increased.

4.8.2 Effect of molar ratio of methanol/oil

The stoichiometric molar ratio of methanol/oil for transesterification reaction requires 3 moles of methanol to one mole of triglyceride. Because the transesterification is a reversible reaction, an excess methanol/oil molar ratio is required to drive the reaction forward. In this part, to study effect of molar ratio of methanol/oil, we investigated under different molar ratio from 3:1-30:1. An agitation speed of 1000 rpm, temperature of 190 °C and a catalyst amount of 0.5 wt.% were used. The results are shown in Figure 4.40, at the stoichiometric molar ratio 3:1, methyl ester yield slightly increase with time. When the methanol/oil molar ratios were increase from 3:1-30:1, the yield of FAME increased considerably. The molar ratios higher than 18:1, the FAME product are identical.

Figure 4.41 (a) showed the un-methyl ester concentration versus time. As increases an amount of methanol, the triglycerides concentrations are decreases as time increases. The results in Figure 4.41 (b) showed that increasing the methanol/oil molar ratio increase the rate of reaction, at the ratios higher than 18:1, the FAME contents are slightly changed.

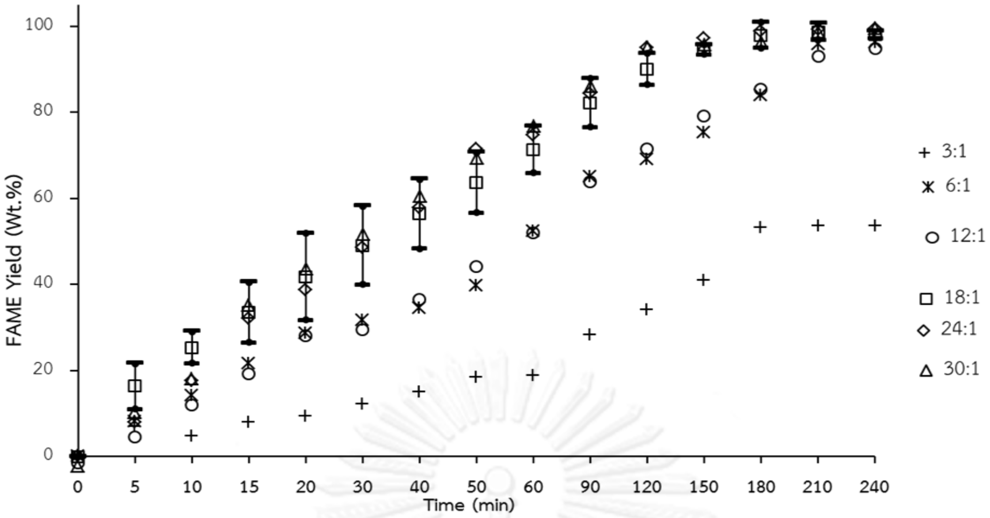
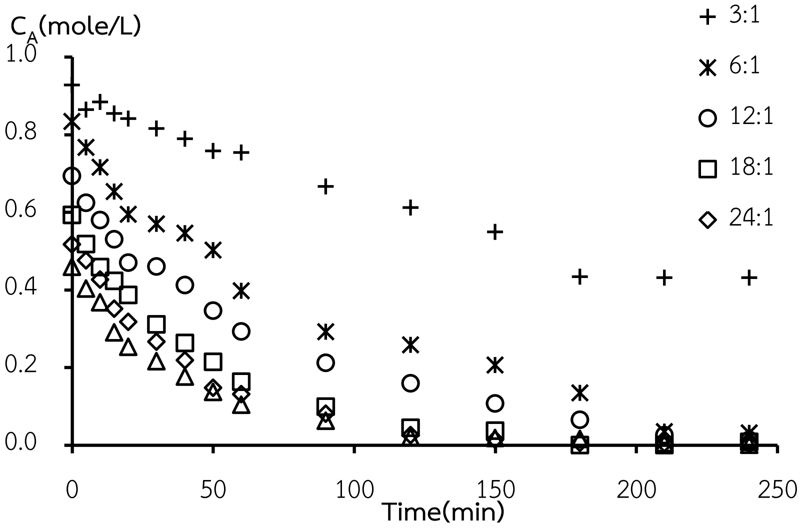
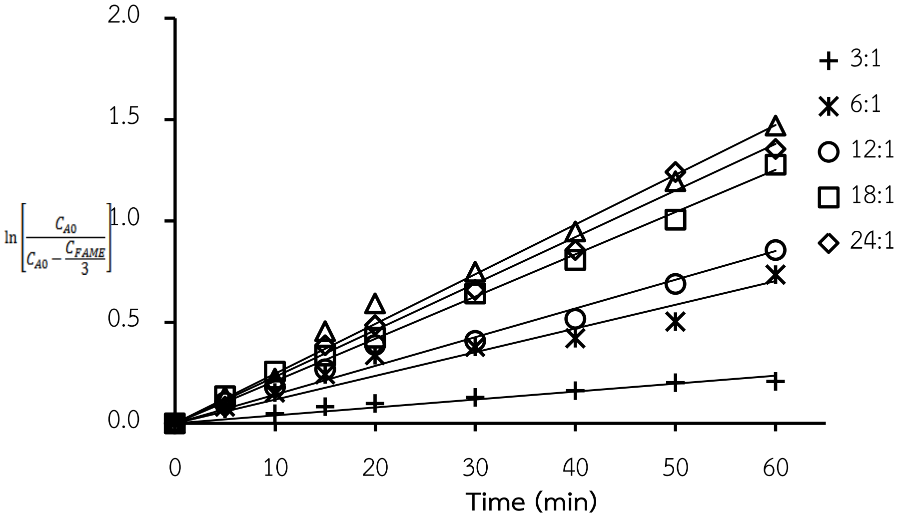


Figure 4. 40 Effect of molar ratio of methanol/oil on FAME yield. Molar ration of methanol/oil: 3:1-30:1. Agitation speed: 1000 rpm. Temperature: 190 °C. Amount of Na_3PO_4/Al_2O_3 equivalent to 0.5 wt.% Na_3PO_4.



(a) Plot of un-methyl ester concentration versus time.



(b) Initial rate of reaction from 0-60 minutes.

Figure 4. 41 Effect of methanol/oil molar ratio from 3:1-30:1. Agitation speed: 1000 rpm. Temperature: 190°C. Amount of catalyst: 0.5 wt.% Na_3PO_4. (a) Un-methyl ester concentration (mono-, di-, tri-glycerides) versus time. (b) Initial rate of reaction from 0-60 minutes.

Normally, the reaction rate can be increased by increasing the ratio of methanol/oil. Increasing the amount of methanol past a certain threshold does not affect the rate of reaction. This research found that a methanol ratio of methanol / oil of 18:1 is enough to accelerate the rate of reaction.

4.8.3 Effect of reaction temperature

Temperature has the most influence the transesterification reaction. However, the reaction occurs at different temperature depending on the type of catalyst and alcohol used. The influences of reaction temperature on the formation of FAME were investigated with 4 different temperatures from 190–250 °C. The agitation speed of 1000 rpm, the molar ratio of methanol/oil of 18:1, and the catalyst amount is equivalent to 0.5 wt.% of Na_3PO_4 were used. The results are shown in Figure 4.42, the methyl ester contents increased as the reaction temperature increased. In Figure 4.43 (a), shows the concentration versus time. It was found the concentration decreases as temperature increasing. Figure 4.43 (b) showed the rate of reaction depending on temperature, at higher temperatures are shown higher FAME product on time. However, it was found at the reaction temperature higher than 210 °C promoted FAME contents change slightly. It was showed a very high 96 wt.% of methyl ester yield after just 40 minutes was observed. This trend is due to the higher energy level of molecules as temperature is increased, resulting in faster diffusion into the continuous phase. The improved solubility of triglycerides in alcohol at elevated temperature is also partially responsible for this behavior, as the improved solubility improves the reaction rate [141].

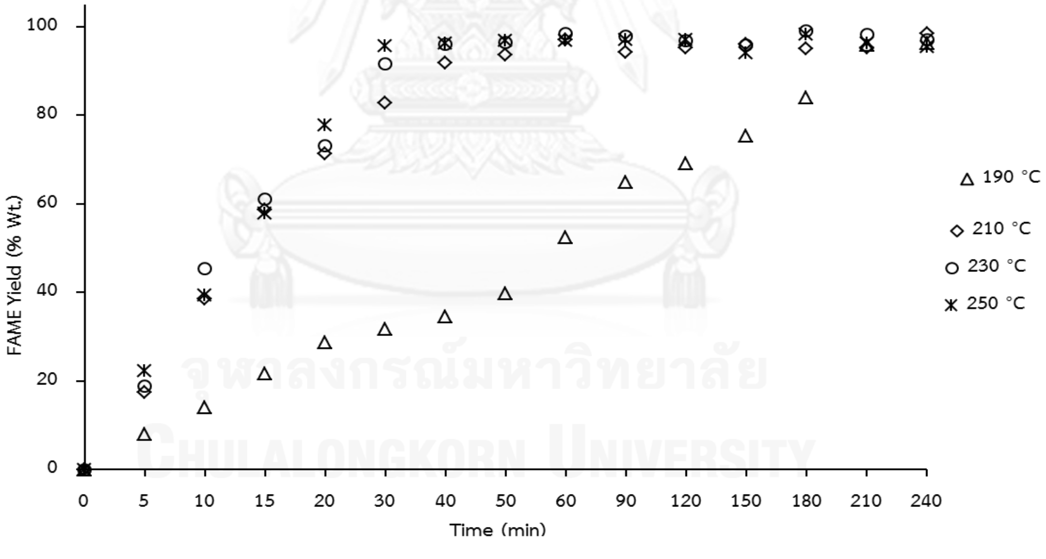
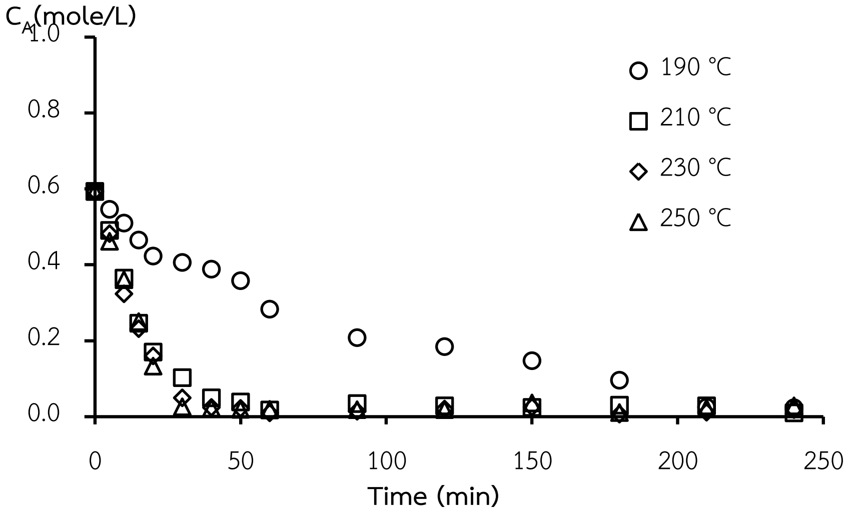
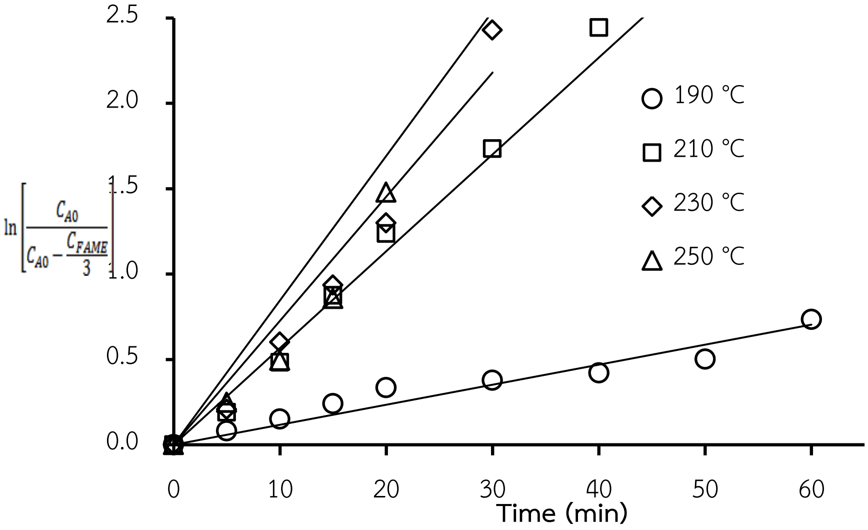


Figure 4. 42 Effect of reaction temperature on FAME yield. Temperature: 190–250 °C. Agitation speed: 1000 rpm. Molar ratio of methanol/oil: 18:1. Amount of Na_3PO_4/Al_2O_3 equivalent to 0.5 wt.% of Na_3PO_4.



(a) Plot of un-methyl ester concentration versus time.



(b) Initial rate of reaction from 0-60 minutes.

Figure 4. 43 Effect of reaction temperature: 190-250°C. Agitation speed: 1000 rpm. Molar ratio of methanol/oil: 18:1. Amount of Na_3PO_4/Al_2O_3 equivalent to 0.5 wt.% Na_3PO_4. (a) Un-methyl ester concentration (mono-, di-, tri-glycerides) versus time. (b) Initial rate of reaction from 0-60 minutes.

4.8.4 Effect of catalyst amount

The influences of the catalyst amount on product formation were investigated. The catalyst loading was varied from 0-2 wt.%, and the reaction condition were fixed at an agitation rate of 1000 rpm, methanol to oil molar ratio of 18:1, and the temperature of 210 ℃. The results are illustrated in Figure 4.44. The results showed transesterification reaction can occur without catalyst present in the system, but the methyl ester content increased only slightly over time in this case. When the catalyst amount was increased, product formation was increased as well as in Figure 4.45 (a), the concentration of un-methyl ester decrease as the catalyst increasing. Figure 4.45 (b), showed the rate of reaction increase as the catalyst amount increasing. In heterogeneous system, mass transfer and reactant adsorption onto the catalyst surface is very important. Increasing the amount of catalyst present increase the number of active catalyst sites available for reaction.

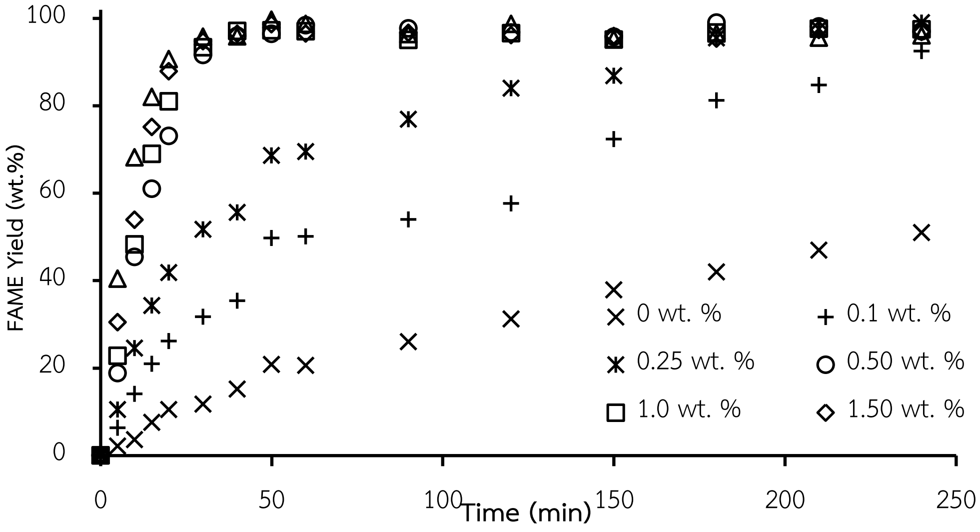
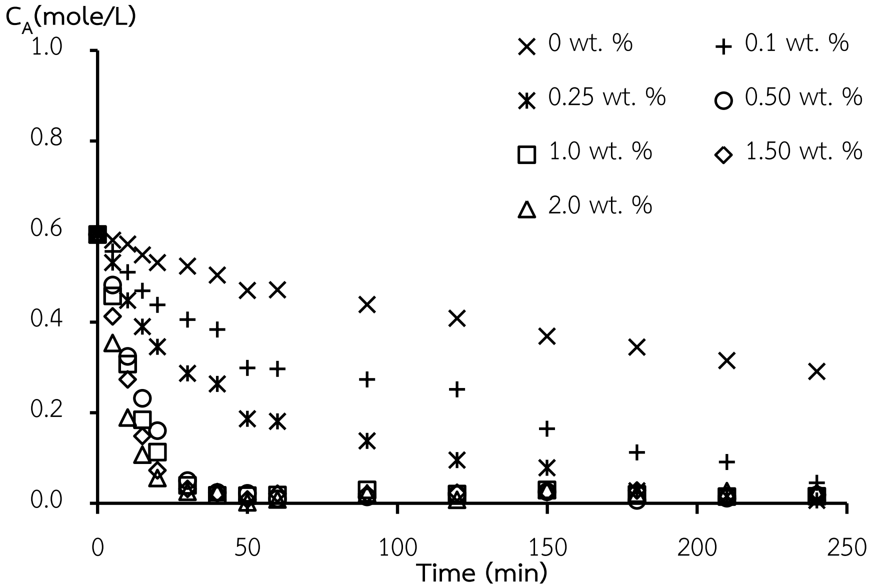
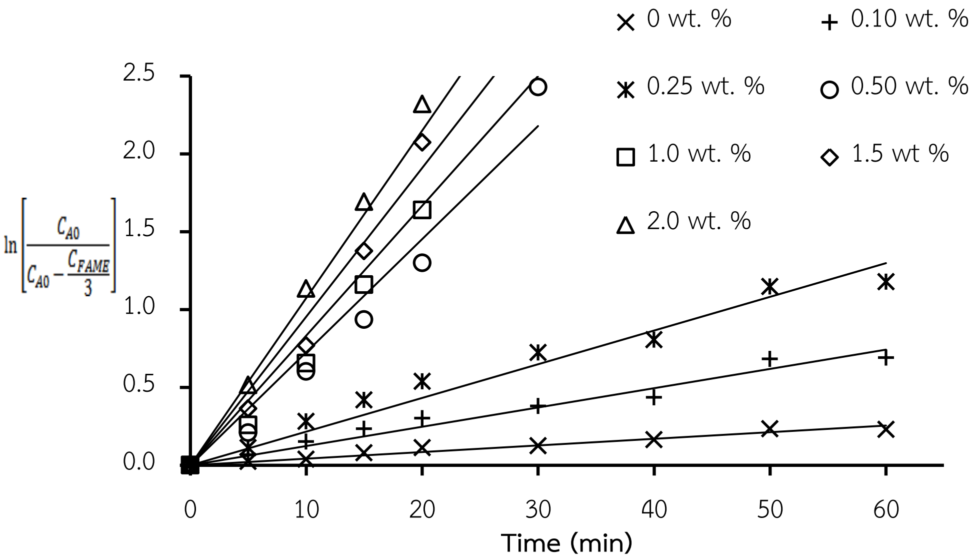


Figure 4. 44 Effect of catalyst amount on FAME yield. Amount of Na_3PO_4/Al_2O_3: equivalent to 0–2.0 wt.% Na_3PO_4. Agitation speed: 1000 rpm. Temperature: 210 ℃. Molar ratio of methanol/oil: 18:1.



(a) Plot of un-methyl ester concentration versus time.



(b) Initial rate of reaction.

Figure 4. 45 Effect of catalyst amount. Agitation speed: 1000 rpm. Molar ratio of methanol/oil: 18:1. Temperature: 210°C. Amount of Na_3PO_4/Al_2O_3 equivalent to 0.5-2.0 wt.% Na_3PO_4. (a) Un-methyl ester concentration (mono-, di-, tri-glyceride) versus time. (b) Initial rate of reaction from 0-60 minutes.

4.8.5 Catalyst degradation

The main problem of heterogeneous catalysts is the dissolution of active component into the reaction products. Catalyst degradation can be caused by the presence of polar substances such as methanol, water, free fatty acid, and glycerol, which can dissolve the active component [142]. In addition, the leaching of catalyst is dependent upon the reaction conditions, and the degree of leaching affects the catalyst's reusability as well as the quality of final product. From an economic point of view, the separation and reuse of catalysts in consecutive batches is of great importance for industrial applications.

To study catalyst reusability, the experiments were performed at a mixing speed of 1000 rpm, the methanol to oil molar ratio of 18:1, the temperature of 210°C, and a catalyst amount equivalent to 1.0 wt.% of Na_3PO_4/Al_2O_3. The experiments were conducted for 240 minutes. In this work, we explored the leaching of catalyst and catalyst reusability under relevant reaction conditions. At the end of each transesterification reaction, the catalyst was separated the reaction mixture, and the catalyst was further used in subsequent runs without regeneration. Five consecutive reactions were performed using the same catalyst and reaction conditions. Figure 4.46 compared the methyl ester content as a function of time for various runs, Figures 4.47 (a) showed the un-methyl ester concentration as a function of time and Figure 4.47 (b) showed the rate of initial time.

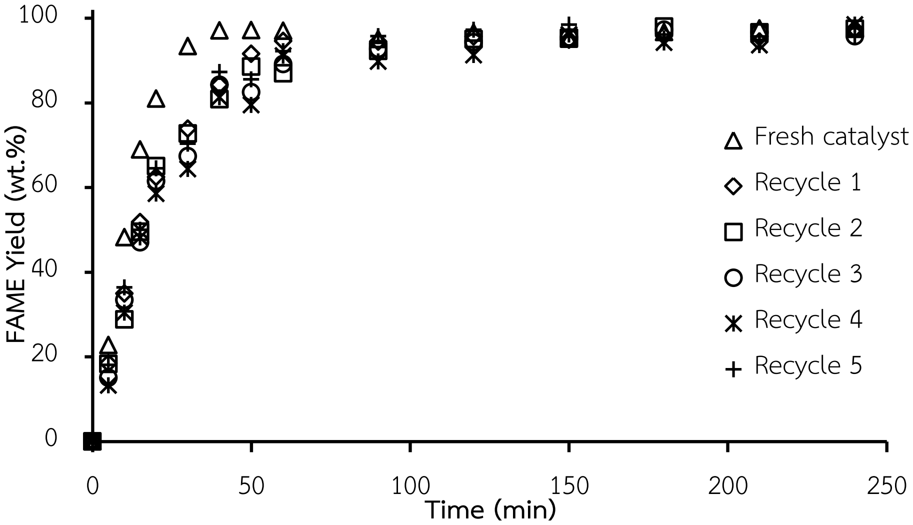
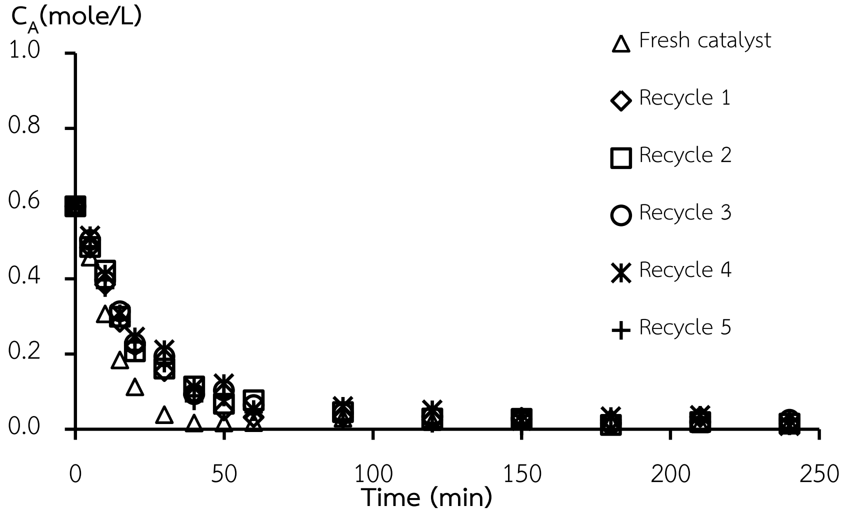
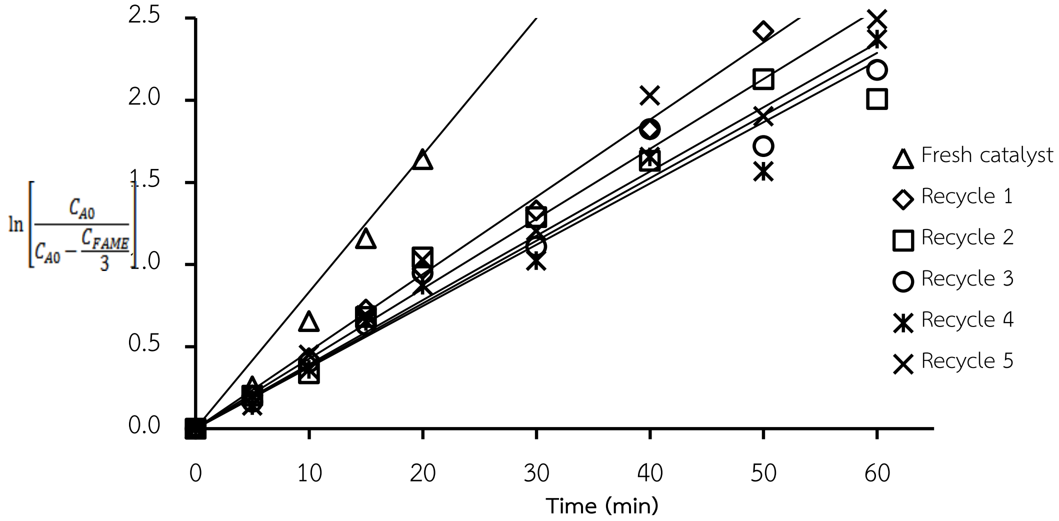


Figure 4. 46 The catalyst reusability. Agitation speed: 1000 rpm. Methanol/oil molar ratio: 18:1. Temperature: 210 °C. Amount of Na_3PO_4/Al_2O_3 equivalent to 0.5 wt.% Na_3PO_4.



(a) Plot of un-methyl ester concentration versus time.



(b) Initial rate of reaction.

Figure 4. 47 Catalyst reusability. Agitation speed: 1000 rpm. Molar ratio of methanol/oil: 18:1. Temperature: 210°C. Amount of Na_3PO_4/Al_2O_3 equivalent to 0.5 wt.% Na_3PO_4. (a) Un-methyl ester concentration (mono-, di-, tri-glyceride) versus time. (b) Initial rate of reaction from 0-60 minutes.

As the catalyst was recycled, a significant drop in methyl ester content was observed between the first and second runs. Slightly differences in methyl ester content were observed for subsequence runs. However, this initial drop in catalyst activity is likely due to leaching of sodium into the product, however this is a very small quantity [142].

The reaction products collected at the end of each reaction were further analyzed for sodium and phosphorus using ICP-OES. Table 4.7 shows the amount of catalyst leached into the reaction products at the end of reaction. When analyzing catalyst solubility in the reaction products, sodium and phosphorus were analyzed together. This catalyst stability is likely due to the bonding of Na and P to the alumina structure to form Na-P-Al, as shown in FT-IR results.

This is much cause from the small amount of Na leached into the product. Despite the leaching, the catalyst maintained a FAME yield higher than 95 % after six cycles without regeneration. The slight decrease of catalytic activity during the repeated experiments might be due to some adsorbed intermediates, methyl esters and glycerol on the catalyst surface and in catalyst pores. The elemental analyst was confirmed that a very small amount of Na, P leached from the solid phases. The catalyst stability from phase change of attached from Na and P have boned with alumina structure to Na-P-Al, as shown in Fig. 4.34, FT-IR spectra of phosphate adsorbed onto alumina, that is very strong, and very stable in transesterification reaction. The ICP results showed support this hypothesis. In Table 4.7 indicated that slightly dissolved of Na compared to the fresh run, but the result not found P.

Table 4. 7 Catalyst leaching under reaction condition.

Run	Catalyst leaching (mg/kg)	
	Na	P
Fresh run	85.27	< 1
Recycle-1	55.37	< 1
Recycle-2	47.93	< 1
Recycle-3	37.42	< 1
Recycle-4	36.99	< 1
Recycle-5	30.15	< 1

Many previous work have been reported about the deterioration of catalyst. Verziu et al. [108] studied transesterification using mesoporous alumina supported alkaline fluorides, they showed that the conversion drop after 6th runs caused from glycerol covering the surface of catalyst. It was reported that the activity of powdered alumina supported catalyst such as, KI, KF, HNO_3, KCO_3, $NaNO_3$, were reduced after successive reuse due to the leaching of active species during reaction [37, 42, 50, 108, 143]. Alonso et al. [50] showed that 85 wt.% of K leached after 4th runs. They concluded that the leaching of K caused by alcohol and formed of bicarbonate. Wan et al. [103] also studied transesterification using $NaAlO_2$, the results showed slight decrease in catalytic activity by repeating the transesterification for 3 times. They summarized the reaction contained homogeneous and heterogeneous in the same time. Liu et al. [105] synthesized a CaO/KF, they found the leakage of K and Ca to the water and methanol and the occupation of active sites by oleic acid were the main reasons for decrease of triglyceride conversion during repeated use of the catalyst. However, about 3.0 and 1.5 mg of F were dissolved into methanol and glycerol.

Technical analysis by SEM showed in Figure 4.48, compared to alumina and the new catalyst, the recycled catalyst is convex. This phenomenon may due to products clogging the catalyst pores. Such clogging could explain why the recycled catalyst does not perform as well as the fresh catalyst. Because catalysts have a highly porous surface area, the molecular size of the substrate is an important consideration for catalyst design.

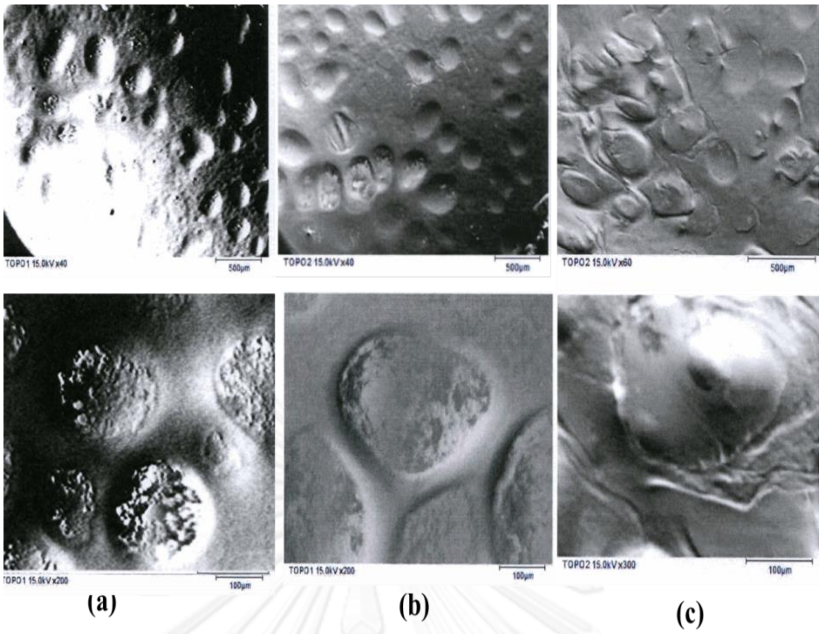


Figure 4. 48 SEM-images of the samples, Al_2O_3 (a), fresh Na_3PO_4/Al_2O_3 (b), and spend Na_3PO_4/Al_2O_3 (c).

According to Fernandez et al [45], the critical diameter, defined as the diameter of the smaller cylinder through which a molecule can pass without distortion, of a triglyceride molecule is approximately 2 nm. Lopez G. et al. [135] reported that methyl oleate has a diameter approximately 2.5 nm, and the diameter of triglycerides is at least two time larger. The preparation of alumina - supported catalyst should therefore have a pore size greater than the triglyceride molecule's critical diameter. The use of meso-structured supports has been shown to improve catalyst performance compared to micro-structured supported, as the larger pores in the meso-structured supports likely reduce mass transfer resistance [47, 48].

4.9 Comparison of Na_3PO_4 in powdered form and prepared on Al_2O_3

In this section, a comparative analysis of the catalyst in two different catalysts forms, in powder form of Na_3PO_4 and prepared on Al_2O_3–supported catalyst. By comparing two forms of catalyst on the reaction rate, the variables such as the agitation speed, the methanol to oil molar ratio, the reaction temperature and the catalyst amount, were compared using the best reaction condition of both systems.

4.9.1 Comparison of the effect of agitation speed

Comparison of agitation speed on the rate of reaction, of the catalyst in powdered form and the catalyst prepared on alumina. The experimental conditions, at the agitation speed of 600 rpm, the methanol/oil molar ratio of 18:1, the reaction temperature of 190 °C, and the catalyst amount of 0.5 wt. % of Na_3PO_4. Then, plot a graph comparing the effect of the speed of the catalyst in two forms, powder form of Na_3PO_4 and Na_3PO_4/Al_2O_3. Figure 4.49 shows the comparison of methyl ester product, Figure 4.50 (a) shows the comparison of un-methyl ester concentration (mono-, di-, tri-glycerides) decreases versus time, and Figure 4.50 (b) shows the rate of reaction at initial time from 0-60 minutes.

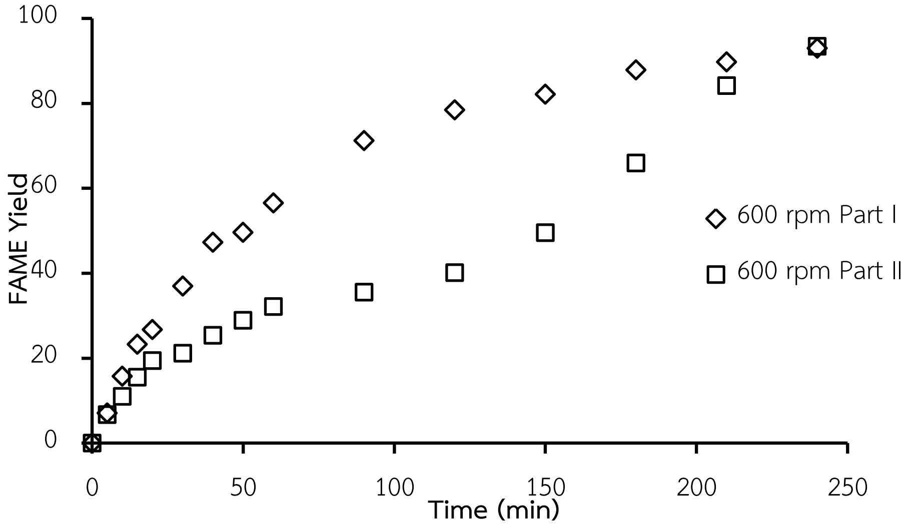


Figure 4. 49 Compares the effect of agitation speed on FAME yield, of Na_3PO_4 in powdered form and Na_3PO_4/Al_2O_3. The molar ratio of methanol/oil: 18:1. Temperature: 190°C. Catalyst amount: 0.5 wt.% Na_3PO_4.

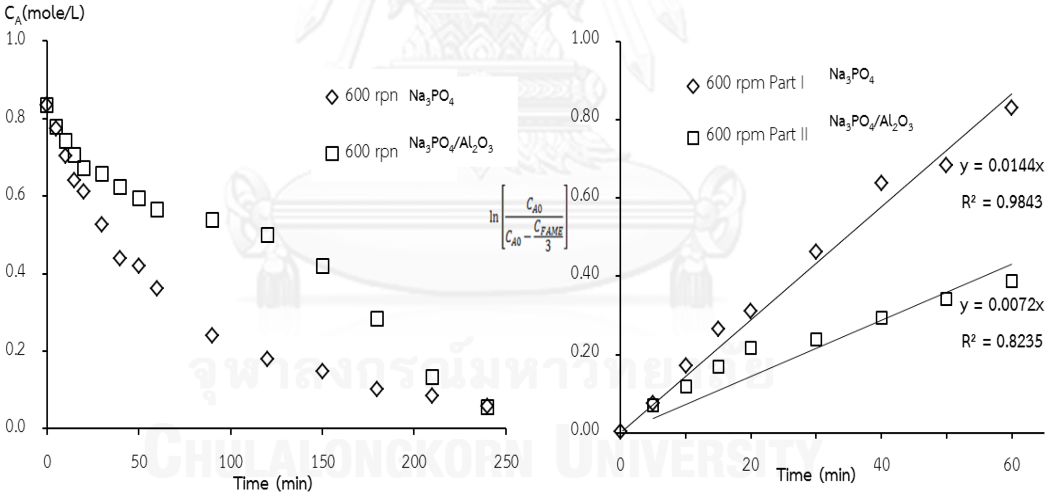


Figure 4. 50 Compares the effect of agitation speed on FAME yield of Na_3PO_4 in powdered form and Na_3PO_4 prepared on Al_2O_3.

In heterogeneous system, the external mass transfer resistance is high. In order to reduce the external mass transfer resistance can be achieved by increasing the speed of agitation until the overall reaction rate was not affected by the external mass transport. From Figure 4.49-4.50, it can be seen in the system using

Na_3PO_4/Al_2O_3, the rate of reaction is slower than the system using powdered form of Na_3PO_4. The study found that the shape of catalyst is strongly affected the external mass transfer, it has been reported that a big shape of catalyst cause to higher mass transfer resistance than a small shape [144]. Hence, a big shape of catalyst used higher mechanical speeds to reduce the mass transfer resistance term, until the speed does not further influence the reaction rate. Data plotted in Figure 4.5-4.52, compares the agitation speeds of 2 forms of catalyst. It can be seen that agitation speed of 600 rpm is enough to eliminate the mass transfer resistance of the catalyst in powdered form. In case of Na_3PO_4/Al_2O_3, the speed of 600 rpm showed a slow rate of reaction and at the speed of 1000 rpm showed the suitable speed of the experiments using Na_3PO_4/Al_2O_3, the reaction rate does not increase at a speed higher than 1000 rpm.

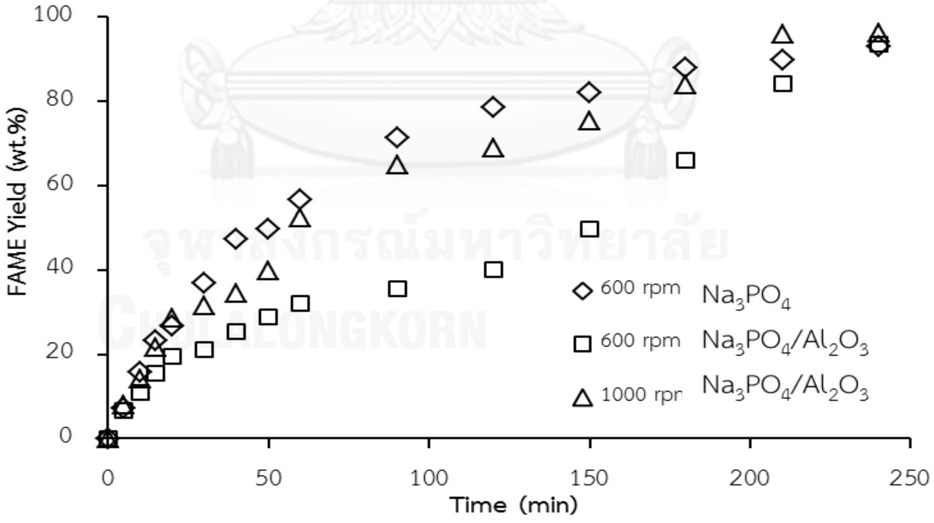


Figure 4. 51 Compares the effect of agitation speed on FAME yield of Na_3PO_4 in powdered form and Na_3PO_4 prepared on Al_2O_3. Molar ratio of methanol/oil: 18:1. Temperature: 190°C. Amount of catalyst: 0.5 wt.% Na_3PO_4.

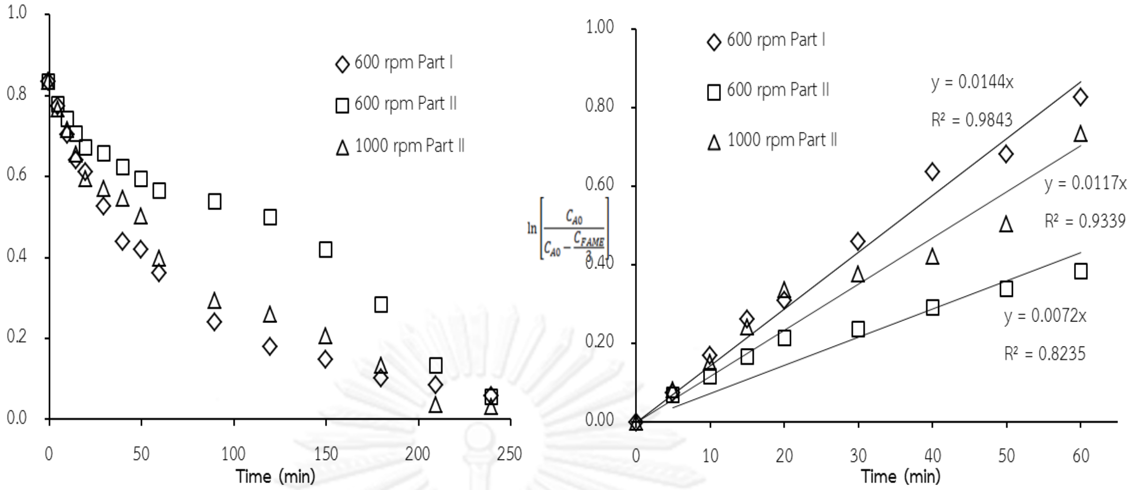


Figure 4. 52 Plot of the effect of agitation speed of Na_3PO_4 in powdered form and Na_3PO_4 prepared on Al_2O_3, (a) concentration versus time, and (b) initial rate of reaction.

The previous research have done by Viola et al. [145], compared of the use of CaO, SrO and K_3PO_4 in powdered form and pellet. They concluded that at three hours of the operating time, the yield of catalyst in powdered form and granular are not different, and longtime of operating condition obtained the same yield. The system will approach the equilibrium conversion at the same value.

4.9.2 Comparison of the effect of methanol/oil molar ratio

Comparison of the effect of methanol to oil molar ration between powdered form of Na_3PO_4 and the prepared Na_3PO_4/Al_2O_3 was analyzed under the methanol/oil molar ratio of 18:1, the amount of Na_3PO_4 of 0.5 wt.%, the reaction temperature of 190 °C, the agitation speed of 600 rpm of powdered form of Na_3PO_4 and 1000 rpm of Na_3PO_4/Al_2O_3. The comparison is shown in Figure 4.53-4.54 (a, b), compares the methyl ester product, compares the un-methyl ester concentration (a), compares the rate of reaction (b).

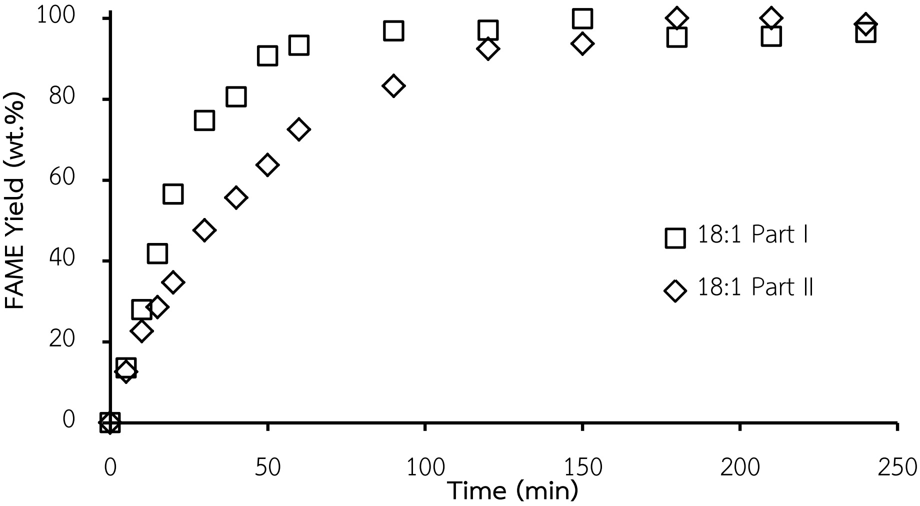


Figure 4. 53 Compares the effect of methanol/oil molar ratio on FAME yield of Na_3PO_4 in powdered form and Na_3PO_4 prepared on Al_2O_3. Molar ratio of methanol/oil: 18:1. Temperature: 210°C. Amount of catalyst: 0.5 wt.% Na_3PO_4.

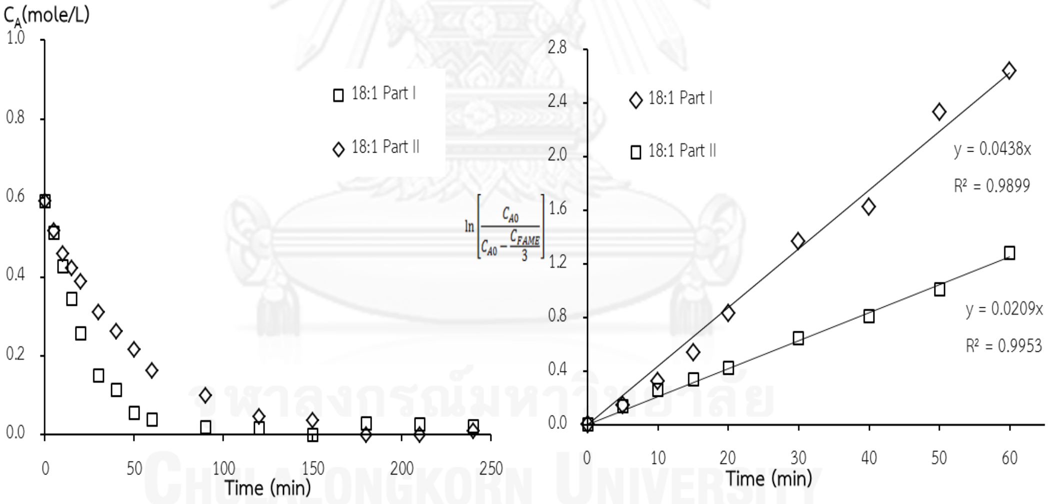


Figure 4. 54 Plot of the effect of molar ratio of methanol/oil of Na_3PO_4 in powdered form and Na_3PO_4 prepared on Al_2O_3. Molar ratio of methanol/oil: 18:1. Temperature: 190°C. Amount of catalyst: 0.5 wt.% Na_3PO_4. (a) Un-methyl ester concentration (mono-, di-, tri-glycerides) versus time. (b) Initial rate of reaction from 0-60 minutes.

The rate reaction was faster at initial step of reaction, however, the system approach the equilibrium conversion at the same value. In powdered form of Na_3PO_4, the equilibrium time was 60 minutes, and 120 minutes for Na_3PO_4/Al_2O_3. But, when compares the equilibrium yield of the system used Na_3PO_4 and Na_3PO_4/Al_2O_3, showed the same value. According research of Viola et al. [145], compare the system used powdered form of catalyst and pellet. They found that the pellet catalyst obtained the equilibrium conversion at 3 hours. The big shape of catalyst affected mass transfer resistance, resulted in low reaction rate.

4.9.3 Comparison of the effect of reaction temperature

Comparison of the effect of reaction temperature on the rate of reaction using the powdered form of Na_3PO_4, and the prepared Na_3PO_4/Al_2O_3, was compared under the methanol/oil molar ratio of 18:1, the reaction temperature of 210 °C, the catalyst amount of 0.5 wt.% of Na_3PO_4. The agitation speed was 600 rpm, and 1000 rpm for Na_3PO_4, and Na_3PO_4/Al_2O_3, respectively. The comparison results are shown in Figure 4.55, compare of FAME product, Figure 4.56 (a), compare of un-methyl ester concentration, and Figure 4.56 (b), compare of the rate of reaction.

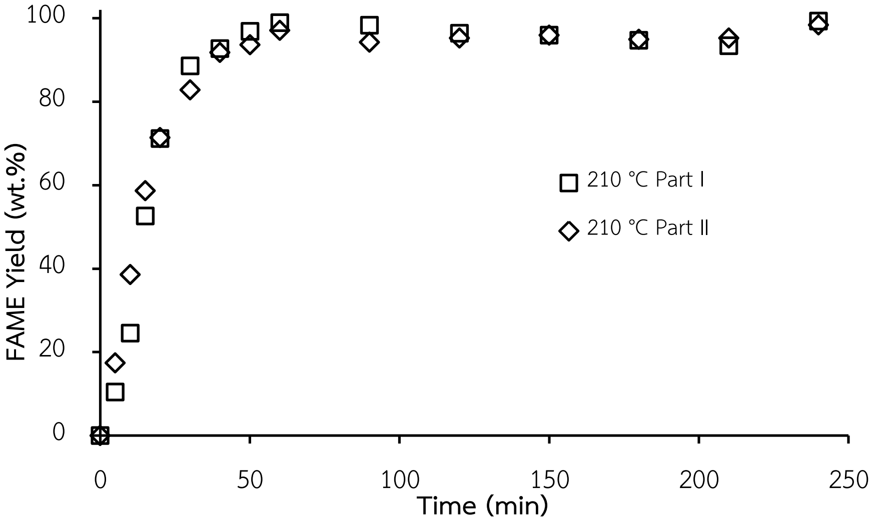


Figure 4. 55 Plot of the effect of molar ratio of methanol/oil of Na_3PO_4 in powdered form and Na_3PO_4 prepared on Al_2O_3, (a) concentration versus time, and (b) initial rate of reaction.

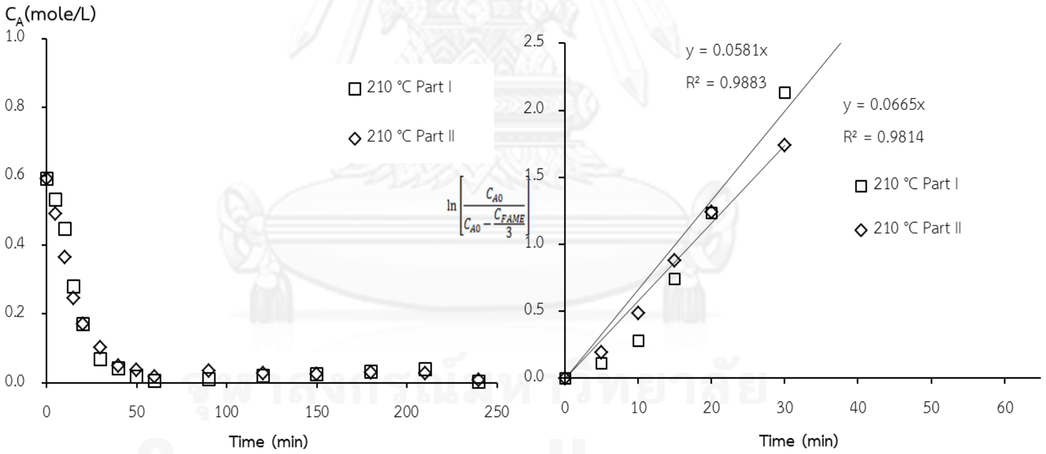


Figure 4. 56 Plot of the effect temperature of Na_3PO_4 in powdered form and Na_3PO_4 prepared on Al_2O. Molar ratio of methanol/oil: 18:1. Temperature: 190°C. Catalyst amount: 0.5 wt.% Na_3PO_4. (a) Un-methyl ester concentration (mon-, di-, tri-glyceride) versus time. (b) Initial rate of reaction from 0-60 minutes.

It can be seen that at the reaction temperature of 210 °C, the formation of FAME product on time are shown no difference. The results showed that at a temperature of 210 °C, the shape of the catalyst affected slightly on the rate of reaction, due to at high reaction temperature the mass transfer resistance had a very little effect. Saka et al. have been reported that a non-polar of triglycerides can be dissolved well with polar of alcohol to form single phase of reactants, result in the shape of catalyst is not affected on the rate of reaction anymore.

4.9.4 Comparison of the effect of catalyst amount

Comparison of the effect of catalyst amount on the rate of reaction of Na_3PO_4, and Na_3PO_4/Al_2O_3 was compared under the methanol/oil molar ratio of 18:1, reaction temperature of 210 °C with 0.5 wt.% of catalyst. The agitation speed was 600 rpm, and 1000 rpm, of Na_3PO_4 and Na_3PO_4/Al_2O_3, respectively. The comparison results are shown in Figure 4.57, compared of FAME product from 0-240 minutes, Figure 4.58 (a), compared of concentration, and Figure 4.58 (b), compared of the initial rate of reaction.

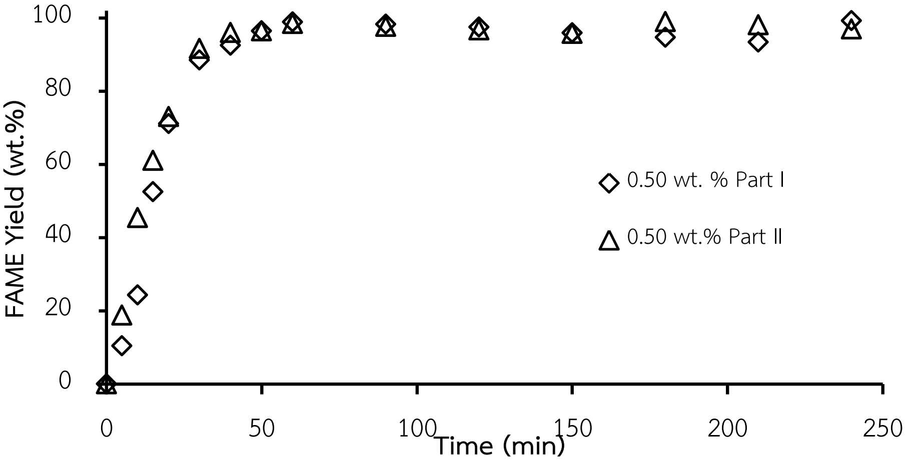


Figure 4. 57 Compares the effect of catalyst amount on FAME yield of Na_3PO_4 in powdered form and Na_3PO_4 prepared on Al_2O_3. Molar ratio of methanol/oil: 18:1. Temperature: 190°C. Amount of catalyst: 0.5 wt.% Na_3PO_4.

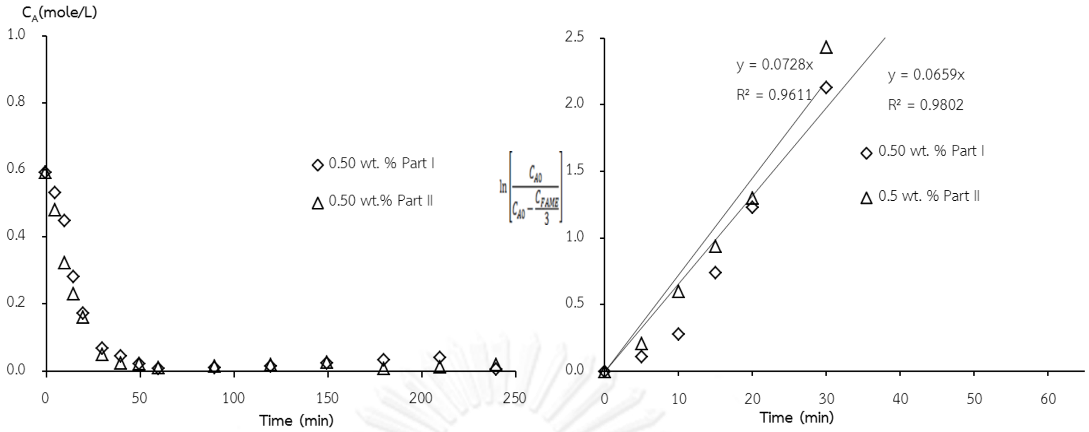


Figure 4. 58 Plot of the effect of catalyst amount of Na_3PO_4 in powdered form and Na_3PO_4 prepared on Al_2O_3. Molar ratio of methanol/oil: 18:1. Temperature: 190°C. Amount of catalyst: 0.5 wt.% Na_3PO_4. (a) Un-methyl ester concentration (mono-, di-, tri-glyceride) versus time. (b) Initial rate of reaction from 0-60 minutes.

It can be seen that at the compared conditions, the reaction rate of two systems occurred similar. The results showed in accordance to the comparison of effect of reaction temperature, which concluded that at 210 °C the polar methanol can be dissolved well in non-polar triglyceride, resulting in high reaction rate.

4.10 Fuel properties of the synthesized biodiesel

Table 4.8 shows the physical and fuel properties of the biodiesel produced from palm olein via the transesterification with methanol over Na_3PO_4/Al_2O_3. The quality of fuel was determined according to standard of diesel fuel and biodiesel issued by the department of Energy Business, Ministry of Energy of Thailand.

Table 4. 8 Comparison of the properties of biodiesel produced in this work with the standards of diesel fuel.

Properties	Standard	Method	Biodiesel in this work
Methyl ester (wt.%)	min 96.5	EN14103-11	98.1
Mono-glyceride (wt.%)	max 0.8	EN14105	0.37
Di-glyceride (wt.%)	max 0.2	EN14105	0.13
Tri-glyceride (wt.%)	max 0.2	EN14105	0.14
Free glycerin (wt.%)	max 0.02	EN14105	0.01
Total glycerin (wt.%)	max 0.025	EN14105	0.14
Cetane number	min 51	ASTM D6890	81
Flash Point PM (°C)	min 120	ASTM D93	169
Density, 15°C (kg/m^3)	860 - 900	ASTM D405	875
Cloud point (°C)	-	ASTM D5771	11
Iodine value (g Iodine/100g)	max 120	EN1411	38
Heating Value (Gross)		ASTM D240	39,933 J/g

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This dissertation has described studies of the catalytic activity of sodium phosphate as a heterogeneous catalyst for transesterification reaction of palm olein and methanol. The catalysts were tested in this work are prepared in powder form and facilitated on a big shape, extrudes industrial form. The powder form and the prepared catalyst were mean by XRD, FT-IR, SEM-EDX, TGA, and ICP-OES.

The results sodium phosphate in powder form can be used effectively as a heterogeneous catalyst. It was found that the rate of reaction depends on the reaction conditions, such as the molar ratio of methanol/oil, the operating temperature, and the amount of catalyst used. Increasing the molar ratio of methanol/oil results in a faster rate of reaction, but at ratios higher than 18:1, the reaction rate is identical. Higher operating temperatures tend to accelerate the rate of reaction but reduce the glycerol by-product quality. The addition of even a small amount of catalyst into the system significantly increased FAME yields. Under study conditions, such as an agitation speed of 600 rpm, methanol/oil molar ratio of 18:1, reaction temperature of 210°C and 1 wt.% Na_3PO_4, nearly complete conversion occurred with 30 minutes. The presence of water and FFAs affect the system during the initial stages of the reaction, but they do not reduce the yield of FAME at equilibrium. When large amounts of methanol were used, the experimental results agreed with the irreversible 1st order kinetic model, and the activation energy was found to be 43.60 kJ/mol palm olein.

This research showed sodium phosphate is a potential catalyst for use in transesterification reactions, since it insoluble in the reaction mixtures. However, powder form is difficult to separate from the reaction product, the preparation of Na_3PO_4 in the commercially useful forms to facilitate the separation of the solid phase from the reactants and products. In this work, Na_3PO_4 was prepared on a big shape in order to easy separate from the reaction product at the end of reaction. Alumina loaded with sodium phosphate, which was prepared by incipient-wetness impregnation on ¼ inch-alumina extrudates support with an aqueous solution of Na_3PO_4 followed by calcination at 500°C in air. The prepared catalyst was continue to test its catalytic activity in transesterification reaction of palm olein and methanol, Na_3PO_4/Al_2O_3 was tested its catalytic activity. Under the study condition with agitation speed of 1000 rpm, methanol/oil molar ratio of 18:1, temperature of 210°C, the amount of catalyst 1.0 wt.% of Na_3PO_4/Al_2O_3, the catalyst show high catalytic activity with 96% of product yield in 30 minutes. After the reaction, the prepared catalyst was separated easily from the reaction products.

The catalyst reused for 5 recycles showed the FAME content at initial time drops significantly from fresh run, but for the next run is showed slightly drop, compared with the fresh run. However, the catalyst is still showed high FAME yield even though 5 recycle. The leaching of catalysts into products was analyzed by IC-OES, the results found a small amount of sodium in the product sample but not found the phosphorus. The phosphate adsorbed on alumina formed by salt-support interaction was probably the main reasons for the strong bonds between support and the catalyst. This work can be summarized that sodium phosphate is a promising catalyst with anti-leaching even though at high reaction temperature, high conversion is achieved even after 5 recycles.

5.2 Recommendation

Our research showed sodium phosphate is a potential catalyst for use in transesterification reactions because it does not dissolve in the reaction mixtures. However, in powdered form is difficult to separate from the reaction product. Our work further performed on the preparation of Na_3PO_4 in the commercially useful forms of rings to facilitate the separation of the solid phase from the reactants and products. The prepared Na_3PO_4/Al_2O_3 showed both high activity and good stability for the transesterification reaction. It could be used in a continuous production process.

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APPENDIX

Appendix A
Sample of calculation

Characterization of palm olein oil

Palm olein used in this research is analyzed it physical properties and fatty acid composition.

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

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

Apparatus

Oil sample bottles 250 ml Erlenmeyer flasks.

Reagents

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

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

FFA range (%)	Sample (g)	Alcohol (ml)	Strength of alkali
0.0 to 0.2	56.4 ± 0.2	50	0.1 N
0.2 to 0.1	28..2 ± 2.2	50	0.1 N
1.0 to 3.0	7.05 ± 0.05	75	0.25 N
30.0 to 50.0	7.05 ± 0.05	100	0.25 N 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 $^{\circ}$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.

Calculation

1. The percentage of free fatty acids in the most types of fats and oils is calculated as palmitic acid, in term of palm oil.

   Free fatty acids as palmitic, % = $\frac{\text{ml of alkali x N x 25.6}}{\text{mass,g of sample}}$
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, 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% toluene and iso-propanol molar ratio 1:1 add 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 potassium hydroxide used = v

Normality of potassium hydroxide = N

Molecular weight of the fatty acids = M

Acid value of palm olein oil

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

$$\text{Acid Value} = \frac{56.1\ x\ 0.10\ x\ 1.3}{10}$$

Acid value = 0.7 milligram KOH/g.oil

A-3 Saponification Value, AOCS Recommended Cd 3a-94

Definition: The saponification value (SV) is the amount of alkali necessary to saponify a definite of the sample. It is expressed as the mg of potassium hydroxide (KOH) required 1 g of the sample.

Scope: The saponification value is calculated from the normalized fatty acid composition determined by gas-liquid chromatography (Notes, 1). The method may be applied to all normal fats and oils, including linseed oil, provided they contain low concentrations of free fatty acids (≤0.1%) and mono- and diglycerides (≤0.1%). To meet this specification a freshly deodorized oil would have to be chromatographically fractionated over 5 % water-deactivated silica gel to isolate the pure triglyceride fraction. The method is not directly applicable to fats and oils having a large un-saponifiable fraction.

Procedure

Determine the normalized fatty acid composition (FAC) of the sample by accepted, validated methodology, e.g., AOCS Official Methods Ce 1-62, Cd 1c-89 or Ce 1e-91.

Calculation

1. Determine the fractional molecular weight of each fatty acid in the sample by multiplying the fatty acid percentage (divided by 100) by its molecular weight.
2. Saponification value, $SV = \frac{3\ X\ 56.1\ X\ 1000}{[(m\ m\ wt\ X3) + 92.09] - (3X18)}$

   where m wt. = mean molecular weight (sum of fractional) weights, determined as noted in Calculations, 1, of all fatty acids in the sample.

   56.1 = molecular weight of KOH

   92.09 = molecular weight of glycerol

Example

From fraction of soybean oil calculated following AOCS Recommended Cd 3a-94 $C_{16:0}$ (10.6%), C18:0 (4.2%), C18:1 (22.7%), C18:2 (54.5%), C18:3 (8.0%), the m m wt of the fatty acids is 278.36 and,

$$\text{Saponification value, SV} = \frac{3\ X\ 56.1\ X100}{[(278.36)\ X\ 3) + 92.09 - (3*18)} = \frac{168{,}300}{873.17} = 192.8$$

Note: The method has not been applied to fatty acid composition data based on mass/mass.

The average fatty acid calculated in this work is 271.86 (Data from Table A-2).

$$\text{Sponification value, SV} = \frac{3\ X\ 56.1\ X100}{[(271.86)\ X\ 3)+92.09-(3*18)} = \frac{168{,}300}{873.08} = 197.07$$

Table A-2 FAC of palm olein

FFA	Structure	FAC, wt.%	MW
Lauric	12:0	0.53	200.3
Myristic	14:0	1.04	228.4
Palmitic	16:0	38.67	256.4
Palmitoleic	16:1	0.23	254.4
Stearic	18:0	4.10	284.4
Oleic	18:1	42.90	282.45
Linoleic	18:2	10.92	280.45
Linolenic	18:3	0.24	278.43
Arachidic	20:0	0.35	312.54
Behenic	22:0	0.80	340.59
Eracic	22:1	0.22	338.57

A-4 Molecular weight of palm olein

Table A-3 The molecular weight of palm olein is calculated by the following method

FFA	Structure	FAC, wt.%	MW	Avg. of MW
Lauric	12:0	0.53	200.3	338.09
Myristic	14:0	1.04	228.4	751.09
Palmitic	16:0	38.67	256.4	31175.75
Palmitoleic	16:1	0.23	254.4	184.05
Stearic	18:0	4.10	284.4	3649.82
Oleic	18:1	42.90	282.45	37938.62
Linoleic	18:2	10.92	280.45	9591.58
Linolenic	18:3	0.24	278.43	209.35
Arachidic	20:0	0.35	312.54	341.12
Behenic	22:0	0.80	340.59	847.02
Eracic	22:1	0.22	338.57	231.60
		SUM		**85258.07**
		Average of molecular weigh		**852.58 gmol^{-1}**

The molecular weight calculated from this research was 852.58 gmol^{-1}.

Appendix B

Calculation of concentration of methyl ester

B-1 Response factor of methyl ester

The response factor is defined as:

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

Response factor calculations are based on the data from the chromatograph of standard methyl esters. Respond Factor calculation of FAME:

$$\text{Response of methyl caprylate} = \frac{226989 \times 8.0}{250252 \times 8.0}$$

R. F. of methyl caprylate = 0.91

$$\text{Response of methyl laurate} = \frac{256235 \times 8.0}{250252 \times 8.0}$$

R. F. of methyl laurate = 1.02

$$\text{Response of myristate} = \frac{261436 \times 8.0}{250252 \times 8.0}$$

R. F. of methyl myristate = 1.04

$$\text{Response of methyl palmitate} = \frac{375779 \times 8.0}{250252 \times 11.0}$$

R. F. of methyl palmitate = 1.09

$$\text{Response of methyl palmitoleate} = \frac{166883 \times 8.0}{250252 \times 5.0}$$

R. F. of methyl palmitoleate = 1.07

$$\text{Response of methyl stearate} = \frac{278608 \times 8.0}{250252 \times 8.0}$$

R. F. of methyl stearate = 1.11

Response of methyl oleic = $\frac{175389 \times 8.0}{250252 \times 5.0}$

R. F. of methyl oleic = 1.12

Response of methyl linoleate = $\frac{170485 \times 8.0}{250252 \times 5.0}$

R. F of methyl linoleate = 1.09

Response of methyl linolenate = $\frac{169017 \times 8.0}{250252 \times 5.0}$

R. F. of methyl linolenate = 1.08

Response of methyl Arachidate = $\frac{281151 \times 8.0}{250252 \times 8.0}$

R. F. of methyl Arachidate = 1.12

Response of methyl Behenate = $\frac{283725 \times 8.0}{250252 \times 8.0}$

R. F. of methyl Behenate = 1.14

Response of methyl erucate = $\frac{175267 \times 8.0}{250252 \times 5.0}$

R. F. of methyl erucate = 1.13

Response of methyl Lignocerate = $\frac{287715 \times 8.0}{250252 \times 8.0}$

R. F. of methyl Lignocerate = 1.15

Table B-1 Summary of response factor calculation of FAME

No.	Fatty acid methyl ester	Structure	RF
1	Methy Caprylic	C8:0	0.86
2	Methyl Capric	C10:0	1.00
3	Methyl Lauric	C12:0	1.02
4	Methyl Myristic	C14:0	1.05
5	Methyl Palmitic	C16:0	1.10
6	Methyl Palmitoleic	C16:1	1.07
7	Methyl Stearate	C18:0	1.12
8	Methyl Oleic	C18:1	1.13
9	Methyl Linoleic	C18:2	1.10
10	Methyl Linoleate	C18:3	1.09
11	Methyl Arachidate	C20:0	1.13
12	Methyl Behenate	C22:0	1.14
13	Methyl Erucate	C22:1	1.13
14	Methyl Lignocerate	C24:1	1.15

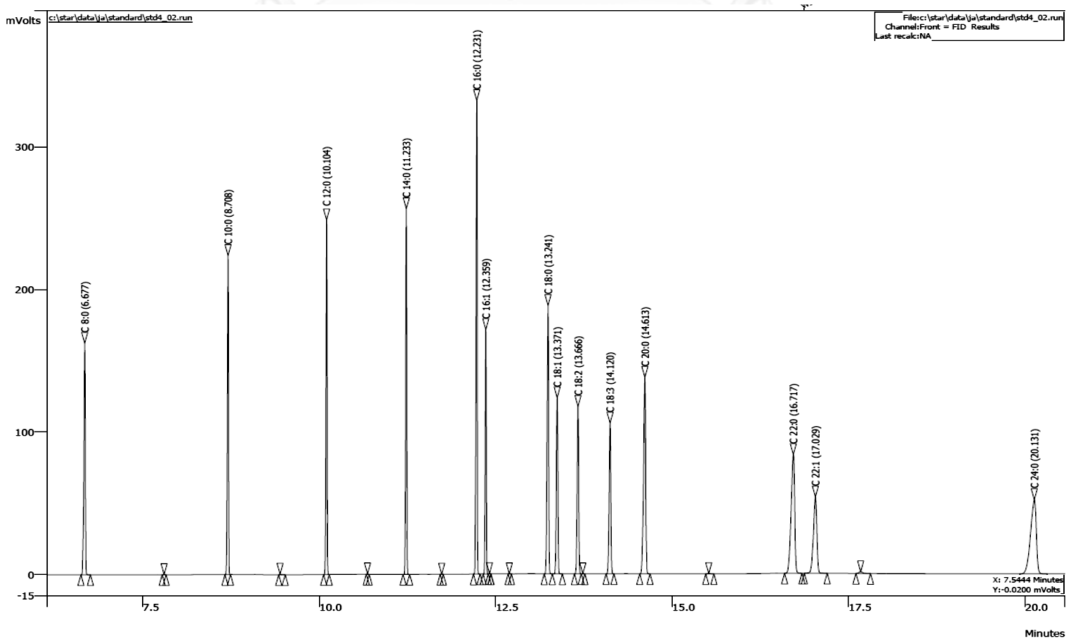
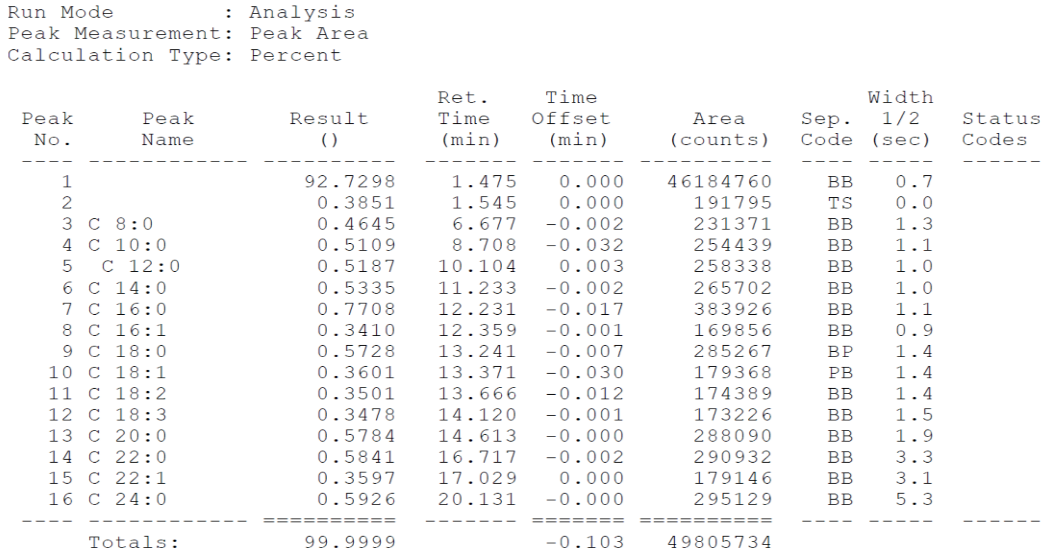


Figure B-1 Chromatogram of methyl ester in the standard at retention time



```
Run Mode          : Analysis
Peak Measurement: Peak Area
Calculation Type: Percent

                                    Ret.    Time                       Width
 Peak       Peak        Result      Time   Offset       Area     Sep.   1/2   Status
  No.       Name          ()        (min)   (min)     (counts)   Code  (sec)  Codes
 ---- ------------ ----------    ------- -------- ----------   ---- -----  ------
    1                 92.7298     1.475    0.000   46184760     BB    0.7
    2                  0.3851     1.545    0.000     191795     TS    0.0
    3 C 8:0            0.4645     6.677   -0.002     231371     BB    1.3
    4 C 10:0           0.5109     8.708   -0.032     254439     BB    1.1
    5  C 12:0          0.5187    10.104    0.003     258338     BB    1.0
    6 C 14:0           0.5335    11.233   -0.002     265702     BB    1.0
    7 C 16:0           0.7708    12.231   -0.017     383926     BB    1.1
    8 C 16:1           0.3410    12.359   -0.001     169856     BB    0.9
    9 C 18:0           0.5728    13.241   -0.007     285267     BP    1.4
   10 C 18:1           0.3601    13.371   -0.030     179368     PB    1.4
   11 C 18:2           0.3501    13.666   -0.012     174389     BB    1.4
   12 C 18:3           0.3478    14.120   -0.001     173226     BB    1.5
   13 C 20:0           0.5784    14.613   -0.000     288090     BB    1.9
   14 C 22:0           0.5841    16.717   -0.002     290932     BB    3.3
   15 C 22:1           0.3597    17.029    0.000     179146     BB    3.1
   16 C 24:0           0.5926    20.131   -0.000     295129     BB    5.3
 ---- ------------ ==========    ------- ======= ==========   ---- -----  ------
      Totals:         99.9999             -0.103   49805734
```

Figure B-2 Peak area of standard

B-2 Analysis of Methyl Ester

To Analysis of methyl ester in the product sample is by using gas chromatography (GC). The retention time of the products is different. To identify the type of methyl by compare the retention time with standard FAME mixed from Supleco. The retention time of sample are shown in Table B-2, and chromatogram of sample and standard are shown in Figure. 1, and Figure. 2.

Example B-2: Methyl ester calculation

Methyl decanoate used as internal standard for methyl esters calculation and n-heptane used as solvent. Stock solution of internal standard solution was prepared in ratio 20:1(wt.%). Weighing the solution 1.0 g and the sample 0.1 g. Then mixed well and to continues analysis by GC method. Unit of calculation are gram to calculate % yield.

$$\text{Yield of Fatty Acid Methyl Ester (FAME)} = \frac{\sum \text{Wt.of FAME (g)}}{\text{Wt. of sample (g)}} \text{ X } 100\ \%$$

Table B-2 Retention time of methyl esters

	Structure	Peak identified with standard
1.475	C_7H_{10}	N-heptane (solvent)
5.645	C8:0	Methyl Caprylate
8.124	C10:0	Methyl Decanoate (Internal Standard)
9.556	C12:0	Methyl Laurate
10.722	C14:0	Methyl Myristate
11.728	C16:0	Methyl Stearate
11.845	C16:1	Methyl Linoleate
12.639	C18:0	Methyl Stearate
12.735	C18:1	Methyl Oleic
12.956	C18:2	Methyl Linoleate
13.299	C18:3	Methyl Linolenate
13.710	C20:0	Methyl Arachidate
15.260	C22:0	Methyl Behenate
15.469	C22:1	Methyl Erucate
16.50	C24:0	Methyl Lignocerate

Table B-3 Sample of Calculation of FAME products

FAME Product	Peak Area	FAME (g)	FAME (wt.%)	RF	FAME/RF (wt.%)
C10:0	1811862	-	-	1	-
C12:0	22070	0.00059	0.544	1.02	0.534
C14:0	43960	0.00119	1.084	1.05	1.033
C16:0	43960	0.04638	42.38	1.10	38.58
C16:1	8042	0.00022	0.198	1.07	0.19
C18:0	186124	0.00502	4.591	1.12	4.10
C18:1	1961680	0.05288	48.393	1.13	42.83
C18:2	485478	0.01309	11.976	1.10	10.89
C18:3	10810	0.00029	0.267	1.09	0.25
C20:0	16126	0.00044	0.398	1.13	0.35
C22:0	37004	0.00100	0.913	1.14	0.80
C22:1	37004	0.00027	0.245	1.12	0.22
Sum	6320151	0.12140	111.05		99.87 %

B-3 Basic Strength

The basic strength of the catalyst (H_) was determined following Hammett indicator method to qualitatively measure the base amount. The Hammett indicators were used:

Table B-4 Basic Strength

Chemical	Basic Strength H_
Neutral red	6.8
Bromothymol blue	7.2
Phenolphthalein	9.3
2, 4-dinitroaniline	15.0
4-nitroaniline	18.4

Method

Approximately 100 mg of the catalysts was shaken with Hammett indicator and methanol, then left to equilibrate until no further color changes were observed. The base strength of the catalyst was defined as being stronger than the Hammett indicator if it showed a color change, but weaker if it showed no color change.

Appendix C

Sample of calculation

C-1: Properties of sodium phosphate

Molecular weight of $Na_3PO_4.12H_2O$ = 380 g/mol.

Molecular weight of Na_3PO_4 = 164 g/mole.

Solubility in water = 1.5 g/100 ml H_2O (0 ^{o}C)

= 8.8 g/100 ml H_2O (25 ^{o}C)

Density = 1.620 g/cm^3 (Anhydrous)

Melting point = 73.5 ^{o}C

Insoluble in alcohol

C-2: Summarized of the calculation

The volume of each experiment was fixed at value 800 cm^3.

Density of oil: 0.89 g/mol (25^{o}C)

Density of methanol: 0.79 g/mol (25^{o}C)

Boiling point of methanol: 64.7 ^{o}C at ambient.

Table C-1 Reaction condition using Na_3PO_4

MeOH/oil molar ratio	Oil (g)	MeOH (g)	Oil (cm^3)	MeOH (cm^3)	Weight of Na_3PO_4 (g)					
					0.10 (wt.%)	0.25 (wt.%)	0.50 (wt.%)	1.0 (wt.%)	1.50 (wt.%)	2.0 (wt.%)
3:1	631.5	71	710	90	0.63	1.58	3.16	6.32	9.47	12.63
6:1	567.5	128	638	162	0.57	1.42	2.83	5.67	8.51	11.35
9:1	515.5	175	579	221	0.52	1.29	2.58	5.16	7.73	10.31
12:1	472	213	530	270	0.47	1.18	2.36	4.72	7.08	9.44
18:1	403.5	274	453	346	0.40	1.01	2.02	4.04	6.05	8.07
24:1	352.5	319	396	403	0.35	0.88	1.76	3.53	5.29	7.05
30:1	313	354	352	448	0.31	0.78	1.57	3.13	4.70	6.26

C-3 Calculation of the catalyst loading

Example: Determinations of pore volume of Al_2O_3 using water fill into pore. The pore volume of the support was 0.87 ml/g Al_2O_3.

Example

Prepared of 50 g of Al_2O_3

The total pore is 50 x 0.87 = 43.5 cm^3.

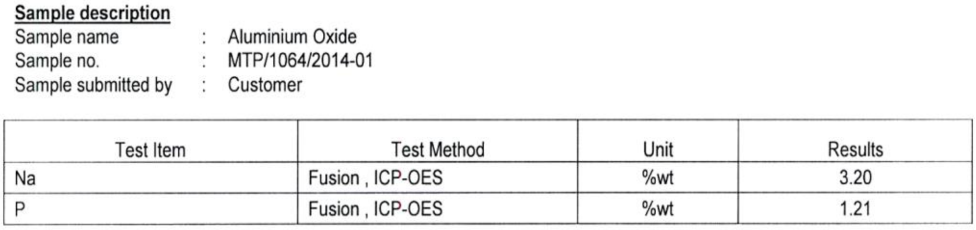
The solubility of Na_3PO_4 = 8.8 wt.% in water.

Hence, Na_3PO_4 amount = 38.28 g dissolved in DI water 43.5 cm^3

Na_3PO_4/H_2O = (8.8 x 87) /(100) = 7.656 g of Na_3PO_4 on Al_2O_3

= (7.656 x 100)/107.656 = 7.11 %

The actual loading was determined using ICP-OES as shown in figure C-1.



Sample description

Sample name : Aluminium Oxide

Sample no. : MTP/1064/2014-01

Sample submitted by : Customer

Test Item	Test Method	Unit	Results
Na	Fusion , ICP-OES	%wt	3.20
P	Fusion , ICP-OES	%wt	1.21

Figure C-1: Elemental analysis of the prepared catalyst by ICP-OES

Table C-2 Reaction condition using the prepared of Na_3PO_4/Al_2O_3

MeOH/oil molar ratio	Oil (g)	MeOH (g)	Oil (cm^3)	MeOH (cm^3)	Weight of Na_3PO_4/Al_2O_3 (g)					
					0.10 (wt.%)	0.25 (wt.%)	0.50 (wt.%)	1.0 (wt.%)	1.50 (wt.%)	2.0 (wt.%)
3:1	631.5	71	710	90	10.25	25.63	51.26	102.52	153.77	205.03
6:1	567.5	128	638	162	9.21	23.03	46.06	92.13	138.19	184.25
9:1	515.5	175	579	221	8.37	20.92	41.84	83.69	125.53	167.37
12:1	472	213	530	270	7.66	19.19	38.31	76.62	114.94	153.25
18:1	403.5	274	453	346	6.55	16.38	32.75	65.50	98.25	131.01
24:1	352.5	319	396	403	5.72	14.31	28.61	57.22	85.84	114.45
30:1	313	354	352	448	5.08	12.70	25.41	50.81	76.22	101.62

C-4 Determination of sodium phosphate in methanol

Determination of sodium phosphate in methanol is performed by the titration method.

Chemical: 1. Standard HCl solution conc. 0.5 molar

2. Methyl Orange used as an indicator
3. Sodium phosphate (Lab grade)

Equation: $3\mathrm{HCl} + \mathrm{Na_3PO_4} \xrightarrow{\mathrm{H_2O}} 3\mathrm{NaCl} + \mathrm{H_3PO_4}$

Table C-3 Titration of sodium phosphate

Wt. Na_3PO_4 (g)	Conc.	Wt. Solution (g)	Amount of HCl 0.5 M		
			1st	2nd	Avg.
0.5	0.305	5	0.6	0.6	0.6
1	0.61	5	1.8	1.8	1.8
2	1.22	50	3.6	3.6	3.5

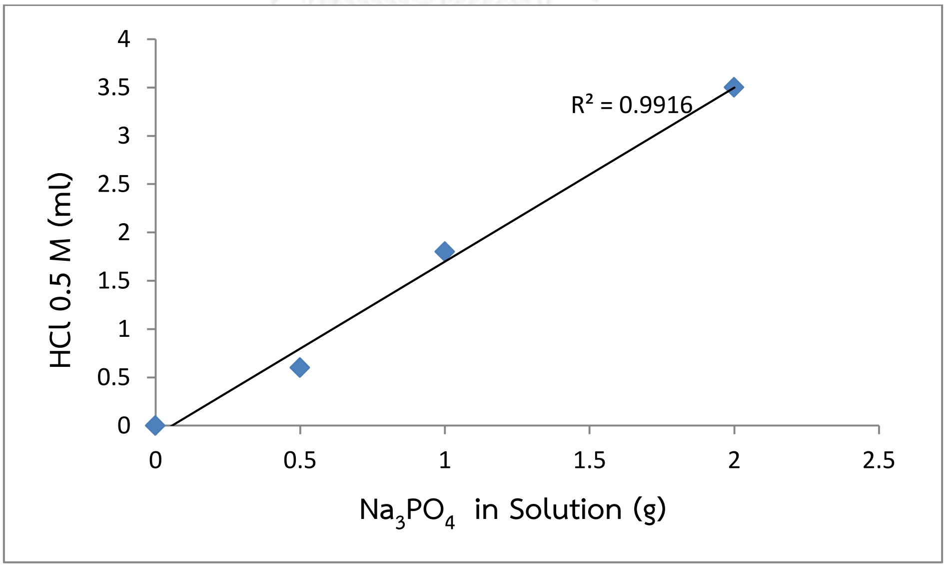


Figure C-1 Standard curve of determination of sodium phosphate in methanol

Appendix D

Experimental analysis

D-1 The experimental result of Part I: Transesterification with Na_3PO_4 as a heterogeneous catalyst in powdered form.

Table D-1 Effect of agitation speed on FAME yield. Agitation speed: 100-800 rpm. Methanol/oil molar ratio: 6:1. Temperature: 190°C. Amount of Na_3PO_4: 0.5 wt. %.

No.	Time (min)	FAME Yield (wt. %)					C_A(mol/L)				
		100 (rpm)	200 (rpm)	400 (rpm)	600 (rpm)	800 (rpm)	100 (rpm)	200 (rpm)	400 (rpm)	600 (rpm)	800 (rpm)
0	0	0.00	0.00	0.00	0.00	0.00	0.83	0.83	0.83	0.83	0.83
1	5	4.83	5.00	5.47	7.07	5.79	0.79	0.79	0.79	0.77	0.79
2	10	11.07	10.30	14.68	15.69	11.59	0.74	0.75	0.71	0.70	0.74
3	15	14.71	14.90	19.65	23.22	24.04	0.71	0.71	0.67	0.64	0.63
4	20	18.84	18.92	24.78	26.68	31.12	0.68	0.68	0.63	0.61	0.57
5	30	23.86	25.42	33.53	36.97	36.71	0.63	0.62	0.55	0.53	0.53
6	40	33.34	33.75	43.67	47.27	45.84	0.56	0.55	0.47	0.44	0.45
7	50	36.73	37.95	51.50	49.62	53.47	0.53	0.52	0.40	0.42	0.39
8	60	44.49	42.47	55.47	56.55	58.27	0.46	0.48	0.37	0.36	0.35
9	90	54.32	54.98	74.67	71.21	68.67	0.38	0.38	0.21	0.24	0.26
10	120	64.16	68.12	78.00	78.40	74.10	0.30	0.27	0.18	0.18	0.22
11	150	72.30	78.32	83.38	82.12	82.74	0.23	0.18	0.14	0.15	0.14
12	180	76.16	81.96	88.77	87.82	84.86	0.20	0.15	0.09	0.10	0.13
13	210	80.02	85.47	88.77	89.72	92.59	0.17	0.12	0.09	0.09	0.06
14	240	85.26	86.72	88.77	92.99	91.31	0.12	0.11	0.09	0.06	0.07

Table D-2 Effect of agitation speed. Initial rate of reaction from 0-60 minutes.

Agitation speed	Linear equation	R^2
100 rpm	Y=0.0096X	0.9928
200 rpm	Y=0.0096X	0.993
300 rpm	Y=0.0139X	0.9952
400 rpm	Y=0144X	0.9843
500 rpm	Y=0.0151X	0.9839

Table D-3 Effect of methanol/oil molar ratio on FAME yield. Methanol/oil molar ratio: 3:1-30:1. Agitation speed: 600 rpm. Temperature: 190°C. Amount of Na_3PO_4: 0.5 wt. %.

No.	Time	FAME Yield (wt. %)							C_A(mol/L)						
	min	3:1	6:1	9:1	12:1	18:1	24:1	30:1	3:1	6:1	9:1	12:1	18:1	24:1	30:1
0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.93	0.83	0.76	0.69	0.59	0.52	0.46
1	5	7.36	7.07	13.75	14.72	13.56	10.54	7.84	0.86	0.77	0.65	0.59	0.51	0.46	0.42
2	10	9.38	15.69	19.12	24.94	27.92	24.62	22.84	0.84	0.70	0.61	0.52	0.43	0.39	0.35
3	15	10.97	23.22	31.56	38.33	41.79	45.24	41.64	0.83	0.64	0.52	0.43	0.34	0.28	0.27
4	20	16.21	26.68	35.72	44.63	56.56	59.48	54.63	0.78	0.61	0.49	0.38	0.26	0.21	0.21
5	30	21.38	36.97	43.53	52.11	74.75	76.07	70.60	0.73	0.53	0.43	0.33	0.15	0.12	0.14
6	40	26.54	47.27	51.34	65.12	80.59	83.43	81.65	0.68	0.44	0.37	0.24	0.11	0.09	0.08
7	50	30.15	49.62	62.78	75.26	90.70	89.12	95.12	0.65	0.42	0.28	0.17	0.06	0.06	0.02
8	60	32.19	56.55	66.53	78.45	93.31	94.32	96.52	0.63	0.36	0.25	0.15	0.04	0.03	0.02
9	90	37.04	71.21	78.12	86.12	96.87	97.09	99.33	0.58	0.24	0.17	0.10	0.02	0.02	0.00
10	120	47.08	78.40	84.57	93.79	97.04	98.27	94.05	0.49	0.18	0.12	0.04	0.02	0.01	0.03
11	150	51.17	82.12	86.59	94.57	99.85	99.58	99.93	0.45	0.15	0.10	0.04	0.00	0.00	0.00
12	180	59.00	87.82	89.41	94.41	95.29	96.55	97.73	0.38	0.10	0.08	0.04	0.03	0.02	0.01
13	210	62.51	89.72	90.19	93.37	95.52	99.80	95.53	0.35	0.09	0.07	0.05	0.03	0.00	0.02
14	240	65.0	92.99	92.47	95.32	96.47	97.09	96.6	0.32	0.06	0.06	0.03	0.02	0.02	0.02

Table D-4 Effect of molar ratio of methanol to oil. Initial rate of reaction from 0-60 minutes.

Molar ratio of methanol/oil	Linear equation	R^2
3:1	Y = 0.0072X	0.9564
6:1	Y = 0.0144X	0.9843
9:1	Y = 0.0189X	0.9809
12:1	Y = 0.0264X	0.9895
18:1	Y = 0.0421X	0.9742
24:1	Y = 0.0441X	0.965
30:1	Y = 0.0382X	0.9685

Table D-5 Effect of reaction temperature on FAME yield. Temperature: 150-250°C. Agitation speed: 600 rpm. Methanol/oil molar ratio: 6:1. Temperature: 190°C. Amount of Na_3PO_4: 0.5 wt. %.

No.	Time (min)	FAME Yield (wt. %)						C_A(mol/L)					
		150 (°C)	170 (°C)	190 (°C)	210 (°C)	230 (°C)	250 (°C)	150 (°C)	170 (°C)	190 (°C)	210 (°C)	230 (°C)	250 (°C)
0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.59	0.59	0.59	0.59	0.59	0.59
1	5	3.37	3.10	13.56	10.40	15.08	31.84	0.57	0.57	0.51	0.53	0.50	0.40
2	10	5.35	9.95	27.92	24.49	36.43	68.85	0.56	0.53	0.43	0.45	0.38	0.18
3	15	10.93	31.02	41.79	52.59	67.45	91.78	0.53	0.41	0.35	0.28	0.19	0.05
4	20	17.58	38.11	56.56	71.16	80.11	94.22	0.49	0.37	0.26	0.17	0.12	0.03
5	30	28.84	42.90	74.75	88.52	93.18	96.58	0.42	0.34	0.15	0.07	0.04	0.02
6	40	40.32	47.69	80.59	92.68	96.52	96.14	0.35	0.31	0.12	0.04	0.02	0.02
7	50	47.96	61.74	90.70	96.83	96.18	97.31	0.31	0.23	0.06	0.02	0.02	0.02
8	60	55.93	66.77	93.31	98.94	97.17	99.29	0.26	0.20	0.04	0.01	0.02	0.00
9	90	69.12	80.11	96.87	98.28	95.40	99.48	0.18	0.12	0.02	0.01	0.03	0.00
10	120	80.02	91.80	97.04	96.39	95.77	95.32	0.12	0.05	0.02	0.02	0.03	0.03
11	150	98.58	92.99	99.85	95.94	92.97	95.11	0.01	0.04	0.00	0.02	0.04	0.03
12	180	97.39	94.18	95.29	94.68	94.03	95.80	0.02	0.03	0.03	0.03	0.04	0.02
13	210	98.75	94.35	95.52	93.42	95.95	95.82	0.01	0.03	0.03	0.04	0.02	0.02
14	240	98.5	97.78	96.47	99.32	96.93	96.6	0.01	0.01	0.02	0.00	0.02	0.02

Table D-6 Effect of reaction temperature. Initial rate of reaction from 0-60 minutes.

Temperature (°C)	Linear equation	R^2
150	Y = 0.0126X	0.971
170	Y = 0.0184X	0.9668
190	Y = 0.0438X	0.9899
210	Y = 0.0665X	0.9814
230	Y = 0.0804X	0.9529
250	Y = 0.1232X	0.0921

Table D-7 Effect of catalyst amount on FAME yield. Amount of Na_3PO_4: 0.0 wt. %-1.0 wt. %. Methanol/oil molar ratio: 18:1. Agitation speed: 600 rpm. Temperature: 210°C.

No.	Time (min)	FAME Yield (wt. %)					C_A(mol/L)				
		0 (wt.%)	**0.1 (wt.%)**	**0.25 (wt.%)**	**0.5 (wt.%)**	**1.0 (wt.%)**	**0 (wt.%)**	**0.1 (wt.%)**	**0.25 (wt.%)**	**0.5 (wt.%)**	**1.0 (wt.%)**
0	0	0.00	0.00	0.00	0.00	0.00	0.59	0.59	0.59	0.59	0.59
1	5	2.50	5.62	4.82	10.40	38.97	0.58	0.56	0.56	0.53	0.36
2	10	2.22	8.81	15.37	24.29	63.54	0.58	0.54	0.50	0.45	0.22
3	15	2.95	14.60	27.29	52.51	90.77	0.58	0.51	0.43	0.28	0.05
4	20	4.30	22.91	35.44	71.16	95.96	0.57	0.46	0.38	0.17	0.02
5	30	4.58	26.36	51.37	88.52	100.00	0.57	0.44	0.29	0.07	0.00
6	40	4.85	29.81	65.23	92.50	98.56	0.56	0.42	0.21	0.04	0.01
7	50	6.27	37.44	82.58	96.47	99.09	0.56	0.37	0.10	0.02	0.01
8	60	3.38	37.89	84.91	98.94	98.75	0.57	0.37	0.09	0.01	0.01
9	90	5.03	47.81	96.68	98.28	98.89	0.56	0.31	0.02	0.01	0.01
10	120	5.80	70.43	99.34	97.52	100.00	0.56	0.18	0.00	0.01	0.00
11	150	14.32	74.40	100.00	95.94	96.50	0.51	0.15	0.00	0.02	0.02
12	180	13.79	86.72	99.36	94.68	100.00	0.51	0.08	0.00	0.03	0.00
13	210	10.71	92.48	98.63	93.42	98.00	0.53	0.04	0.01	0.04	0.01
14	240	13.08	94.31	100	99.22	100	0.52	0.03	0.02	0.00	0.00

Table D-8 Effect of catalyst amount. Initial rate of reaction from 0-60 minutes.

Catalyst amount (wt.%)	Linear equation	R^2
0 wt.%	Y = 0.0011X	0.1139
0.1 wt.%	Y = 0.0089X	0.9473
0.25 wt.%	Y = 0.0296X	0.9534
0.5 wt.%	Y = 0.0659X	0.9802
1.0 wt.%	Y = 0.164X	0.9618

Table D-9 Effect of FFAs content in raw materials on FAME yield. Amount of FFAs: 0.0 wt.% oil-10 wt.% oil. Amount of Na_3PO_4: 0.5 wt. %. Methanol/oil molar ratio: 18:1. Agitation speed: 600 rpm. Temperature: 210°C.

No.	Time (min)	FAME Yield (wt. %)				C_A(mol/L)			
		0.0 (wt.%)	**3.0 (wt.%)**	**5.0 (wt.%)**	**10.0 (wt.%)**	**0 .0 (wt.%)**	**3.0 (wt.%)**	**5.0 (wt.%)**	**10.0 (wt.%)**
0	0	0.00	0.00	0.00	0.00	0.59	0.59	0.59	0.59
1	5	38.97	19.46	14.94	16.61	0.36	0.45	0.52	0.53
2	10	63.54	36.94	27.35	27.49	0.22	0.40	0.44	0.43
3	15	90.77	58.05	43.86	39.92	0.05	0.31	0.38	0.38
4	20	95.96	75.65	55.36	53.40	0.02	0.20	0.30	0.31
5	30	98.66	96.40	71.74	67.29	0.00	0.08	0.15	0.19
6	40	98.56	96.78	77.44	72.30	0.01	0.02	0.09	0.11
7	50	99.09	99.81	83.74	77.00	0.01	0.00	0.06	0.07
8	60	97.05	99.23	88.07	85.71	0.01	0.01	0.01	0.03
9	90	98.89	99.78	98.46	95.77	0.01	0.00	0.02	0.01
10	120	99.45	99.35	100.00	99.64	0.00	0.01	0.00	0.00
11	150	96.50	99.63	97.85	99.34	0.02	0.03	0.03	0.02
12	180	97.64	94.26	95.45	97.15	0.00	0.00	0.02	0.01
13	210	98.00	93.89	100.00	98.78	0.01	0.02	0.00	0.01
14	240	100	95.05	99.87	99.85	0.00	0.03	0.00	0.00

Table D-10 Effect of FFAs content in oil. Initial rate of reaction from 0-60 minutes.

FFAs in oil	Linear equation	R^2
0 wt.%	Y = 0.164X	0.9618
3 wt.%	Y = 0.0845X	0.9317
5 wt.%	Y = 0.0364X	0.9902
10 wt.%	Y = 0.032X	0.9825

Table D-11 Effect of water content in raw materials on FAME yield. Amount of water: 0.0 wt.% oil-10 wt.% methanol. Amount of Na_3PO_4: 0.5 wt. %. Methanol/oil molar ratio: 18:1. Agitation speed: 600 rpm. Temperature: 210°C.

No.	Time (min)	FAME Yield (wt. %)				C_A(mol/L)			
		0.0 (wt.%)	3.0 (wt.%)	5.0 (wt.%)	10.0 (wt.%)	0 .0 (wt.%)	3.0 (wt.%)	5.0 (wt.%)	10.0 (wt.%)
0	0	0.00	0.00	0.00	0.00	0.59	0.59	0.59	0.59
1	5	38.97	24.85	11.59	11.44	0.36	0.48	0.50	0.49
2	10	63.54	33.25	26.10	27.07	0.22	0.37	0.43	0.43
3	15	90.77	47.16	36.03	36.67	0.05	0.25	0.33	0.36
4	20	95.96	65.42	48.97	48.00	0.02	0.14	0.26	0.28
5	30	100.00	86.52	74.01	68.26	0.01	0.02	0.17	0.19
6	40	98.56	96.71	84.39	81.63	0.01	0.02	0.13	0.16
7	50	99.09	99.26	90.52	88.29	0.01	0.00	0.10	0.14
8	60	98.75	98.38	98.30	95.22	0.02	0.00	0.07	0.08
9	90	98.89	99.35	97.46	98.06	0.01	0.00	0.01	0.03
10	120	100.00	97.78	100.00	99.21	0.00	0.00	0.00	0.00
11	150	96.50	95.51	94.38	97.27	0.02	0.00	0.01	0.00
12	180	100.00	99.19	97.10	98.58	0.01	0.03	0.03	0.02
13	210	98.00	97.45	100.00	98.13	0.01	0.04	0.00	0.01
14	240	98.13	97.5	96.45	98.52	0.01	0.04	0.02	0.01

Table D-12 Effect of water content in oil. Initial rate of reaction from 0-60 minutes.

Water in oil	Linear equation	R^2
0 wt.%	Y = 0.0164X	0.9618
3 wt.%	Y = 0.0728X	0.9333
5 wt.%	Y = 0.0516X	0.9205
10 wt.%	Y = 0.0436X	0.9674

D-2 The experimental result of Part II: Transesterification with Na_3PO_4 /Al_2O_3 as a heterogeneous catalyst.

Table D-13 Effect of agitation speed on FAME yield. Agitation speed: 600 rpm-1200 rpm. Methanol/oil molar ratio: 6:1. Amount of Na_3PO_4/Al_2O_3: 0.5 wt. %. Temperature: 190°C.

No.	Time (min)	FAME Yield (wt. %)				C_A(mol/L)			
		600 (rpm)	800 (rpm)	1000 (rpm)	1200 (rpm)	600 (rpm)	800 (rpm)	1000 (rpm)	1200 (rpm)
0	0	0.00	0.00	0.00	0.00	0.83	0.83	0.83	0.83
1	5	6.72	11.91	7.96	7.90	0.78	0.73	0.77	0.77
2	10	11.01	15.33	14.07	14.27	0.74	0.71	0.72	0.71
3	15	15.46	18.81	21.59	22.32	0.70	0.68	0.65	0.65
4	20	19.42	25.00	28.67	27.68	0.67	0.63	0.59	0.60
5	30	21.14	27.25	31.58	30.77	0.66	0.61	0.57	0.58
6	40	25.35	31.38	34.50	38.99	0.62	0.57	0.55	0.51
7	50	28.87	33.64	39.72	44.80	0.59	0.55	0.50	0.46
8	60	32.13	38.37	52.32	60.01	0.57	0.51	0.40	0.33
9	90	35.55	46.71	64.91	67.50	0.54	0.44	0.29	0.27
10	120	40.12	53.30	69.01	71.72	0.50	0.39	0.26	0.24
11	150	49.56	61.99	75.20	77.61	0.42	0.32	0.21	0.19
12	180	65.90	79.98	83.88	86.97	0.28	0.17	0.13	0.11
13	210	84.12	97.59	95.77	96.34	0.13	0.02	0.04	0.03
14	240	93.4	97.41	96.17	97.96	0.06	0.02	0.03	0.02

Table D-14 Effect of agitation speed. Initial rate of reaction from 0-60 minutes.

Agitation speed	Linear equation	R^2
600 rpm	Y = 0.0111X	0.9905
800 rpm	Y = 0.0148X	0.9254
1000 rpm	Y = 0.0163X	0.9964
1200 rpm	Y = 0.0162X	0.9978

Table D-15 Effect of methanol/oil molar ratio on FAME yield. Methanol/oil molar ratio: 3:1-30:1. Agitation speed: 1000 rpm. Amount of Na_3PO_4/Al_2O_3: 0.5 wt. %. Temperature: 190°C.

No.	Time (min)	FAME Yield (wt. %)						C_A(mol/L)					
		3:1	6:1	12:1	18:1	24:1	30:1	3:1	6:1	12:1	18:1	24:1	30:1
0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.93	0.83	0.69	0.59	0.52	0.46
1	5	6.80	7.96	9.90	12.59	7.86	12.27	0.86	0.77	0.62	0.52	0.48	0.40
2	10	4.65	14.07	16.38	22.68	17.50	19.88	0.88	0.72	0.58	0.46	0.43	0.37
3	15	7.94	21.59	23.48	28.56	32.05	36.73	0.85	0.65	0.53	0.42	0.35	0.29
4	20	9.31	28.67	32.16	34.67	38.57	44.90	0.84	0.59	0.47	0.39	0.32	0.25
5	30	12.10	31.58	33.61	47.55	48.41	52.91	0.82	0.57	0.46	0.31	0.27	0.22
6	40	14.90	34.50	40.50	55.63	57.75	61.49	0.79	0.55	0.41	0.26	0.22	0.18
7	50	18.29	39.72	50.00	63.71	71.44	70.08	0.76	0.50	0.35	0.22	0.15	0.14
8	60	18.76	52.32	57.75	72.47	74.56	77.36	0.75	0.40	0.29	0.16	0.13	0.10
9	90	28.17	64.91	69.43	83.24	84.29	86.36	0.67	0.29	0.21	0.10	0.08	0.06
10	120	34.04	69.01	76.96	92.44	95.06	95.36	0.61	0.26	0.16	0.04	0.03	0.02
11	150	40.80	75.20	84.49	93.72	97.29	95.93	0.55	0.21	0.11	0.04	0.01	0.02
12	180	53.22	83.88	90.59	100.00	98.82	96.50	0.43	0.13	0.07	0.00	0.01	0.02
13	210	53.47	95.77	96.24	100.00	99.13	98.86	0.43	0.04	0.03	0.00	0.00	0.01
14	240	53.47	96.18	99.06	98.53	99.43	99.68	0.43	0.03	0.01	0.01	0.00	0.00

Table D-16 Initial rate of reaction from 0-60 minutes.

Molar ratio of methanol/oil	Linear equation	R^2
3:1	Y = 0.0039X	0.8852
6:1	Y = 0.0117X	0.9339
12:1	Y = 0.0142X	0.9689
18:1	Y = 0.0209X	0.9953
24:1	Y = 0.023X	0.99
30:1	Y = 0.0246X	0.9953

Table D-17 Effect of temperature on FAME yield. Methanol/oil molar ratio: 18:1. Temperature: 190°C-250°C. Agitation speed: 1000 rpm. Amount of Na_3PO_4/Al_2O_3: 0.5 wt. %.

No.	Time (min)	FAME Yield (wt. %) 190 (°C)	210 (°C)	230 (°C)	250 (°C)	C_A(mol/L) 190 (°C)	210 (°C)	230 (°C)	250 (°C)
0	0	0.00	0.00	0.00	0.00	0.59	0.59	0.59	0.59
1	5	7.96	17.40	18.81	22.16	0.55	0.49	0.48	0.46
2	10	14.07	38.52	45.44	39.26	0.51	0.36	0.32	0.36
3	15	21.59	58.61	61.04	57.82	0.46	0.25	0.23	0.25
4	20	28.67	71.36	73.08	77.64	0.42	0.17	0.16	0.13
5	30	31.58	82.78	91.65	95.67	0.41	0.10	0.05	0.03
6	40	34.50	91.77	96.01	96.23	0.39	0.05	0.02	0.02
7	50	39.72	93.62	96.43	96.79	0.36	0.04	0.02	0.02
8	60	52.32	97.07	98.45	96.84	0.28	0.02	0.01	0.02
9	90	64.91	94.27	97.71	96.93	0.21	0.03	0.01	0.02
10	120	69.01	95.22	96.74	97.03	0.18	0.03	0.02	0.02
11	150	75.20	95.94	95.78	93.93	0.15	0.02	0.03	0.04
12	180	83.88	94.95	99.01	98.28	0.10	0.03	0.01	0.01
13	210	95.77	95.27	98.13	96.27	0.03	0.03	0.01	0.02
14	240	96.18	98.40	97.00	95.32	0.02	0.01	0.02	0.03

Table D-18 Initial rate of reaction from 0-60 minutes.

Temperature (°C)	Linear equation	R^2
190	Y = 0.0117X	0.9339
210	Y = 0.0564X	0.9926
230	Y = 0.0727X	0.9613
250	Y = 0.0847X	0.9009

Table D-19 Effect of amount of Na_3PO_4/Al_2O_3 on FAME yield. Amount of Na_3PO_4/Al_2O_3: 0.0-2.0 wt. % of Na_3PO_4. Methanol/oil molar ratio: 18:1. Temperature: 210°C. Agitation speed: 1000 rpm.

No	Time (min)	FAME Yield (wt. %)							C_A(mol/L)						
		0.0	**0.1**	**0.25**	**0.5**	**1.0**	**1.5**	**2.0**	**0.0**	**0.1**	**0.25**	**0.5**	**1.0**	**1.5**	**2.0**
0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.59	0.59	0.59	0.59	0.59	0.59	0.59
1	5	2.17	6.33	10.49	18.81	22.81	30.50	40.43	0.58	0.56	0.53	0.48	0.46	0.41	0.35
2	10	3.60	14.06	24.52	45.44	48.26	53.91	68.19	0.57	0.51	0.45	0.32	0.31	0.27	0.19
3	15	7.56	20.93	34.30	61.04	68.96	75.12	82.01	0.55	0.47	0.39	0.23	0.18	0.15	0.11
4	20	10.52	26.16	41.80	73.08	81.00	87.86	90.63	0.53	0.44	0.35	0.16	0.11	0.07	0.06
5	30	11.76	31.73	51.70	91.65	93.40	94.78	95.76	0.52	0.40	0.29	0.05	0.04	0.03	0.03
6	40	15.16	35.37	55.58	96.01	97.11	96.42	95.89	0.50	0.38	0.26	0.02	0.02	0.02	0.02
7	50	20.80	49.70	68.61	96.43	97.22	98.63	99.70	0.47	0.30	0.19	0.02	0.02	0.01	0.00
8	60	20.61	50.07	69.53	98.45	97.00	96.55	98.71	0.47	0.30	0.18	0.01	0.02	0.02	0.01
9	90	26.04	53.96	76.88	97.71	95.06	96.66	96.37	0.44	0.27	0.14	0.01	0.03	0.02	0.02
10	120	31.23	57.61	83.99	96.74	96.61	96.19	98.73	0.41	0.25	0.09	0.02	0.02	0.02	0.01
11	150	37.88	72.35	86.83	95.78	95.12	95.96	95.26	0.37	0.16	0.08	0.03	0.03	0.02	0.03
12	180	41.93	81.20	95.47	99.01	96.74	95.32	96.53	0.34	0.11	0.03	0.01	0.02	0.03	0.02
13	210	46.93	84.73	97.53	98.13	97.60	97.35	95.57	0.31	0.09	0.01	0.01	0.01	0.02	0.03
14	240	50.94	92.46	98.97	97.00	97.47	99.88	96.07	0.29	0.04	0.01	0.02	0.02	0.02	0.02

Table D-20 Initial rate of reaction from 0-60 minutes.

Catalyst Amount (wt.%)	Linear equation	R^2
0	Y = 0.0042X	0.9663
0.1	Y = 0.0124X	0.966
0.25	Y = 0.0216X	0.9637
0.5	Y = 0.0727X	0.9613
1.0	Y = 0.0833X	0.9815
1.5	Y = 0.0955X	0.9868
2.0	Y = 0.1075X	0.9894

Table D-21 Catalyst reusability. Agitation speed: 1000 rpm. Methanol/oil molar ratio: 18:1. Amount of Na_3PO_4/Al_2O_3: 1.0 wt. %. Temperature: 210°C.

No.	Time (min)	FAME Yield (wt. %)						C_A(mol/L)					
		Fresh	Re 1	Re 2	Re 3	Re 4	Re 5	Fresh	Re 1	Re 2	Re 3	Re 4	Re 5
0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.59	0.59	0.59	0.59	0.59	0.59
1	5	22.81	18.48	18.31	15.10	13.22	18.09	0.46	0.48	0.48	0.50	0.51	0.49
2	10	48.26	34.97	28.79	33.42	30.41	36.41	0.31	0.39	0.42	0.39	0.41	0.38
3	15	68.96	51.81	49.58	47.04	48.20	50.03	0.18	0.29	0.30	0.31	0.31	0.30
4	20	81.00	62.50	65.07	61.52	58.52	64.52	0.11	0.22	0.21	0.23	0.25	0.21
5	30	93.40	73.89	72.78	67.36	64.35	70.35	0.04	0.15	0.16	0.19	0.21	0.18
6	40	97.11	84.24	80.83	84.29	81.29	87.29	0.02	0.09	0.11	0.09	0.11	0.08
7	50	97.22	91.56	88.54	82.52	79.51	85.51	0.02	0.05	0.07	0.10	0.12	0.09
8	60	97.00	94.63	86.99	89.19	91.12	92.18	0.02	0.03	0.08	0.06	0.05	0.05
9	90	95.06	94.44	92.30	92.75	89.75	95.75	0.03	0.03	0.05	0.04	0.06	0.03
10	120	96.61	95.69	95.09	94.30	91.29	97.29	0.02	0.03	0.03	0.03	0.05	0.02
11	150	95.12	94.93	95.36	95.48	96.13	98.47	0.03	0.03	0.03	0.03	0.02	0.01
12	180	96.74	95.83	98.00	97.24	94.24	95.24	0.02	0.02	0.01	0.02	0.03	0.03
13	210	97.60	94.50	96.67	96.68	93.67	94.67	0.01	0.03	0.02	0.02	0.04	0.03
14	240	97.47	97.41	97.47	95.74	98.5	96.00	0.02	0.02	0.02	0.03	0.01	002

Table D-22 Initial rate of reaction from 0-60 minutes.

Catalyst Recycle	Linear equation	R^2
Fresh catalyst	Y = 0.0833X	0.9815
Recycle 1	Y = 0.047X	0.9975
Recycle 2	Y = 0.0392X	0.9509
Recycle 3	Y = 0.0381X	0.9636
Recycle 4	Y = 0.0373X	0.9653
Recycle 5	Y = 0.0426X	0.9669

D-3 Experimental Error

Table D-23 The repeatability of the effect of agitation speed on FAME yield. Agitation speed: 600 rpm. Methanol/oil molar ratio: 6:1. Temperature: 190°C. Amount of Na_3PO_4: 0.5 wt. %.

No.	Time (min)	FAME Yield (wt. %)					
		Run 1	Run 2	Mean	SD	Mean-SD	Mean+SD
0	0	0.00	0.00	0.00	0.00	0.00	0.00
1	5	5.47	12.41	8.94	4.91	13.85	13.85
3	10	14.68	22.92	18.80	5.83	24.63	24.63
3	15	19.65	19.19	19.42	0.32	19.74	19.74
4	20	24.78	28.70	26.74	2.77	29.51	29.51
5	30	33.53	38.98	36.25	3.86	40.11	40.11
6	40	43.67	49.26	46.47	3.95	50.42	50.42
7	50	51.50	51.03	51.27	0.33	51.60	51.60
8	60	55.47	61.36	58.41	4.16	62.57	62.57
9	90	74.67	80.43	77.55	4.08	81.63	81.63
10	120	78.00	86.80	82.40	6.22	88.62	88.62
11	150	83.38	93.16	88.27	6.92	95.19	95.19
12	190	88.77	94.90	91.83	4.34	96.17	96.17
13	210	88.77	94.49	91.63	4.05	95.68	95.68
14	240	88.77	93.69	91.23	3.48	94.71	94.71

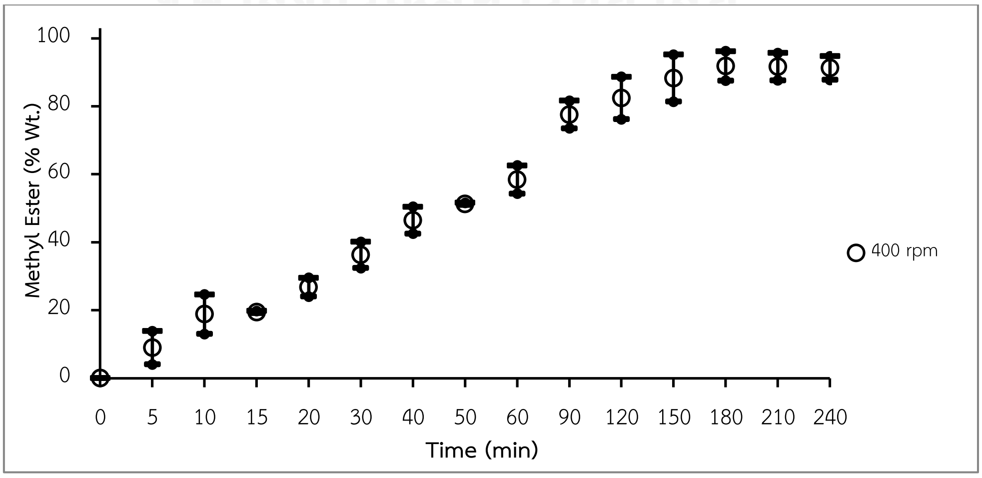


Figure D-1 Plot of the experimental error test of effect of methanol/oil molar ratio.

Table D-24 The repeatability of effect of methanol/oil molar ratio on FAME yield. Methanol/oil molar ratio: 18:1. Agitation speed: 600 rpm. Temperature: 190°C. Amount of Na_3PO_4: 0.5 wt. %.

No.	Time (min)	FAME Yield (wt. %)					
		Run 1	Run 2	Mean	SD	Mean-SD	Mean+SD
0	0	0.00	0.00	0	0	0.0	0
1	5	13.56	7.84	10.70	4.04	6.7	14.74
2	10	27.92	22.84	25.38	3.59	21.8	28.98
3	15	41.79	41.64	41.71	0.11	41.6	41.82
4	20	56.56	54.63	55.59	1.36	54.2	56.95
5	30	74.75	70.60	72.67	2.94	69.7	75.61
6	40	80.59	81.65	81.12	0.75	80.4	81.87
7	50	90.70	95.12	92.91	3.12	89.8	96.03
8	60	93.31	96.52	94.92	2.27	92.6	97.19
9	90	96.87	99.33	98.10	1.74	96.4	99.83
10	120	97.04	94.05	95.54	2.12	93.4	97.66
11	150	99.85	99.93	99.89	0.06	99.8	99.94
12	190	95.29	97.73	96.51	1.72	94.8	98.23
13	210	95.52	95.53	95.52	0.01	95.5	95.53
14	240	96.47	96.60	96.53	0.09	96.4	96.62

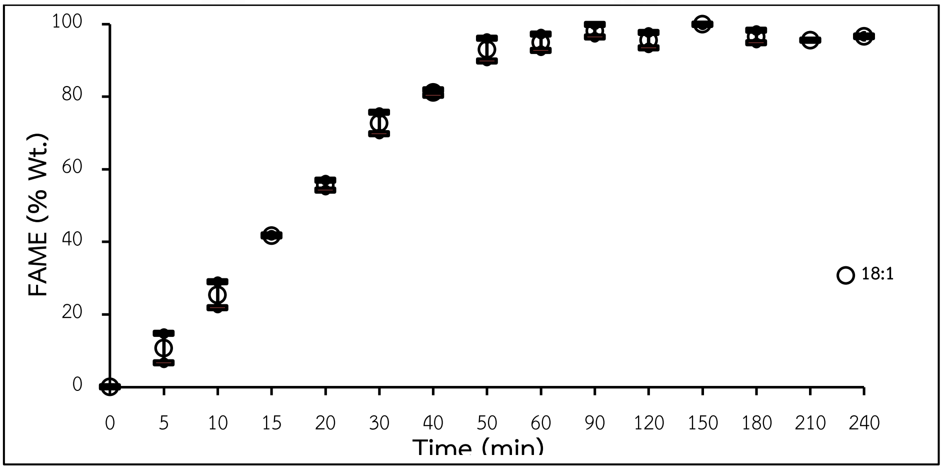


Figure D-2 Plot of the experimental error test of effect of molar ratio of methanol/oil.

Table D-25. The repeatability of effect of reaction temperature on FAME yield. Methanol/oil molar ratio: 18:1. Agitation speed: 600 rpm. Temperature: 210°C. Amount of Na_3PO_4: 0.5 wt. %.

No.	Time (min)	FAME Yield (wt. %)					
		Run 1	Run 2	Mean	SD	Mean-SD	Mean+SD
0	0	0.00	0.00	0.00	0.00	0.00	0.00
1	5	10.40	13.27	11.84	2.03	9.8	13.9
2	10	24.49	17.53	21.01	4.92	16.1	25.9
3	15	52.59	48.72	50.66	2.74	47.9	53.4
4	20	71.16	78.46	74.81	5.16	69.6	80.0
5	30	88.52	83.97	86.25	3.22	83.0	89.5
6	40	92.68	90.02	91.35	1.88	89.5	93.2
7	50	96.83	95.55	96.19	0.91	95.3	97.1
8	60	98.94	97.43	98.18	1.06	97.1	99.2
9	90	98.28	97.56	97.92	0.51	97.4	98.4
10	120	96.39	98	97.20	1.14	96.1	98.3
11	150	95.94	97.23	96.58	0.92	95.7	97.5
12	190	94.68	92.02	93.35	1.88	91.5	95.2
13	210	93.42	96.46	94.94	2.15	92.8	97.1
14	240	99.32	96.02	97.67	2.33	95.3	100.0

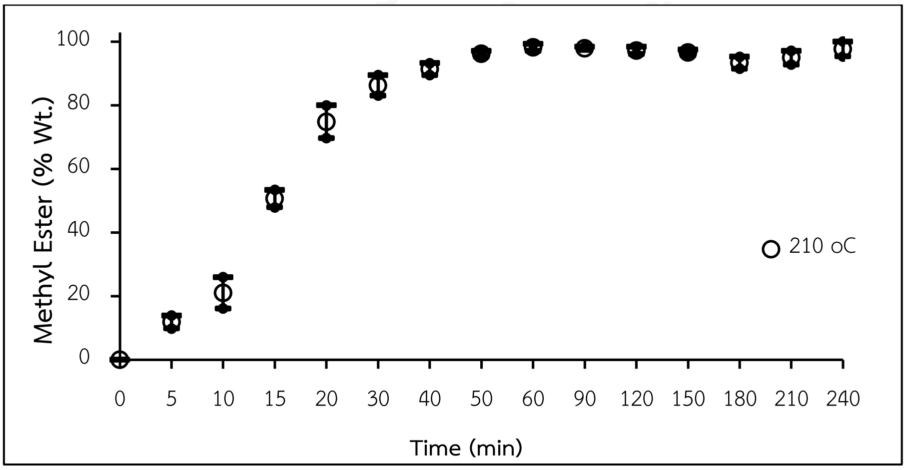


Figure D-3 Plot of the experimental error test of effect of temperature.

Table D-26 The repeatability of effect of catalyst amount on FAME yield. Methanol/oil molar ratio: 18:1. Agitation speed: 600 rpm. Temperature: 210°C. Amount of Na_3PO_4: 0.5 wt. %.

No.	Time (min)	FAME Yield (wt. %)					
		Run 1	Run 2	Mean	SD	Mean-SD	Mean+SD
0	0	0.0	0	0	0	0.0	0.0
1	5	10.4	8.79	9.60	1.14	8.5	10.7
2	10	24.3	18.12	21.21	4.37	16.8	25.6
3	15	52.5	46.33	49.42	4.37	45.0	53.8
4	20	71.2	84.43	77.79	9.39	68.4	87.2
5	30	88.5	90.25	89.39	1.22	88.2	90.6
6	40	92.5	93.42	92.96	0.65	92.3	93.6
7	50	96.5	95.32	95.90	0.82	95.1	96.7
8	60	98.9	93	95.97	4.20	91.8	100.2
9	90	98.3	94.48	96.38	2.69	93.7	99.1
10	120	97.5	98.3	97.91	0.55	97.4	98.5
11	150	95.9	96.35	96.14	0.29	95.9	96.4
12	190	94.7	95.55	95.11	0.62	94.5	95.7
13	210	93.4	96.25	94.83	2.00	92.8	96.8
14	240	99.2	98.56	98.89	0.47	98.4	99.4

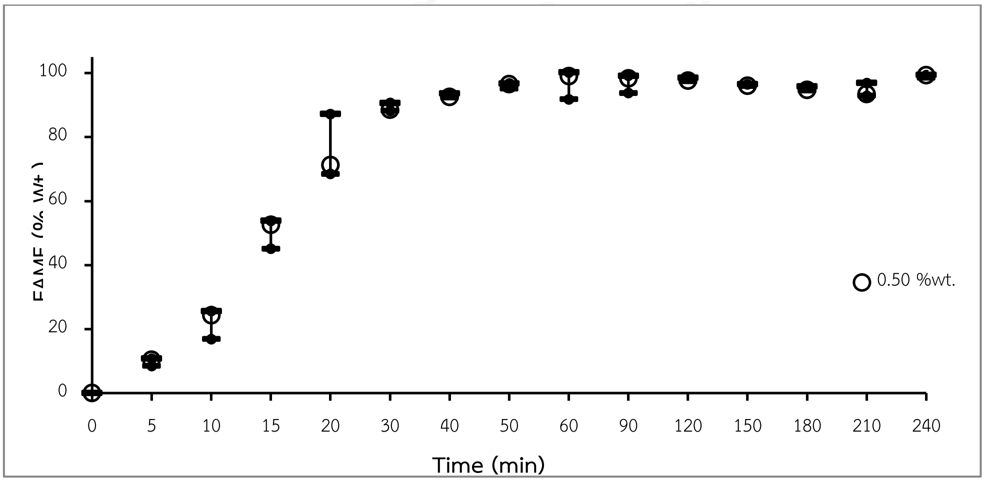


Figure D-4 Plot of the experimental error test of effect of catamount.

D-4 The Analytical Error

Analysis error checking of the experiment is divided into two parts. In the first part, sample preparation 7 times and analyzed by gas Chromatography graph. The analytical results of FAME yield are shown in Table C-8. In the second part, the same samples were analyzed 3 times and the FAME yields are shown in Table C-9.

Table D-27 Analysis error checking by preparation repeated 7 times.

No	FAME Yield (wt.%)								
	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	20:0	Sum
1	0.59	0.89	38.03	4.24	38.49	14.29	0.26	0.35	97.14
2	0.61	0.91	38.70	4.36	39.58	14.60	0.26	0.37	99.39
3	0.62	0.92	39.48	4.41	40.07	14.81	0.26	0.37	100.96
4	0.62	0.92	39.31	4.39	40.00	14.82	0.26	0.37	100.65
5	0.62	0.93	39.11	4.33	39.69	14.69	0.26	0.36	99.97
6	0.64	0.94	39.38	4.38	39.94	14.77	0.26	0.37	100.67
7	0.63	0.92	38.58	4.26	38.89	14.34	0.26	0.36	98.23
								SD	**1.42**

Table D-28 Analysis error checking by injecting sample 3 times.

No	FAME Yield (wt.%)								
	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	20:0	Sum
1	0.60	0.89	38.81	4.01	40.21	13.63	0.25	0.34	98.72
2	0.60	0.87	38.67	4.00	40.13	13.61	0.24	0.34	98.48
3	0.59	0.87	38.92	4.07	40.50	13.72	0.00	0.35	99.00
								SD	**0.26**

Appendix D

List of publications

1. Khritsayaporn Thinnakorn and Jirdsak Tscheikuna, **“Transesterification of Palm Olein Oil using Na_3PO_4 as Heterogeneous Catalyst”**, 2rd International Conference on Energy and Environment Protection. 2013 (ICEEP2013), Guilin, China, April 20-21, 2013. Advance Energy.

2. Khritsayaporn Thinnakorn and Jirdsak Tscheikuna, **“Biodiesel Production via Transesterification of Palm Olein using Sodium Phosphate as a Heterogeneous Catalyst”**, Applied Catalysis A:General, Vol. 476 (2014) 26-33.

3. K. Thinnakorn and J. Tscheikuna, **“Transesterification of Palm Olein using Sodium Phosphate Impregnated on an Alumina Support”**, Applied Catalysis A: General. Impress, Accepted Manuscript.

4. K. Thinnakorn, P. Peungton, S. Somsri and J. Tshcheikuna, **“The activity of Sodium Phosphate used as a Heterogeneous Catalyst in Transesterification of Palm Olein and Methanol”**, Energy and Fuel.

VITA

Miss Khritsayaporn Thinnakorn was born on 23 July, 1978 in Nakhon Si Thammarat, Thailand. She received her Master degree of Science from Chulalongkorn University, from the department of Chemical Technology in 1995. She continued in Doctoral of Engineering from the department of Chemical Engineering, Chulalongkorn in June, 1999.