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Monoglyceride Preparation Over Heterogeneous Catalysts

ชื่อนิสิต นางสาวกมลวรรณ สิงห์พันนา
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คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

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By

Miss Kamonwan Singpanna

A Senior Project Submitted in Partial Fulfillment of the Requirements for

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Thesis Title MONOGLYCERIDE PREPARATION OVER HETEROGENEOUS CATALYSTS
By Miss Kamonwan Singpanna

Accepted by the Department of Chemistry, Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Bachelor Degree

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ชื่อโครงการ การเตรียมโมโนกลีเซอไรด์ด้วยตัวเร่งปฏิกิริยาวิวิธพันธุ์

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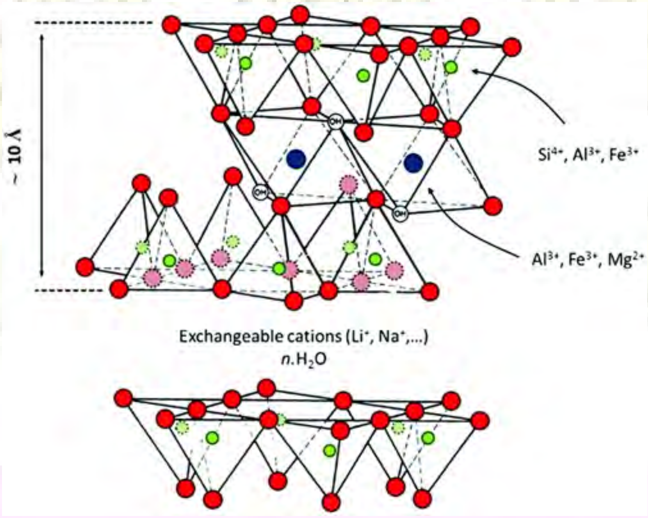
บทคัดย่อ

ในงานวิจัยนี้ศึกษาการใช้ดินเหนียว (clay) เป็นตัวเร่งปฏิกิริยาสำหรับการสังเคราะห์โมโนกลีเซอไรด์ (monoglycerides) ด้วยปฏิกิริยาเอสเทอริฟิเคชันของกรดโอเลอิกกับกลีเซอรอล จุดมุ่งหมายของการศึกษานี้เพื่อปรับปรุงสมบัติของดิน เช่นพื้นที่ผิว ความเป็นรูพรุน และความเป็นกรด ดินที่ถูกปรับสภาพด้วยกรดสามารถเตรียมได้โดยการรีฟลักซ์กับกรดซัลฟิวริกที่อุณหภูมิ 120 องศาเซลเซียส และอบแห้งที่ 100 องศาเซลเซียส ข้ามคืน และนำมาบด จากนั้นนำตัวเร่งปฏิกิริยามาพิสูจน์เอกลักษณ์ของตัวเร่งปฏิกิริยาด้วยเทคนิค XRD SEM N_2 adsorption และไทเทรตหาปริมาณกรด จากศึกษา พบว่า ดินเบนโทไนต์ที่ผ่านการรีฟลักซ์กับกรดซัลฟิวริกเข้มข้น 0.5 โมลาร์ให้ผลการทดลองดีกว่าการปรับสภาพแบบอื่น เมื่อใช้อัตราส่วนโดยโมลของกลีเซอรอลต่อกรดไขมัน เท่ากับ 3:1 ปริมาณตัวเร่งปฏิกิริยา 5 เปอร์เซ็นต์โดยน้ำหนัก 160 องศาเซลเซียส และระยะเวลาทำปฏิกิริยา 30 นาที โดยมีการเปลี่ยนของกรดไขมันอยู่ในช่วง 51.4 ถึง 94.6 เปอร์เซ็นต์ มีความเลือกจำเพาะต่อโมโนกลีเซอไรด์สูงสุด คือ 34.1 และ 66.3 เปอร์เซ็นต์ตามลำดับ



โครงสร้างของดินเหนียว

คำสำคัญ: ดินเหนียว, การเพิ่มความเป็นกรด, โมโนกลีเซอไรด์, เอสเทอริฟิเคชัน, ตัวเร่งปฏิกิริยา

Project Title Monoglyceride preparation over heterogeneous catalysts

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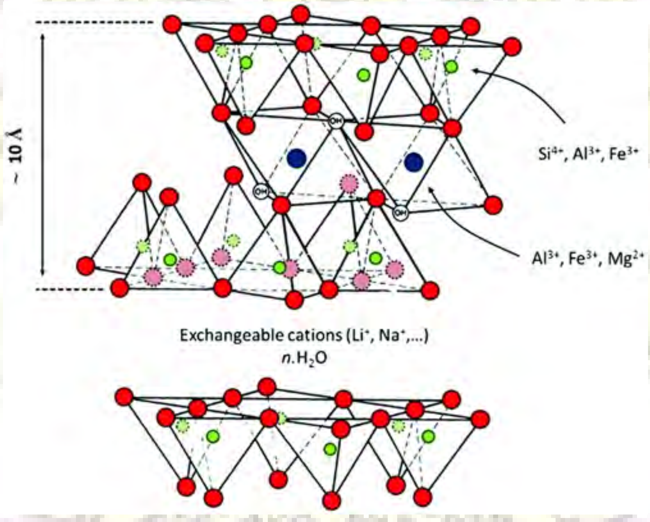
Department of Chemistry, Faculty of Science, Chulalongkorn University, Academic Year 2016

Abstract

Monoglyceride preparation from esterification of oleic acid with glycerol was evaluated with acid-activated clay catalysts. The goal of this study is to obtain an improvement of clay properties such as specific surface area, porosity and acidity. The acid-activated clays were prepared by refluxing the raw clay with sulfuric acid at 120°C, drying in the oven at 100°C overnight and crushing. The catalysts were characterized by XRD, SEM analysis, N_2 adsorption and acid-base titration. From our study, the 0.5 M H_2SO_4 acid- activated bentonite catalyst provided better results than the others. The acid conversions were in range of 51.4% to 94.6% and the highest mono-glyceride yield and selectivity were 34.1% and 66.3% when using 3:1 molar ratio of glycerol:oleic acid, 5.0 wt.% of catalyst, 160°C for 30 min.



Structure of clay

Keywords: Clay, Acid activation, Monoglycerides, Esterification, Catalysts

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SCHEMES

LIST OF ABBREVIATIONS

Å	Angstrom unit
BET	Brunauer, Emmett and Teller equation
BJH	Barret-Joyner-Halender equation
°C	Degree Celsius
F	Feldspar
FAME	Fatty acid methyl ester
FFA	Free fatty acid
g	Gram
GC	Gas chromatography
h	Hour or hours
I	Illite
IS	Internal standard
K	Kaolinite
kV	Kilovolt
L	Liter (s)
M	Molar
Mt	Montmorillonite
min	Minute or minutes
mL	Milliliter (s)
nm	Nanometer (s)
Q	Quartz
RT	Room temperature
S	Smectite
SEM	Scanning electron microscopy
Std	Standard
wt.%	Percent by weight
XRD	X-ray diffraction

CHAPTER I

INTRODUCTION

1.1 Background

Monoglyceride is usually used as an emulsifier in food, pharmaceutical and cosmetic industries because it is a good surfactant that contains a hydrophilic head and a hydrophobic tail. Monoglyceride can be produced from the base-catalyzed transesterification of glycerol with fatty acid methyl esters (FAME) but the FAME is a high-value substance using in industries. The alternative is the acid-catalyzed esterification of glycerol with free fatty acid, as shown in Figure 1.1.

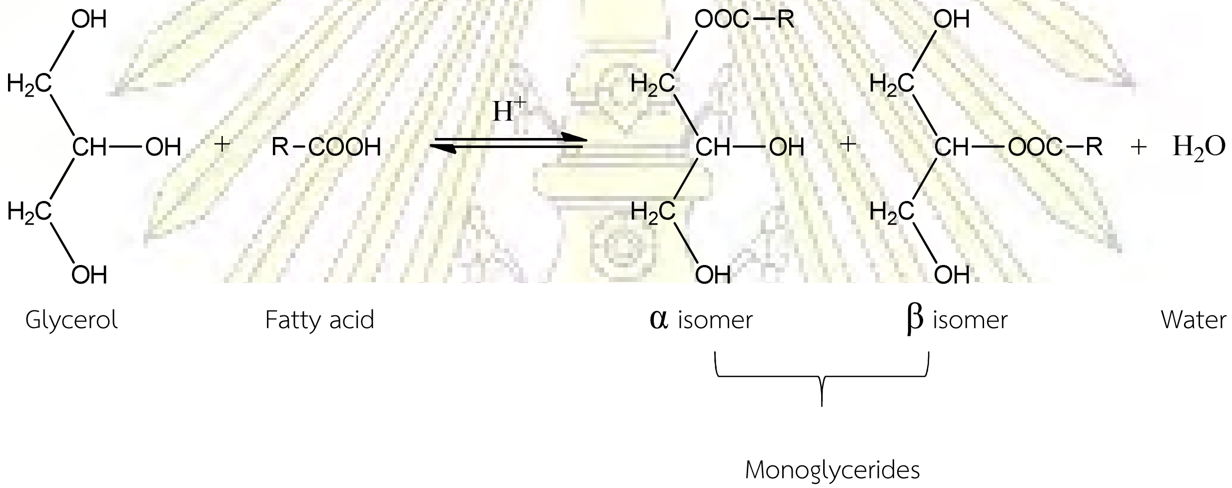


Figure 1.1 Monoglyceride preparation from esterification of free fatty acid and glycerol.

Monoglyceride preparation from acid-catalyzed esterification of glycerol with free fatty acid in an industrial scale usually uses homogeneous catalysts such as sulfuric acid. Sulfuric acid is very active but causes corrosion and presents problems of storage and control[1]. Furthermore, the esterification required high reaction temperature that resulting in mixed products of monoglyceride, diglyceride and triglyceride because monoglyceride could continue reacting with free fatty acid, as shown in Figure 1.2, and the step of neutralizing the acid catalyst increased the volume of waste. The use of a heterogeneous catalyst could simplify the process because it could be removed by filtration without neutralization and could be reused.

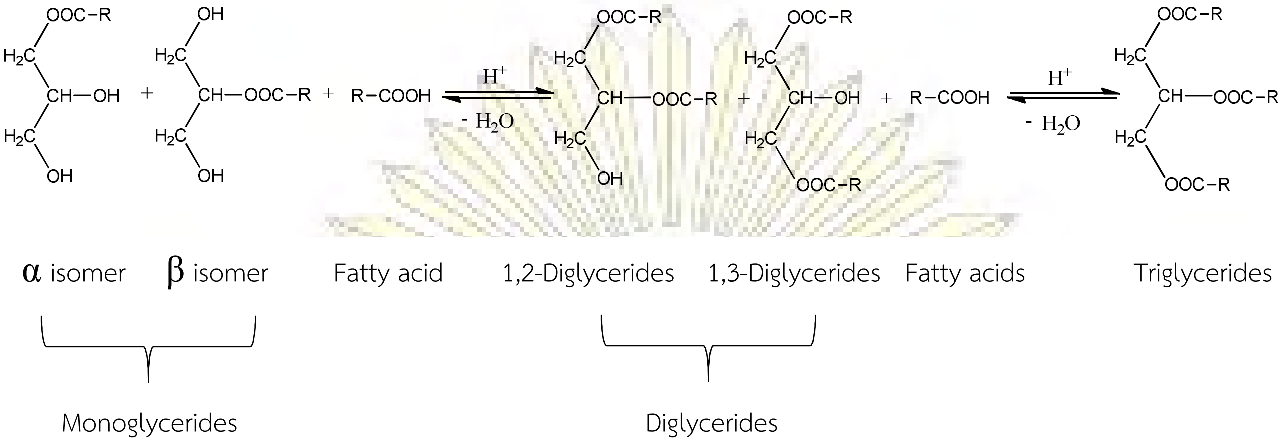


Figure 1.2 Esterification of free fatty acid and monoglycerides.

1.2 Literature reviews on catalyst

Clay minerals find many applications and the variety of uses is still increasing because their properties can be optimized and adjusted to the intended uses such as the swelling behavior, adsorption properties, colloidal and rheological phenomena. The different ways to modify the clay minerals were ion exchange with inorganic and organic cations, binding of inorganic and organic anions, grafting of organic compounds, reaction with acids, pillaring by different types of poly (hydroxo metal) cations, deamination and reaggregation of smectite clay minerals and other techniques. In this research, we focused on the preparation of clay using acid activation method. The acid activation consists of the reaction of clay minerals with a mineral acid solution, usually H_2SO_4. The goal of this is to obtain an improvement of clay properties such as specific surface area, porosity and surface acidity or others. Previously, several researchers studied the modified acidic clay as following below;

In 2010, Eloussaief and Benzina[2] studied the efficiency of natural and acid-activated clays as the adsorbent to remove Pb(II) from aqueous solutions. Four types of clay were raw green clay (RGC), raw red clay (RRC), activated green clay (AGC) and activated red clay (ARC). The acid-activated clay was prepared using 6 M H_2SO_4 solution. The characterization results exhibited that clay samples were mainly composed of kaolinite (K), illite (Il) and chloride (Ch). In addition, raw materials showed the main constituents as silica, alumina and iron oxides whereas acid modified materials indicated the higher silica and alumina amount. Additional, specific surface area, total pore volume, internal porosity and pore size of treated clay were increased when compared to raw material. All prepared clays were used to remove Pb(II) from aqueous solution. Activated green clay showed the highest efficiency for this application at pH 7.0 around 40.75 mg/g of adsorbent.

In 2013, Tong D. S. *et. al.*[3] investigated the hydrolysis of cellulose over acid-activated montmorillonite catalyst. The clay materials were modified with different acid types as H_3PO_4, H_2SO_4, PTSA, CH_3COOH and HCOOH. The effect of acid type and amount were studied. The results showed that the intensity of (001) reflection peak of treated montmorillonite was increased and some interlayer impurities were removed. This suggested that the acid treatment had little influence on the clay layered structure. Additional, the SEM image exhibited the raw material showed large aggregates of platelets mixed with small particles. Conversely, the acid-activated montmorillonite appeared to be composed of relatively smaller particles suggesting that some disaggregation of montmorillonite particles. Finally, the prepared materials were utilized for the hydrolysis of cellulose to reducing sugar. The results showed that H_2SO_4(20)/MMT provided the highest cellulose conversion around 91.2% while H_3PO_4(10)/MMT provided the highest product yield around 16.9%.

In 2013, Catrinescu C. *et al.*[4] determined the methoxylation of limonene over ion-exchanged and acid-activated clays. The raw montmorillonite (SD) material was purified before used (Na-SD). The cation-exchange was prepared by stirred with desired cation solution (Al, Fe or Ni) whereas acid-activated was stirred with different concentration of HCl (1, 3, or 6 M). Raw material was purified in order to eliminate some impurities such as anorthite, feldspar and quartz. The characterization of structure showed that the acid-activated clay was decreased in the basal reflection peak intensity. In addition, the modified clay provided higher specific surface area when compared with raw and cation-exchange materials. All prepared clay exhibited the microporous structure related to type II isotherm. These modified clays were utilized for the methoxylation of limonene in order to produce the α-terpinyl methyl ether. Clay at 1 M acid-activated, SAz-1M-95-30, indicated the highest efficiency to product production when compared with other acid-activated materials.

In 2014, Tong D. S. *et. al.*[5] studied the catalytic cracking of rosin using acid-activated montmorillonite. Clay was modified using 4 M sulfuric acid and studied the effect of acid amount on clay materials. Before acid modification, all materials were purified using DI water in order to remove some impurities. From the XRD results, the acid-activated montmorillonite structure was similar to raw material suggesting that the process did not damage the inherent layered structure of clay. Furthermore, the (001) reflection intensity was increased after acid treatment indicating that some impurities as quartz could be soluble to some extent in sulfuric acid. In addition, the specific surface area and pore volume was increased for acid-activated montmorillonite catalysts. From acidic site analysis, the modified materials showed the medium acidic site related to the NH_3 desorption from the terminal Si-OH groups on the surface of montmorillonite. The acid materials were utilized for the rosin cracking to produce the essential and non-essential oils.

In 2014, Jeenpadiphat S. and Tungasmita D. N.[6] investigated the esterification of oleic acid and high acid content palm oil using an acid-activated bentonite and kaolin as catalyst. The acid catalysts were treated with H_2SO_4 at varying concentration from 0.25 M to 2.0 M or with 0.5 M HNO_3. From the characterization results, the crystallinity of montmorillonite and quartz as the bentonite clay was activated with increasing the H_2SO_4 concentration. Moreover, the modified bentonite with HNO_3 still revealed the montmorillonite and quartz phase similar to raw material, except that the lazulite phase was found. For kaolin samples, both acid treated clays showed the same kaolinite phase as in the raw kaolin. In addition, the specific surface area, total pore volume and acidity of activated bentonite were higher than raw material that TBS-0.5 catalyst provided the highest value. The acidity of treated clay with H_2SO_4 was higher than with HNO_3 because the divalent proton nature of sulfuric acid compared to nitric acid. Finally, all catalysts were applied in esterification reaction fatty acid with methanol. Bentonite was activated with 0.5 M H_2SO_4 showed the best catalytic activity with 100% methyl oleate yield and 99% free fatty acid conversion in the esterification of pure oleic acid and oleic acid in palm oil with methanol, respectively.

In 2016, Rezende and Pinto[7] reported the use of acid-activated smectite natural clay in the esterification of fatty acids at atmospheric pressure and without a co-solvent. The natural clay was modified with 4 M H_2SO_4 to produce the acid-activated material. The XRD results indicated the characteristic peak at 2Theta around 6.5 that related to the typical smectite. Furthermore, after acid treatment, the smectite peak decreased due to a partial destruction of the crystalline phase of clay. The textural properties of natural material were lower specific surface area and pore volume value than acid-activated clay and exhibited type IV isotherm that referred to mesoporous structure. Additional, the number of acid sites was increased with acid-activated clay in every temperature range. These catalysts were used in esterification of fatty acid with methanol. The catalytic activity was compared to the commercial clay as K-10. The results found that the acid-activated smectite clay provided the highest conversion value as 93%.

In 2016, Timofeeva M. N. *et. al.*[8] investigated the catalytic efficiency of acid modified kaolin and metakaolin for the synthesis of octahydro-*2H*-chromen-4-ol from vanillin and isopulegol. For the material preparation, firstly, metakaolin was prepared by calcination of kaolin at 650°C in the air. After that, the materials were modified with HCl solution at different concentration as 0.25, 0.5, 1.0 and 3.0 M to produce the acid catalysts. The composition of kaolin clay was mainly kaolinite phase with little phase of quartz, calcite, illite and illite-smectite. Meanwhile, metakaolin still consisted of quartz, calcite and illite. After acid treatment, both clays showed the similar reflection pattern to raw material suggesting that the clay structure did not destroy by acid condition. The chemical composition as Si/Al ratio of acid activated clay increased with increasing acid concentration due to the leaching of

Al from the framework of the clay. Additional, for textural properties, both acid modified clays exhibited a higher specific surface area than raw material. All prepared clay was applied in the Prins cyclization of (-)-isopulegol with vanillin to octahydro-*2H*-chromen-4-ol in toluene.

1.3 Literature reviews on esterification of free fatty acid

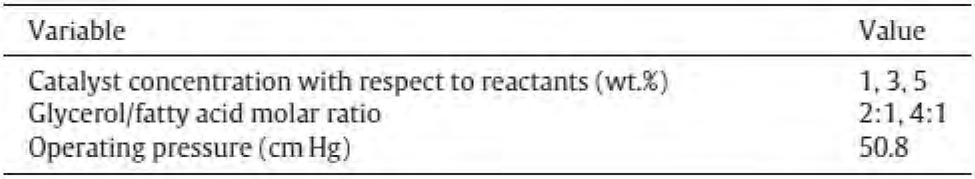
In 1997, Abro S., Pouilloux Y. and Barrault J.[9] studied the synthesis of monoglycerides from glycerol and fatty acids in the presence of solid catalysts. The esterification was carried out at atmospheric pressure in a glass reactor equipped with a stirrer and heated in an oil bath. The reaction was studied at 90°C during 24 h. The molar ratio glycerol/oleic acid was 6.3, the weight ratio oleic acid/catalyst 4.5 and the catalyst weight 1 g. The study showed that the ion-exchange resins are the most active catalysts for the selective preparation of monooleyl glyceride. A comparison between macroporous and gel-type resins shows that the gel-type resins are the most active. Moreover, the selectivity to mono-oleyl glyceride is 90% at a conversion of 54% over the gel resin Amberlyst 31.

In 1999, Pouilloux Y., Abro S., Vanhove C. and Barrault J.[10] studied the preparation of monoglycerides from glycerol and fatty acids in the presence of ion-exchange resins. The esterification was performed in a glass batch reactor equipped with a condenser. The glycerol 9 g and the fatty acid 4.5 g (molar ratio glycerol/fatty acid = 6) were stirred at 800 rpm and heated in an oil bath at 140°C using Amberlyst 31 as a catalyst. The study shows that the decrease of the hydrocarbon chain length of the fatty acid increase the %conversion and %selectivity to monoglyceride because of the greater accessibility to the active sites in the pores. Finally, using lauric acid as a fatty acid in the reaction gave higher %fatty acid conversion and %selectivity to monoglyceride than using oleic acid.

In 2010, Hermida L., Abdullah A. Z. and Mohamed A. R.[11] studied the pore structural properties and catalytic activity of SBA-15 post synthetically functionalized with organo sulfonic acid (HSO_3SBA-15) and with sulfated zirconia (SZSBA-15). The preparation of HSO_3SBA-15: SBA-15 2 g dissolved in 50 mL of dry toluene under mild stirring. 3-(mercaptopropyltrimethoxy)silane (MPTMS) with varied amount (2, 6 and 10 mL) was added and the resulting mixture was refluxed for 20 h. Then the –SH groups were converted to $–SO_3H$ groups by oxidation with H_2O_2 solution, acidified under reflux condition with 10%(w/w)H_2SO_4 then filtered off and dried at 333 K for 12 h. The synthesized catalysts will be donated as HSO_3(1)SBA-15, HSO_3SBA(3)-SBA-15 and HSO_3(5)SBA-15 where values in the brackets represent MPTMS proportion (mL/gram) of SBA-15. The preparation of SZSBA-15: 4 g of SBA-15 was added to solution of zirconium oxychloride and 1.083 g of urea. The mixture was refluxed at 90°C for 5 h, filtered and dried at 100°C 24 h. The reaction condition: lauric acid 0.026 mol (5.21 g), glycerol 0.105 mol (9.67 g) and catalyst 0.7 g were added to the reactor. The system was flushed with nitrogen. The reaction mixture was heated to 160°C. Stirring was started and the reactants were stirred for 6 h. The result has shown that HSO_3SBA-15(1) gave 94% lauric acid conversion and the selectivity to monolaurin is 70%.

In 2011, Hermida L., Abdullah A. Z. and Mohamed A. R.[12] studied the synthesis of monoglyceride through glycerol esterification with lauric acid over propyl sulfonic acid post-functionalized SBA-15 mesoporous catalyst. The SBA-15 mesoporous material was functionalized with propylsulfonic acid by refluxing 2 g of SBA-15 materials with 2 mL of 3-mercaptopropyl trimethoxysilane (MPTMS). Then, soxhlet extraction was carried out for 20 h, followed by mild oxidation using H_2O_2 to form HSO_3SBA-15. The esterification of glycerol with lauric acid using different HSO_3SBA-15 catalysts loadings, lauric acid/glycerols molar ratios and reaction temperatures was carried out in a batch system with continuous removal of water and without the use of any solvent. The condition is given in Table 1.1 for stirring at 750 rpm for 7 h. The results have shown that HSO_3SBA-15 gave the highest %monoglyceride yield and %lauric acid conversion at 433 K (160°C) using a catalyst loading of 5 wt% and molar ratio of 4:1.

Table 1.1 Experimental conditions used for the kinetic study.

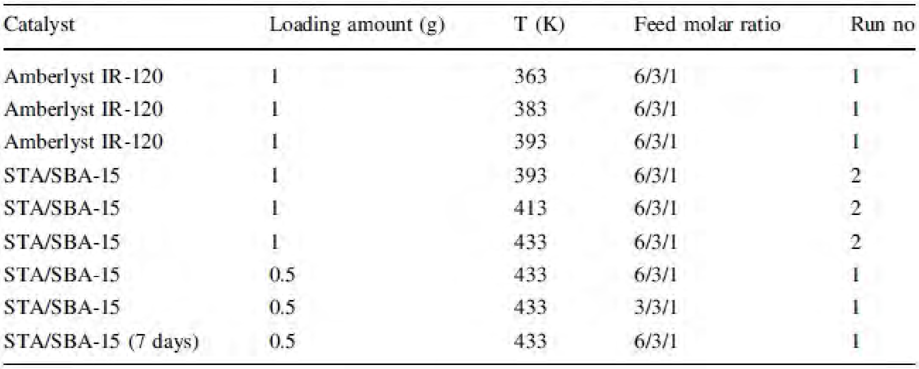


Variable	Value
Catalyst concentration with respect to reactants (wt.%)	1, 3, 5
Glycerol/fatty acid molar ratio	2:1, 4:1
Operating pressure (cm Hg)	50.8

In 2013, Singh D., Patidar D., Ganesh A and Mahajanin S.[13] studied esterification of oleic acid with glycerol in the presence of supported zinc oxide as catalyst. The preparation of ZnO/zeolite: $ZnNO_3$ 1 M is mixed with zeolite in a weight ratio of 1:3 (ZnO/zeolite). Added urea to the mixture to precipitate and stirred at 85°C for 10 h. The mixture was filtered, the solid obtained was dried at 110°C for 14 h. The reactor was charged with 60 g of oleic acid, 80 g of glycerol, and 2.76 g of catalyst are added to a reactor. And 10 mL of n-hexane is added to separate the organic layer from glycerol. The mixture is centrifuged. The parameters like temperature, mole ratio and catalyst loading are varied over a wide range. The synthesized ZnO supported zeolite catalyst shows that esterification of oleic acid gave selectivity as high as 70-80% for monoloein in the conversion range of 60-90% at 160°C using catalyst loading >0.5 wt% and a mole ratio of 4:1.

In 2016, Simsek V., Degirmenci L. and Murtezaoglu K.[14] studied the synthesis of a silicotungstic acid SBA-15 catalyst for selective monoglyceride production. The preparation of STA/SBA-15 (silicotungstic acid/SBA-15) is to prepare a surfactant solution by dissolving 4 g of Pluronic P123 (Sigma-Aldrich) in 1.7 M HCl at 40°C and stirring for 4 h. The amount of tetraethylorthosilicate (TEOS) was determined as 8 g, stirred for 2 h, aged at 100 °C for 48 h. The crystalline sample at the end of aging process was washed with DI water and dried at 80°C for 12h and the reaction condition is given in Table 1.2. The result showed that the synthesized STA/SBA-15 catalyst can be used as an alternative of Amberlyst IR-120 in esterification reactions and give 75-85 % selectivity to monoglyceride and 90% lauric acid conversion at 393 K (120°C) using a catalyst and molar ratio glycerol/ethanol/lauric acid of 6:3:1.

Table 1.2 Experimental conditions applied in esterification reactions.



Catalyst	Loading amount (g)	T (K)	Feed molar ratio	Run no
Amberlyst IR-120	1	363	6/3/1	1
Amberlyst IR-120	1	383	6/3/1	1
Amberlyst IR-120	1	393	6/3/1	1
STA/SBA-15	1	393	6/3/1	2
STA/SBA-15	1	413	6/3/1	2
STA/SBA-15	1	433	6/3/1	2
STA/SBA-15	0.5	433	6/3/1	1
STA/SBA-15	0.5	433	3/3/1	1
STA/SBA-15 (7 days)	0.5	433	6/3/1	1

In 2016, Konwar L. J., Arvela P. M., Kumar N., Mikkola J. P., Sarma A. K. and Deka D.[15] studied sulfonated carbons as heterogeneous catalysts upon the selective esterification of glycerol with lauric and oleic acids. The –SO_3H containing mesoporous carbon catalyst ($ACSO_3H$) was prepared by sulfonation of activated carbon (AC) derived from waste biomass while nonporous carbon catalyst ($HTCSO_3H$) was prepared by direct hydrothermal treatment of the same biomass with con. H_2SO_4. The biomass samples were dried and stored in a desiccator. The reaction condition is that 5 wt% of glycerol mass was added to 10 g of glycerol in a 3-necked flask equipped with a magnetic stirrer bar and the stirring speed was set at 650 rpm. The mixture was heated to the desired temperature. When the preset temperature was reached, an addition of lauric acid or oleic acid (Gly/FA molar ratio = 1) was commenced. The preliminary catalytic experiments with lauric acid using the different acid catalysts. Conditions: 125°C, glycerol to lauric acid molar ratio = 1, stirring speed = 650 rpm and a catalyst loading of 5 wt%. The study has shown that the maximum lauric acid conversion and selectivity to MG at 125°C was $ACSO_3H$. Furthermore, the effect of reaction temperature on lauric and oleic acid conversion and selectivity to monoglyceride during esterification of glycerol and fatty acids has shown that the range of temperature which gave the highest % fatty acid conversion and % selectivity to monoglyceride was 100-125°C.

1.4 Theory

1.4.1 Clay and clay mineral[16]

Clay has been defined as ‘a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden with dried or fired’. The term clay can signify a rock, a sedimentary deposit and the alteration products of primary silicate minerals.

In industrial applications of clays, we can divide clay into four types: (i) bentonites with montmorillonite as the principal clay mineral constituent; (ii) kaolins containing kaolinite; (iii) palygoskite and sepiolite; and (iv) common clays, which often contain illite-smectite mixed-layer minerals, and are largely used for ceramics.

The definition of clay mineral is ‘phyllosilicate minerals (extended sheet of SiO_4 tetrahedral of which 3 in 4 oxygens are joined with adjacent tetrahedral leading to Si:O ratio of 2:5) and minerals which impart plasticity to clay and which harden upon drying or firing’. Phyllosilicate of any size, such as macroscopic mica, vermiculite, and chlorite, may be regarded as clay minerals. Non-phyllosilicate minerals would also qualify as clay minerals if they imparted plasticity to clay and hardened on drying and firing. The clay fraction of soils often contains non-phyllosilicate minerals, such as carbonates, feldspars, and quartz together with the oxide of iron and aluminium. Clay minerals are classified under silicates but since their formulas have more oxygen than Si, Al or Mg, these minerals may be considered as oxide of silicon, aluminium or magnesium. Thus, clay minerals and related layer minerals may be referred to as porous layered oxides.

Clay minerals may be considered as inorganic polymers. The basic monomer is the silica tetrahedron, which is bound on one or both sides to octahedral sheet, as shown in Figure 1.3.

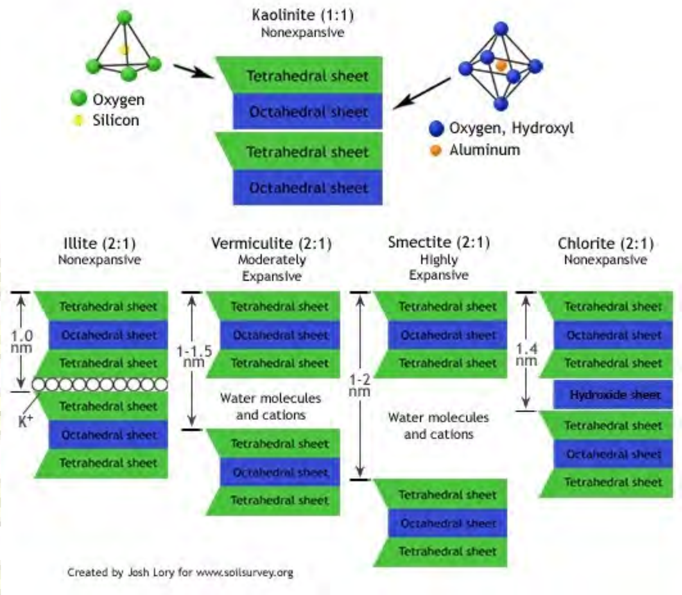


Figure 1.3 Structure of clays

1.4.2 Characterization of materials

1.4.2.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a technique used for characterization of minerals and other crystalline materials. X-rays is directed onto the flat surface of material. XRD can provide additional information beyond basic identification. If the sample is a mixture, XRD data can be analyzed to determine the proportion of the different minerals present. Other obtained information can include the degree of crystallinity of the minerals present and possible deviations of the minerals from their ideal compositions. The diffraction of x-rays was shown in Figure 1.4.

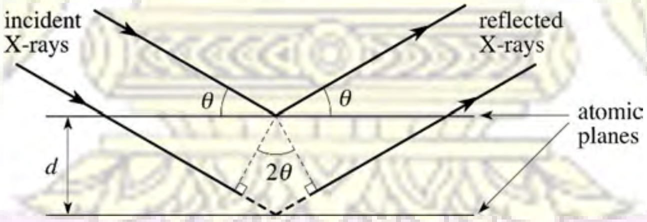


Figure 1.4 Diffraction of X-rays.

$$n\lambda = 2d\sin\theta$$

From the Bragg's equation (above), d is the distance between equivalent atomic planes, θ is the angle between the incident beam and these planes, n is an integer and λ is the wavelength of X-ray source. Then from XRD results, it is able to determine the interplanar spacing of the sample.

1.4.2.2 N_2 adsorption-desorption technique

There are three types of porous materials as shown in Table 1.3. The nitrogen was absorbed on the surface of the materials by physisorption. The van der Waals force attracted between the surface of materials and the nitrogen molecules. However, this attractive force is weak, the absorbed nitrogen molecules could be desorbed by decreasing the pressure or heating.

Table 1.3 The classification of porous materials

Type	Pore size
Microporous	< 20 Å
Mesoporous	20-500 Å
Macroporous	> 500 Å

N_2 adsorption-desorption technique is the technique used to determine the surface area, pore volume, pore diameter and pore size distribution. The adsorption behavior is described by adsorption isotherm. The adsorption isotherm can be classified into six types, as shown in Figure 1.5. According to the IUPAC definition, microporous materials show a Type I adsorption-desorption isotherm. Nonporous or macroporous exhibit types II, III, and VI and mesoporous exhibits types IV and V.

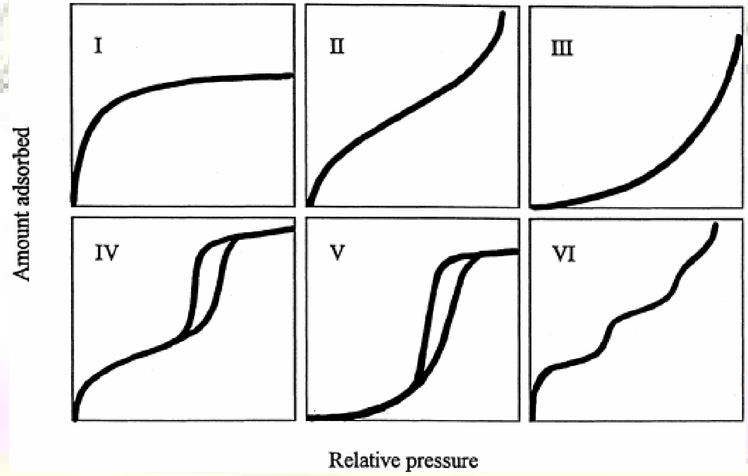


Figure 1.5 The IUPAC classification of adsorption isotherm.

1.4.2.3 Scanning electron microscopy (SEM)

The scanning electron microscopy (SEM) is a technique used to provide the detail about morphology, texture, etc. The SEM images show the three-dimension of materials in black and white. The samples were sputtering coated with a thin layer of gold or other conductive metals if the samples were not conductive. SEM forms a magnified image by scanning the surface of a sample by a convergent electron beam using scanning coils. Several kinds of signals generated from the sample by the injection of the electrons are detected by various detectors arranged near the sample. The detected signals modulate the brightness of a display at the console of SEM, which is synchronized with the scan by the electron probe.

1.4.3 Esterification reaction

Esters are chemical compounds derived from a carboxylic acid and an alcohol. Esterification is a common method for making esters. The mechanisms of acid-catalyzed and base-catalyzed esterifications are presented in Figure 1.6 and 1.7, respectively.

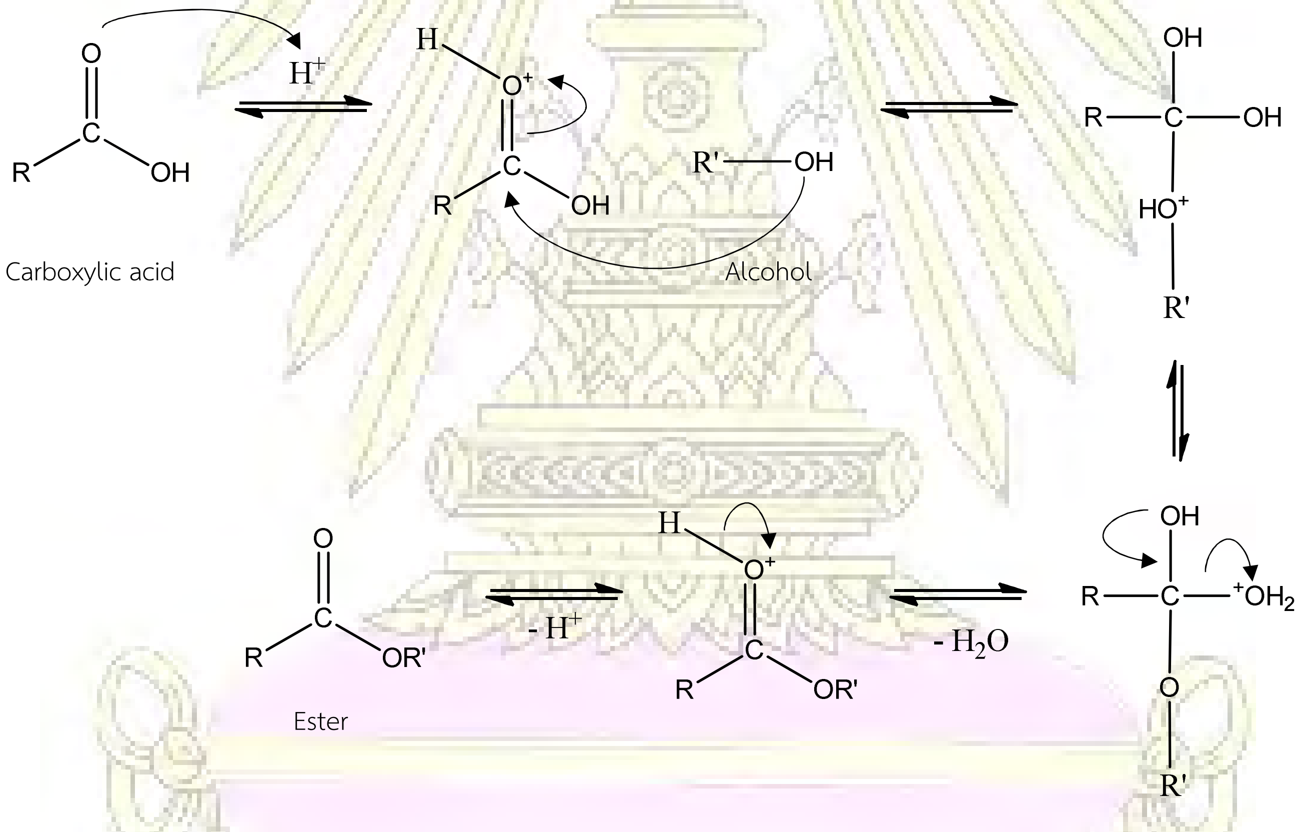


Figure 1.6 Mechanism of acid-catalyzed esterification of fatty acid.

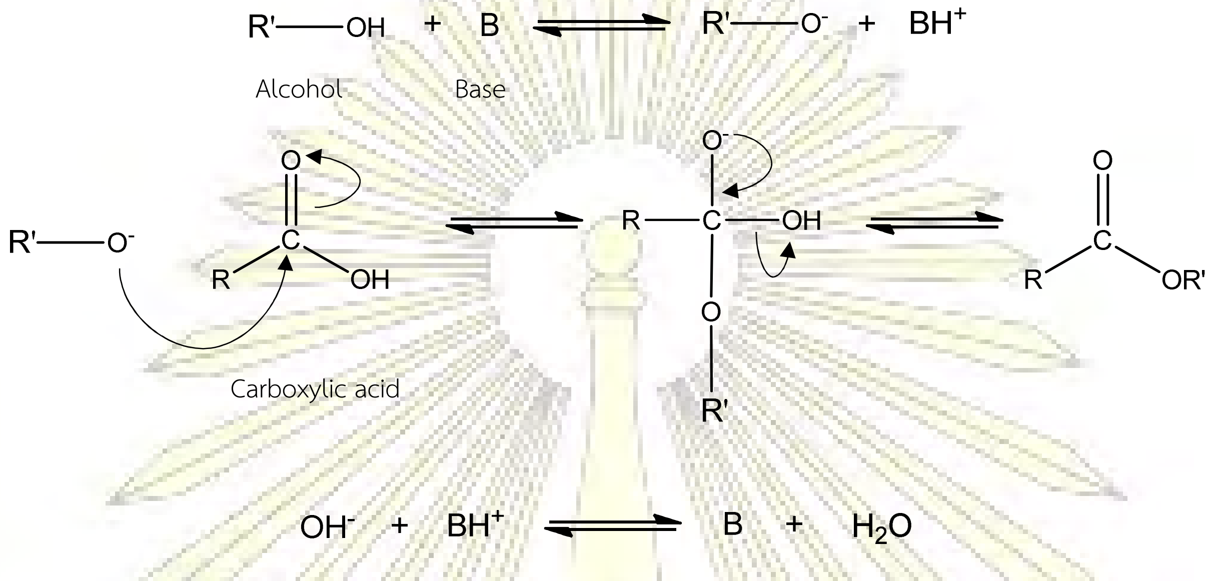


Figure 1.7 Mechanism of base-catalyzed esterification of fatty acid.

1.5 Objectives

1.5.1 To modify natural clays as the heterogeneous catalysts

1.5.2 To test modified clay in the esterification reaction of fatty acid

1.5.3 To investigate the optimum conditions in esterification reaction of fatty acid

CHAPTER II

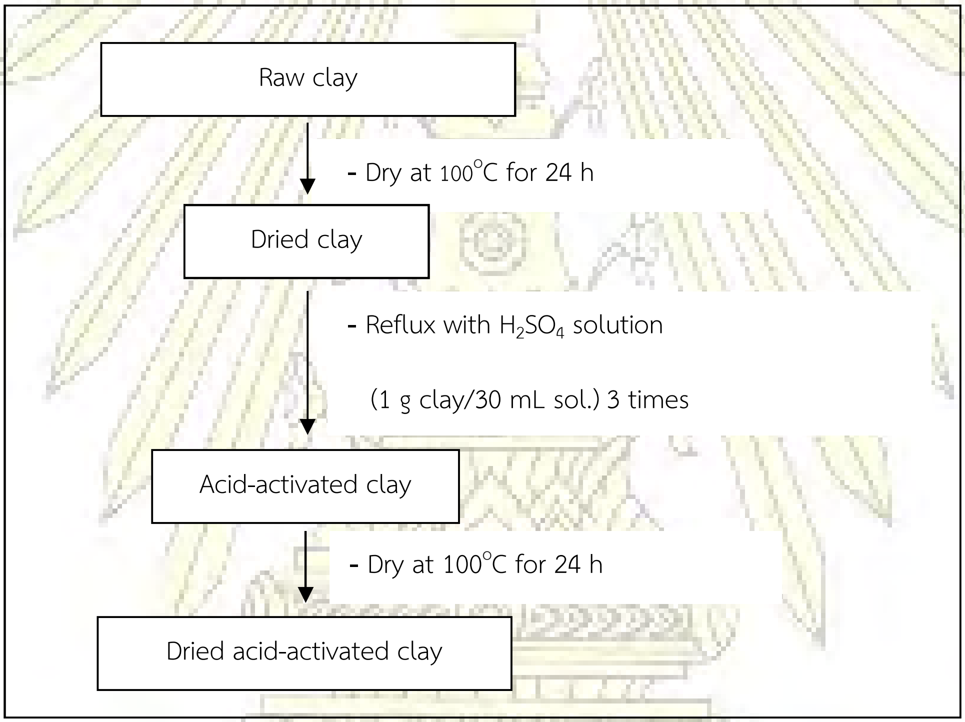
EXPERIMENTAL

2.1 Chemicals

1. Bentonite clay (Siam Valclay Co., Ltd. (Thailand))
2. Lanna White clay (Industrial Mineral Development Ltd. (Thailand))
3. Ranong Fine clay (Industrial Mineral Development Ltd. (Thailand))
4. Cerafast clay (Industrial Mineral Development Ltd. (Thailand))
5. Naraton clay (Industrial Mineral Development Ltd. (Thailand))
6. Sulfuric acid, H_2SO_4 (Merck, 95-97%)
7. Oleic acid, $C_{18}H_{34}O_2$ (Fluka)
8. Ethanol, C_2H_5OH (Merck)
9. Glycerol (Fisher)
10. Eicosane, $C_{20}H_{42}$ (Aldrich)
11. N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA), (Aldrich)
12. Potassium hydroxide (Merck)
13. Sodium hydroxide (Merck)
14. Alpha-monoolein, (Sigma, ≥99%)
15. 1,3-Diolein (Sigma, ≥99%)
16. Tetrahydrofuran (S.T. Baker)
17. Phenolphthalein
18. Alpha-monopalmitin (Sigma, ≥99%)

2.2 Acid-activated clay preparation

The clay samples were prepared using acid-activation method with H_2SO_4 at varying concentrations from 0.25 to 2.0 M. The acid-activated clay was performed by refluxing dried clay powder with H_2SO_4 at 120°C for 1 h at clay: acid solution ratio of 1.0 g: 30 mL. At the end of each run, the mixture was separated by centrifugation and then the collected clay was repeatedly refluxed twice as above for a fresh sample. Finally, the acid-activated clay was dried in air at 100°C overnight. The activated clay samples as above with 0.25, 0.5, 1.0 and 2.0 M H_2SO_4 were denoted as Bent 0.25, Bent 0.5, Bent 1.0 and Bent 2.0, respectively, and Bent 0.5 samples from heating with an oil bath was donated as Bent 0.5 (OB). In addition, there are four Thai clays as the raw material; Lanna white from northern Thailand, Ranong fine and Cerafast from Ranong and Naraton from Narathiwas. The acid-activated Thai clay samples were donated as Lanna white 0.5, Ranong fine 0.5, Cearafast 0.5 and Naraton 0.5, respectively. The preparation process was shown in Scheme 2.1.



Scheme 2.1 Diagram of acid-activated clay preparation.

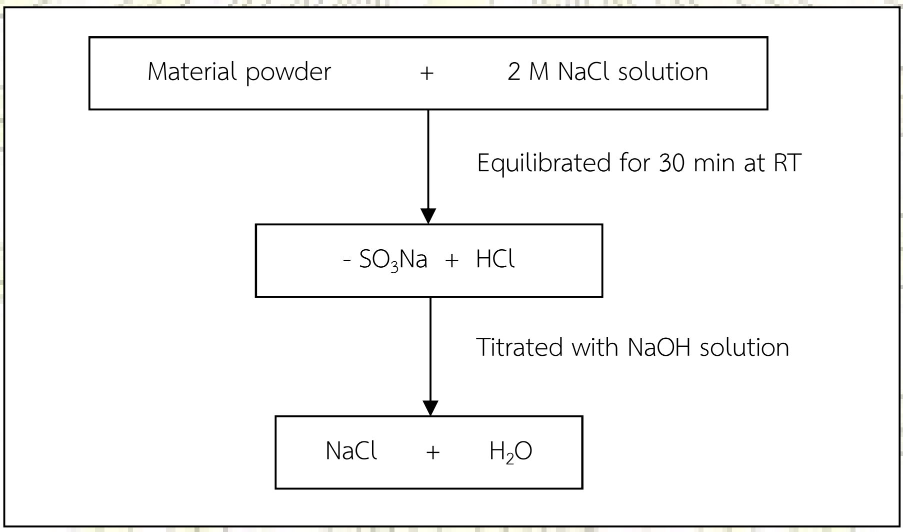
2.3 Catalyst characterization

2.3.1 X-ray diffraction (XRD)

Powder X-ray diffraction patterns of synthesized catalysts were identified with a Rigaku D/MAX-2200 Ultima+ X-ray diffractometer equipped with Cu target X-ray tube (40 kV, 30 mA). The samples were scanned at 2-theta angle in the range of 0.5 to 50.0 degree with 2 degree/min of scan speed. The scattering slit, divergent slit and receiving slit were fixed at 0.5 degree, 0.5 degree and 0.15 nm, respectively.

2.3.2 Acid-base titration

The acid capacities of catalysts were quantified using 2 M NaCl solution as the ion exchange agent. Approximately 0.05 g of catalyst was exchanged with 15 mL of the salt (NaCl) solution and allowed to equilibrate for 30 min at room temperature. After that, the sample solution was titrated with 0.01 M NaOH solution using phenolphthalein as indicator. The acid-base titration process was shown in Scheme 2.2.



Scheme 2.2 Diagram of acid-base titration process.

2.3.3 Specific surface area

Specific surface area, N_2 adsorption-desorption isotherms and pore size distribution of catalysts were determined by a BEL Japan, BELSORP mini instrument. Before measurement, each sample was pretreated at 150°C for 2 h.

2.3.4 Scanning electron microscopy (SEM)

The morphology of synthesized materials was analyzed by JSM-5410 LV scanning electron microscope with 15 kV of acceleration. All samples were coated with sputter gold under vacuum for conductivity.

2.4 Esterification reaction

Esterification reactions were carried out in a laboratory-built apparatus using glycerol and free fatty acid as starting materials at 3:1 mole ratio, 160°C for 5 h. The reaction was studied at 5wt% catalyst loading based on oleic acid. The clay catalyst modified with H_2SO_4 was used. The reaction was under negative pressure (460 mm Hg) in order to remove the water product. After complete reaction, two layers of mixture which the top layer was the product and the bottom layer was excess glycerol.

The determination of fatty acid conversion was used the titration method during the esterification reaction because it was simple and efficient analytical method that could be performed without the need for highly specialized equipment. The titration procedure, 0.1 g sample at time intervals was dissolved in ethanol and used phenolphthalein indicator as indicator. The titration was carried out against aqueous solution of 0.1 M KOH. Acidity and conversion of fatty acid was determined according to the equation given below.

$$\mathrm{Acidity} = \frac{(282.47 \times \mathrm{N} \times \mathrm{V})}{\mathrm{W}}$$

Where

N = Molar concentration of KOH solution

V = Volume of KOH solution employed for titration (mL)

W = Weight of sample (g)

$$\%\ \mathrm{Conversion} = \left(\frac{\mathrm{A_i} - \mathrm{A_t}}{\mathrm{A_i}}\right) \times 100$$

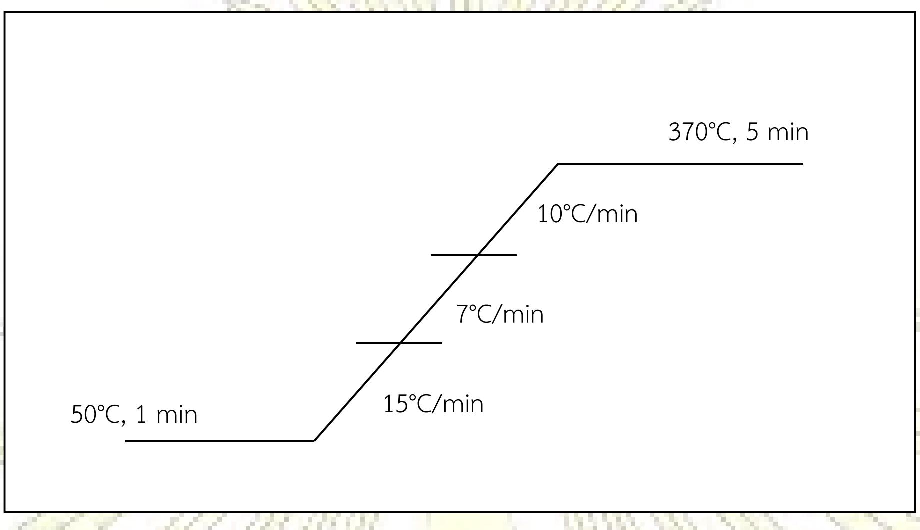
Where

Ai = Initial acidity of oleic acid

At = Acidity at a time

2.5 Gas chromatography analysis (GC)

The monoglyceride yield can be analyzed by Gas Chromatography which was carried out on a VARIAN CP-3800 chromatography equipped with split ratio 1:50, flame ionization detector (FID, N_2 as a carrier gas and a 10 m in length of Metal biodiesel column equivalent to a 0.32-mm diameter and a 0.10 μm film thickness. The capillary column has been had maximum temperature limit of 400°C. Eicosane was used as an internal standard and tetrahydrofuran as a solvent for analysis. Samples were prepared for GC analysis by derivatization using N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) and 1 μL of sample was injected into the column. The GC temperature program for product analysis was 50°C hold for 1 min, programmed at 15°C/min up to 180°C, programmed at 7°C/min up to 230°C, programmed at 10°C/min up to 370°C, final temperature hold for 5 min, it was shown in Scheme 2.3.



Scheme 2.3 The temperature program used for GC analysis of glyceride products.

CHAPTER III

RESULTS AND DISCUSSIONS

3.1 Catalysts characterization

3.1.1 X-ray diffraction

The XRD patterns of raw bentonite (Bent), Bent 0.25, Bent 0.5, Bent 1.0 and Bent 2.0 were shown in Figure 3.1. The raw bentonite consisted of montmorillonite (Mt), illite (I) and quartz (Q). Illite had been disappeared after acid treatment. However, all patterns were slightly different because the structures of acid-activated bentonites were not significantly changed after the treatment.

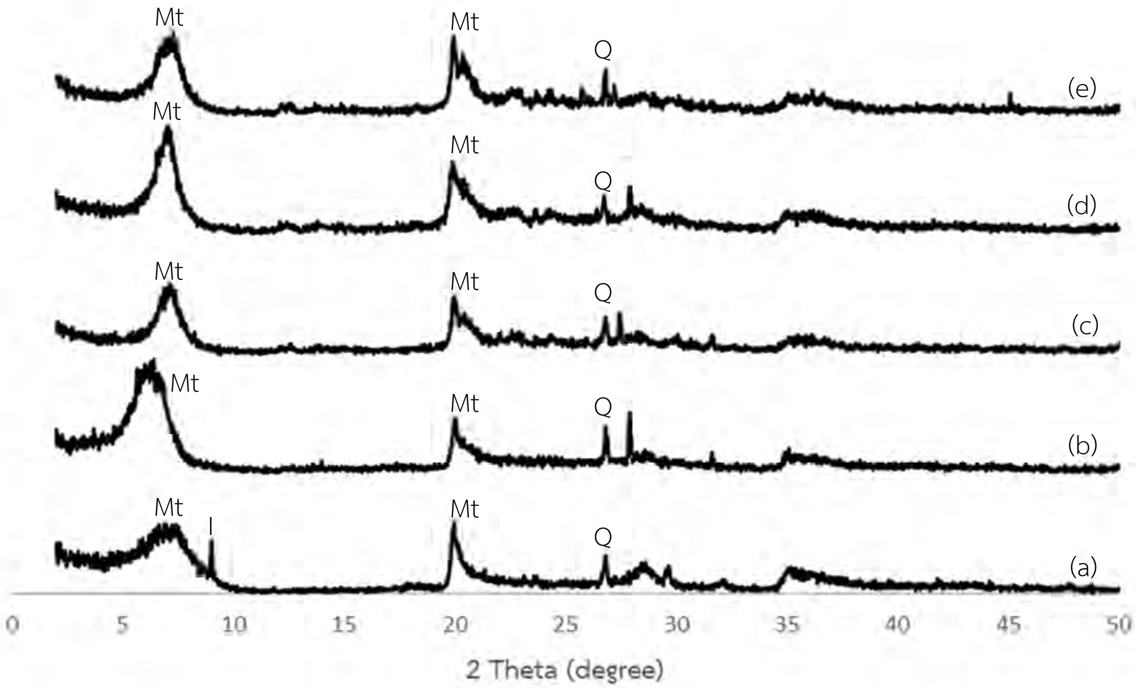


Figure 3.1 Representative XRD patterns of (a) Bent, (b) Bent 0.25, (c) Bent 0.5, (d) Bent 1.0 and (e) Bent 2.0

Montmorillonite in Bent 0.5 (OB) and Bent 1.0 (OB) had a lower intensity compared to the Bent 0.5 and Bent 1.0 as shown in Figure 3.2, suggesting that heating with an oil bath can cause a partial destruction of the Mt crystalline phases of the clay and octahedral cation passed into the acid solution.[17]

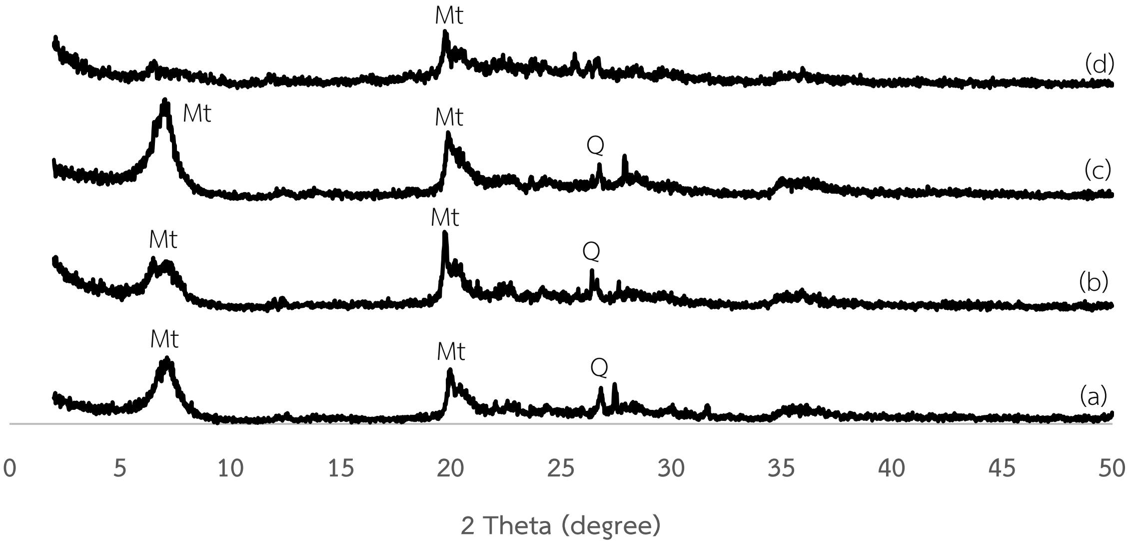


Figure 3.2 Representative XRD patterns of (a) Bent 0.5, (b) Bent 0.5 (OB), (c) Bent 1.0 and (d) Bent 1.0 (OB).

Similarly, the structure of acid-activated Thai clays also insignificantly changed after treating. As can be seen in Figure 3.3, the peaks at 2θ = 12.1° and 24.4° suggest the presence of kaolinite[18] and feldspar[19] in all Thai clays. The XRD analysis investigated that kaolin is the dominant mineral in the four Thai clays. Illite-smectite[18] (2θ = 8.8°) and quartz[18] (2θ = 26.6°) also be presented in Lanna white, Ranong fine and Cerafast.

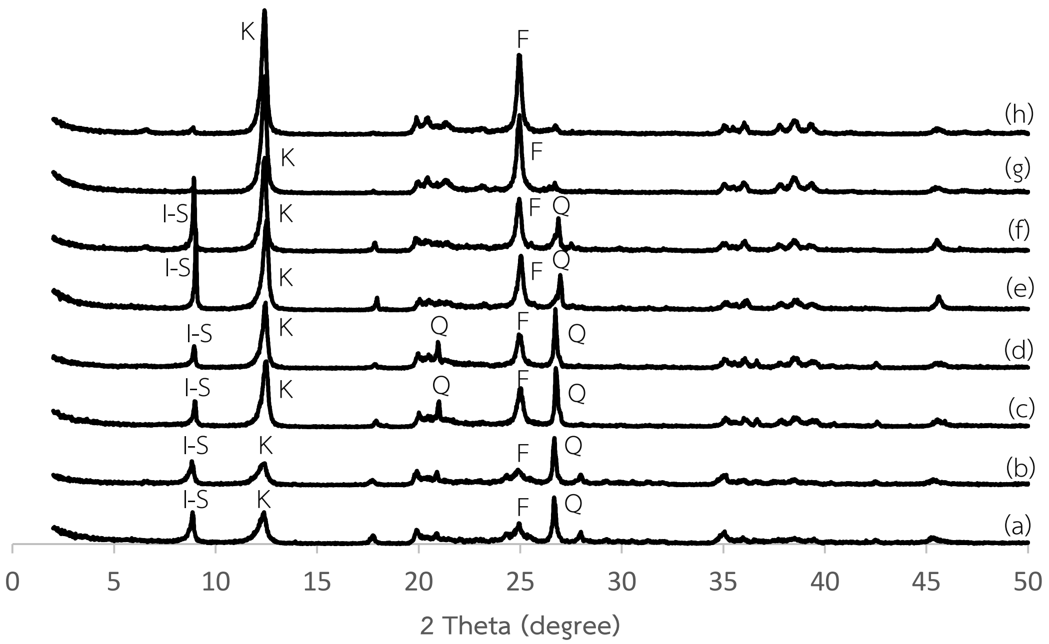


Figure 3.3 Representative XRD patterns of (a) Lanna white, (b) Lanna white 0.5, (c) Ranong fine, (d) Ranong fine 0.5, (e) Cerafast, (f) Cerafast 0.5, (g) Naraton and (h) Naraton 0.5

3.1.2 Acid-base titration

The acid amount values of all clay samples were shown in Table 3.1. It was significant that acid amount values of the materials were increased as the raw clay was treated with increasing concentration of H_2SO_4.[20] At the acid concentration of 0.5 M seems to be saturated point for bentonite support to be acidified. Then, the acid concentration of 0.5 M was selected to be treated in other clay samples.

Table 3.1 Acid strength of raw clays and acid-activated clays.

Catalyst	Acid amount (mmol/g clay)
Bent	0.08
Bent 0.25	2.41
Bent 0.5	3.86
Bent 1.0	3.87
Bent 2.0	3.92
Lanna white	0.09
Lanna white 0.5	1.03
Ranong fine	0.11
Ranong fine 0.5	1.29
Cerafast	0.09
Cerafast 0.5	1.19
Naraton	0.07
Naraton 0.5	1.55

The acid amount of acid-activated clays which were prepared by heating with an oil bath showed higher values due to a larger surface area, as shown in Table 3.2.

Table 3.2 Acid strength of Bent 0.5 and Bent 1.0 from different preparation.

Catalyst	Acid amount (mmol/g clay)
Bent 0.5	3.86
Bent 0.5 (OB)	4.15
Bent 1.0	3.87
Bent 1.0 (OB)	5.60

3.1.3 Specific surface area

The specific BET surface area (A) and total pore volume (V) of samples were obtained from the standard BET (Brunauer, Emmett and Teller) method and the Barret-Joyner-Halender (BJH) equation, respectively as shown in Table 3.3. The surface area values of bentonite clay are not significantly different which are in range of 3-12.

Table 3.3 BET surface area, total pore volume and average pore diameter of raw clays and acid-activated clays.

Catalyst	BET surface area (m^2/g) (A)	Total pore volume (cm^3/g) (V)	Average pore diameter (nm)
Bent	15.3	0.05	2.43
Bent 0.25	8.6	0.03	3.28
Bent 0.5	8.1	0.02	4.19
Bent 1.0	3.4	0.01	5.41
Bent 2.0	12.4	0.03	3.28
Lanna white	11.0	0.04	3.28
Lanna white 0.5	5.4	0.02	4.19
Ranong fine	11.4	0.04	3.28
Ranong fine 0.5	5.4	0.02	4.19
Cerafast	11.0	0.04	3.71
Cerafast 0.5	7.3	0.02	2.43
Naraton	14.4	0.06	3.28
Naraton 0.5	10.8	0.03	3.28

The surface area, total pore volume and pore diameter of the Bent 0.5 (OB) and Bent 1.0 (OB) were higher than Bent 0.5 and Bent 1.0, respectively, as shown in Table 3.4. These results were caused by the different heating processes.

Table 3.4 BET surface area, total pore volume and average pore diameter of Bent 0.5 and Bent 1.0 from different preparation.

Catalyst	BET surface area (m^2/g) (A)	Total pore volume (cm^3/g) (V)	Average pore diameter (nm)
Bent 0.5	8.1	0.02	4.19
Bent 0.5 (OB)	31.2	0.15	18.58
Bent 1.0	3.4	0.01	5.41
Bent 1.0 (OB)	6.4	0.21	13.17

As can be seen in Figure 3.4, 3.5 and 3.6, the isotherms of all clays showed type IV that referred to mesoporous materials.

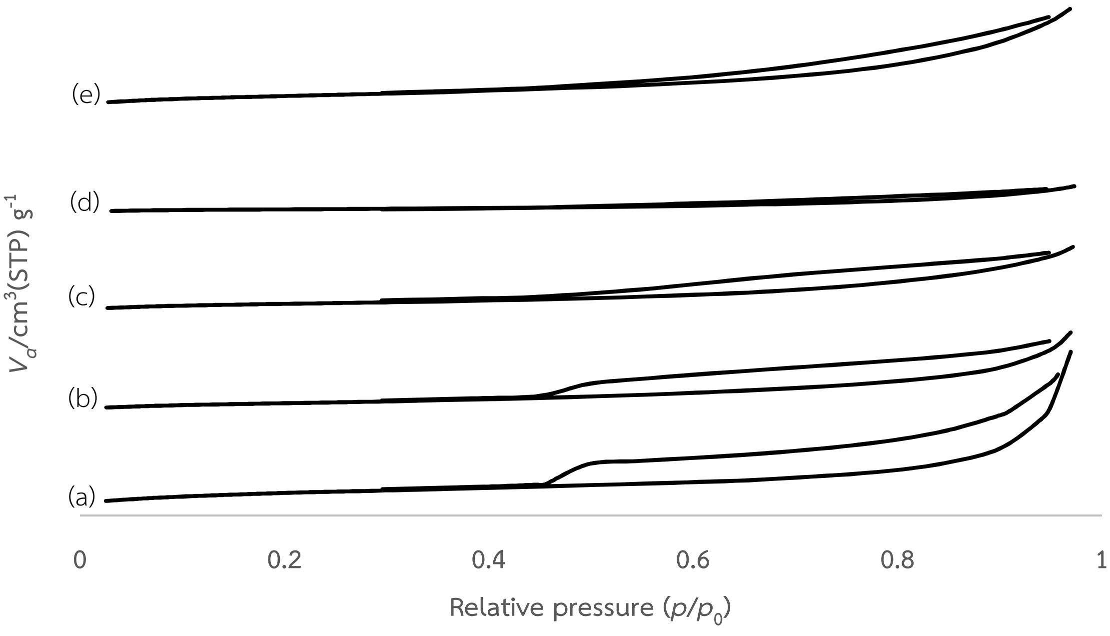


Figure 3.4 Representative N_2 adsorption/desorption isotherms of (a) Bent, (b) Bent 0.25, (c) Bent 0.5, (d) Bent 1.0 and (e) Bent 2.0.

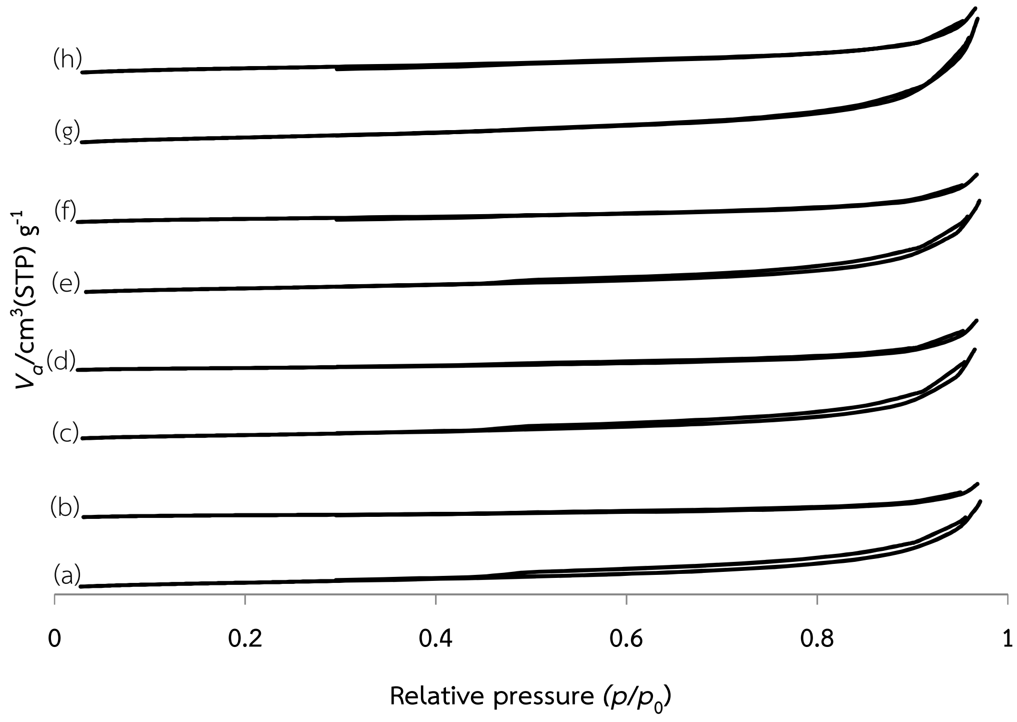


Figure 3.5 Representative N_2 adsorption/desorption isotherms of (a) Lanna white, (b) Lanna white 0.5, (c) Ranong fine, (d) Ranong fine 0.5, (e) Cerafast, (f) Cerafast 0.5, (g) Naraton and (h) Naraton 0.5.

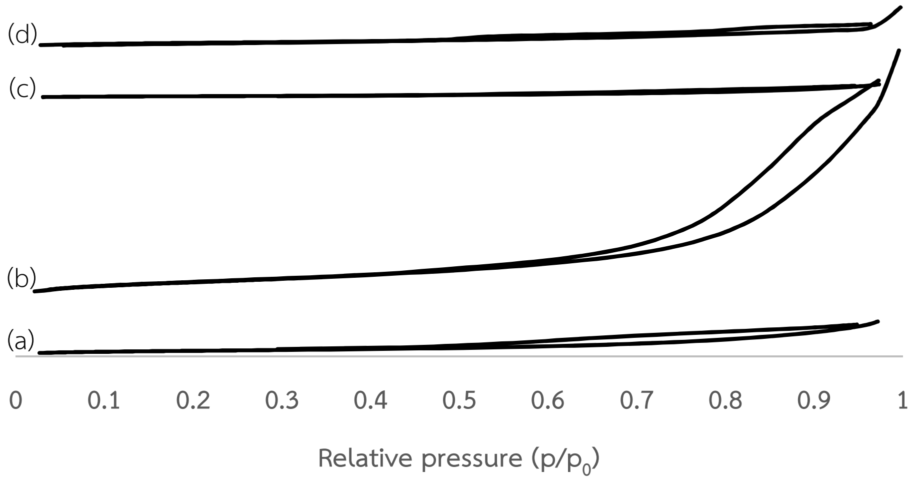


Figure 3.6 Representative N_2 adsorption/desorption isotherms of (a) Bent 0.5, (b) Bent 0.5 (OB), (c) Bent 1.0 and (d) Bent 1.0 (OB).

3.1.4 Scanning electron microscopy (SEM)

The SEM images of Bent, Bent 0.25, Bent 0.5, Bent 1.0 and Bent 2.0 samples at 6,000 magnification were shown in Figure 3.7. The surface of acid-activated bent samples showed rougher than the raw bent because of the dissolution of octahedral aluminium layers in clay.[21]

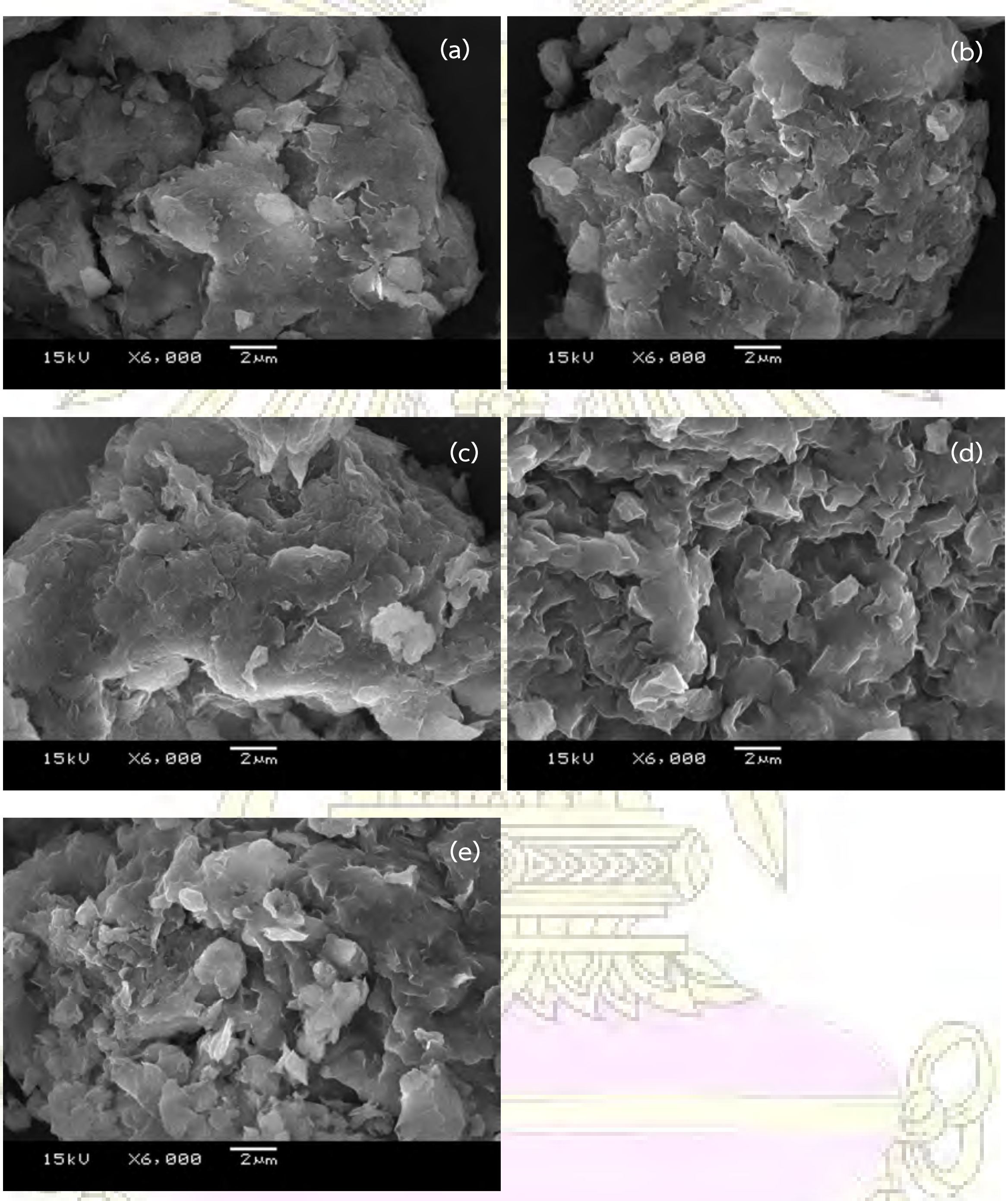


Figure 3.7 Representative SEM images × 6,000 of (a) Bent, (b) Bent 0.25, (c) Bent 0.5, (d) Bent 1.0 and (e) Bent 2.0

The heating process affected the morphology of clay samples. As can be seen in Figure 3.8, the surfaces of both clay samples were sheet-shaped and rougher than Bent 0.5 and Bent 1.0, respectively.

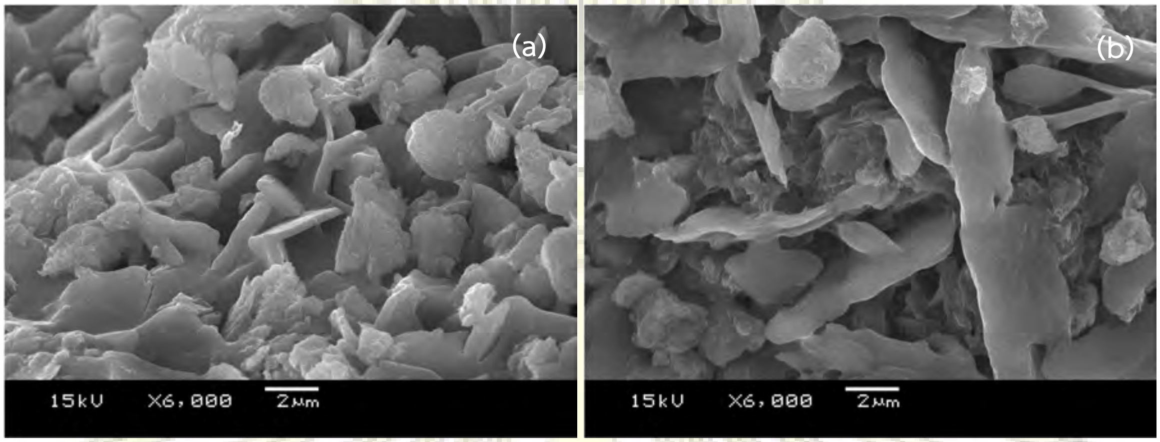
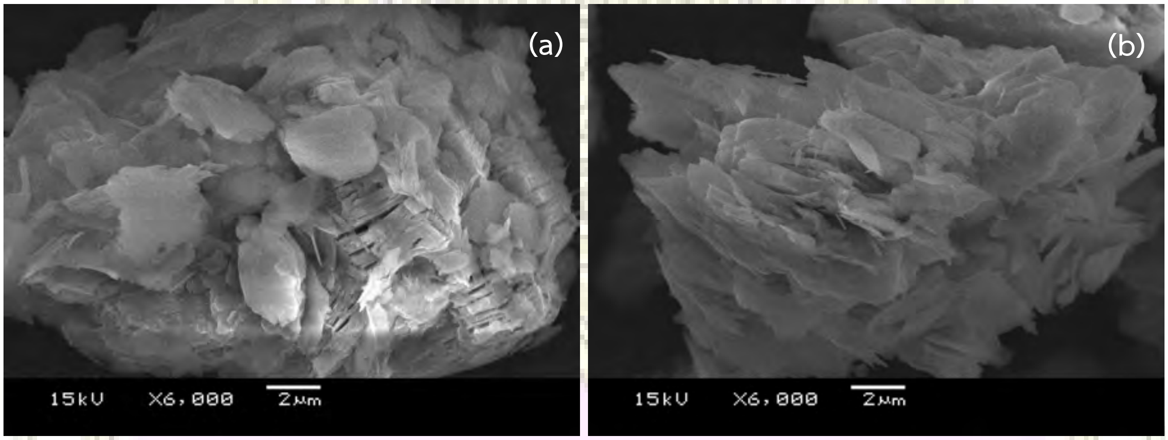


Figure 3.8 Representative SEM images × 6,000 of (a) Bent 0.5 (OB) and (b) Bent 1.0 (OB).

The SEM images of Lanna white, Lanna white 0.5, Ranong fine, Ranong fine 0.5, Cerafast, Cerafast 0.5, Naraton and Naraton 0.5 samples at 6,000 magnification were shown in Figure 3.9. The morphology of acid-activated clays was not significantly changed after treating.



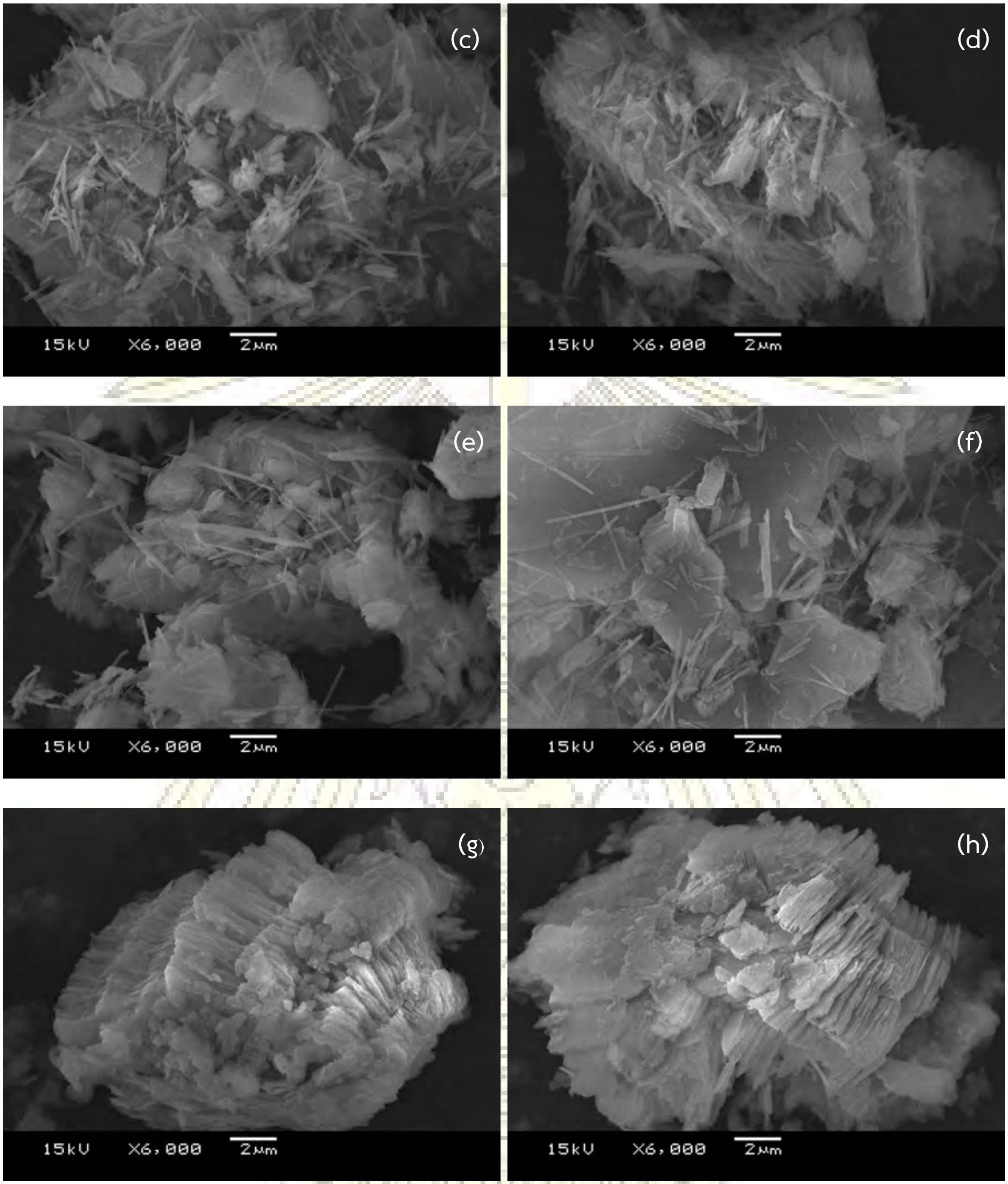


Figure 3.9 Representative SEM images × 6,000 of (a) Lanna white, (b) Lanna white 0.5, (c) Ranong fine, (d) Ranong fine 0.5, (e) Cerafast, (f) Cerafast 0.5, (g) Naraton and (h) Naraton 0.5

3.2 Esterification reaction

3.2.1 Types of clays

As can be seen in Figure 3.10, the catalytic activity of Bent 0.5 catalyst has shown the best conversion due to its highest acid amount. The bentonite presented more acidity than kaolin as confirmed in the acid-base titration results because Bronsted acid sites generated at the external surface of the tetrahedral layers during the acid treatment,[22] and the structure of bentonite composed of 2 tetrahedral sheets and 1 octahedral sheet, while kaolin composed of 1 tetrahedral sheet and 1 octahedral sheet.

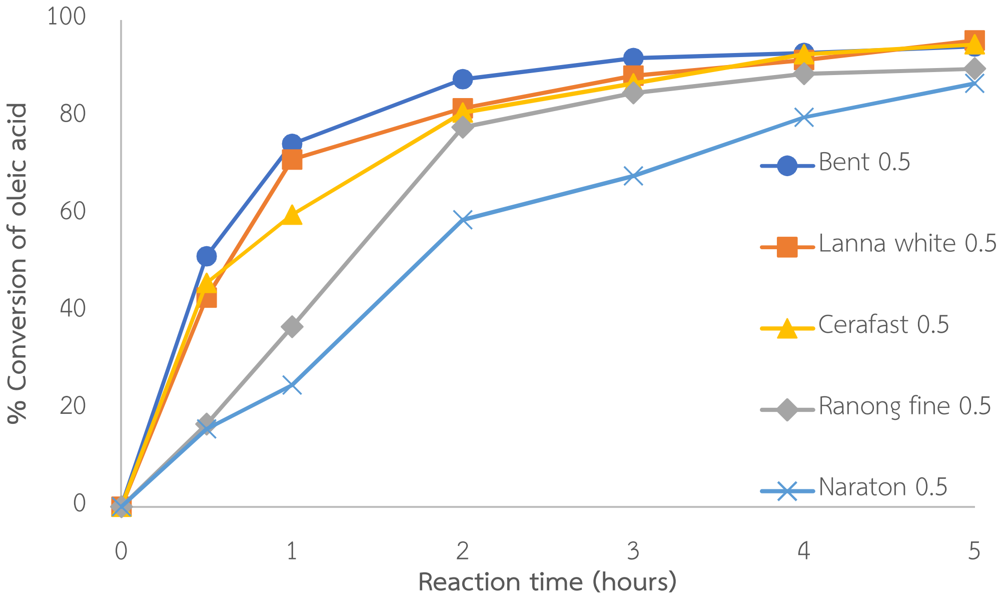


Figure 3.10 Effect of types of clay on conversion of oleic acid using a glycerol/oleic acid molar ratio of 3:1 at 160°C

3.2.2 Effect of reaction temperature

The effect of reaction temperature is shown in Figure 3.11. The Bent 0.5 catalyst had a higher % acid conversion when compared to the Lanna white 0.5. The conversion of oleic acid increased significantly with an increasing reaction temperature due to more energy provided to the system.

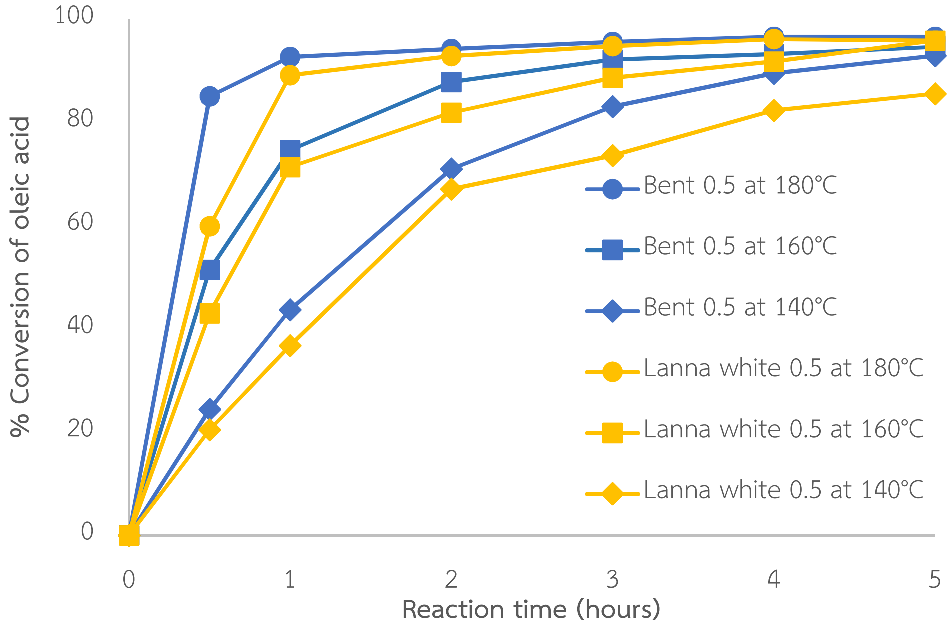


Figure 3.11 Effect of reaction temperature on glycerol esterification using a glycerol/oleic acid molar ratio of 3:1 and a Bent 0.5 catalyst loading of 5wt.%.

3.2.3 Effect of catalyst loading

The effect of catalyst loading on conversion of oleic acid can be seen in Figure 3.12. The results have shown that when using the Bent 0.5 catalyst loading from 0 wt.% to 5.0 wt.% at reaction time of 30 min, the conversion increased from 24% to 48%. This can be suggested that the increase of catalyst loading can increase the number of acid sites for the reaction. However, when using the catalyst loading from 5.0 wt.% to 7.5 wt.%, no further improvement in the conversion was observed because there was an excess of acid sites for the reactants.

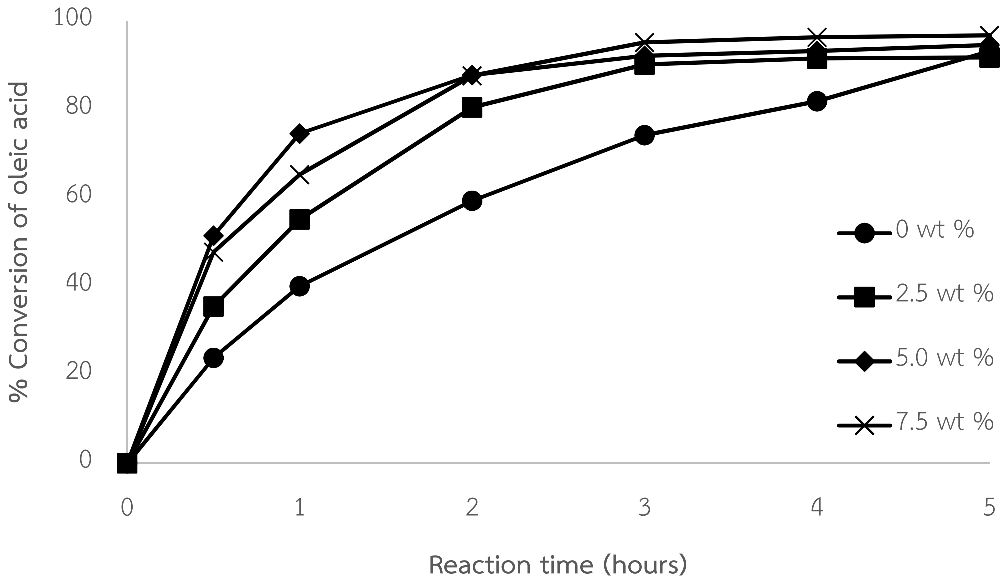


Figure 3.12 Effect of Bent 0.5 catalyst loading on glycerol esterification using a glycerol/oleic acid molar ratio of 3:1 at 160°C.

3.2.5 Gas chromatography analysis

The GC analysis results are shown in Table 3.5 and 3.6. The Bent 0.5 catalyst had a higher % acid conversion, % mono-glyceride yield and % mono-glyceride selectivity when compared to the reaction without catalyst. The monoglyceride selectivity of the both reactions had a downward trend because monoglyceride product could react with free fatty acid and became di- and tri-glycerides, as seen in Figure 3.14. Moreover, the Bent 0.5 gave higher % mono-glyceride selectivity than the Bent 0.5 (OB) due to smaller pore diameter; while the Bent 0.5 (OB) promote di- and tri-glyceride selectivity because of the four times higher of pore diameter, as shown in Figure 3.15. The esterification reaction over Bent 0.5 at 180°C gave the higher % acid conversion but lower % monoglyceride yield and selectivity because most of the product formed di- and tri-glycerides.

Table 3.5 Catalytic activity of acid-activated clays for the esterification of oleic acid and glycerol at a 3:1 glycerol: oleic acid mole ratio and 5.0 wt% catalyst.

Catalyst	**Reaction temperature**	**Reaction time**	**% Conversion**	**% Glyceride yields**			**% Glyceride selectivity**		
				Mono-	**Di-**	**Tri-**	**Mono-**	**Di-**	**Tri-**
No catalyst	160°C	30 min	23.8	11.7	2.0	0	49.1	8.5	0
		1 h	40.1	18.9	8.9	0	47.1	15.8	0
		2 h	59.4	18.9	10.5	0.3	31.8	17.8	0.5
		3 h	74.2	20.0	11.8	1.0	26.9	15.9	1.3
		4 h	81.9	19.8	13.2	0.9	24.2	16.1	1.2
		5 h	93.2	29.0	20.4	0.9	31.4	21.9	1.0
Bent 0.5	160°C	30 min	51.4	34.1	5.4	0	66.3	10.5	0
		1 h	74.6	25.5	5.5	0	34.2	7.4	0
		2 h	87.8	24.4	7.0	0.1	27.8	8.0	0.1
		3 h	92.2	22.3	9.2	0.4	24.2	9.9	0.4
		4 h	93.2	17.0	9.1	0.4	18.2	9.8	0.4
		5 h	94.6	10.5	10.8	2.9	11.1	11.4	3.1
Bent 0.5 (OB)	160°C	30 min	46.8	24.0	5.5	0	51.2	11.7	0
		1 h	63.3	19.4	6.3	0	30.7	10.0	0
		2 h	79.9	21.7	15.5	1.0	27.1	19.4	1.2
		3 h	90.5	13.8	27.4	3.7	15.2	30.3	4.1
		4 h	92.7	4.4	25.6	4.5	4.7	27.6	4.8
		5 h	92.3	3.2	25.3	6.4	3.5	27.4	6.9
Bent 0.5	180°C	30 min	85.0	14.1	1.0	0.2	16.6	1.2	0.2
		1 h	92.6	12.5	2.7	0.4	13.5	2.9	0.4
		2 h	94.2	7.0	2.4	1.1	7.4	2.5	1.1
		3 h	95.6	2.9	3.0	1.1	3.1	3.2	1.2
		4 h	96.6	2.6	3.0	0.8	2.7	3.1	0.8
		5 h	96.5	1.9	3.0	1.1	2.0	3.2	1.1

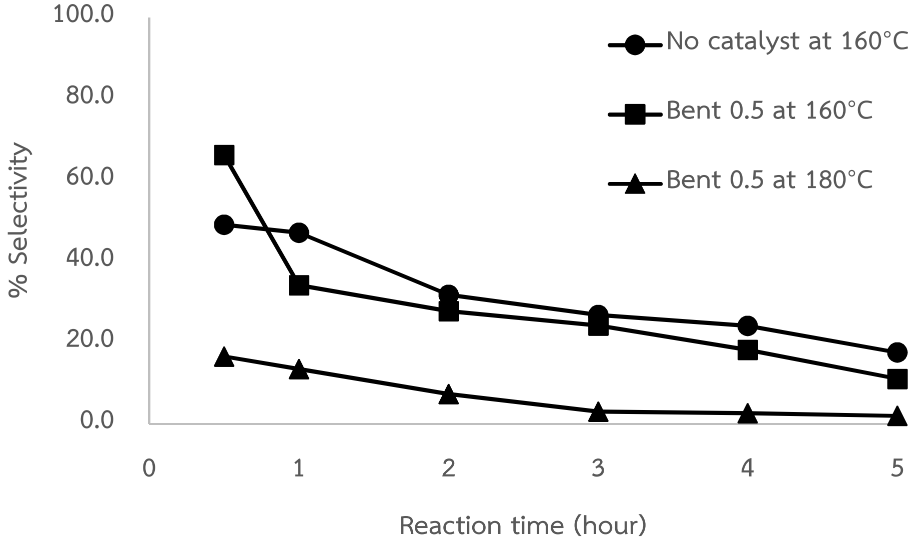


Figure 3.13 Effect of temperature on selectivity to monoolein.

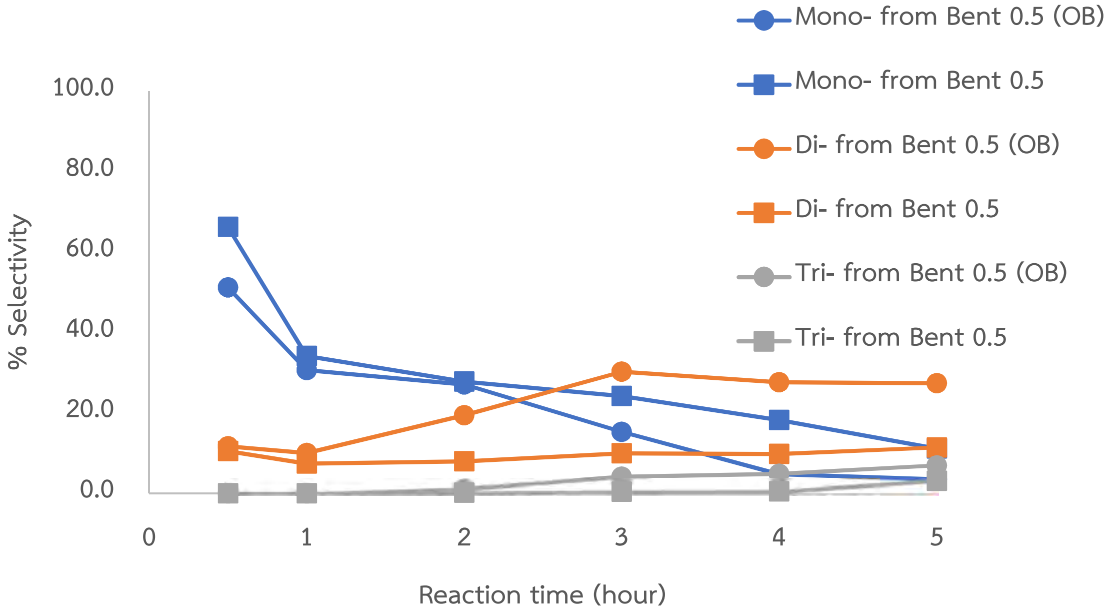


Figure 3.14 Selectivity to glycerides using 5.0 wt.% catalyst and a glycerol/oleic acid molar ratio of 3:1 at 160°C.

CHAPTER IV

CONCLUSIONS

Clay is one of the interesting heterogeneous catalysts which be used in esterification of glycerol and free fatty acid. The XRD analysis indicated that montmorillonite and kaolin are the dominant minerals in the bentonite and four Thai clays, respectively. The acid activation method was used to modify physical and chemical properties. The acid strength of acid-activated clay samples increased as the raw material was treated with increasing concentration of H_2SO_4 and at the acid concentration 0.5 M was the saturated point for bentonite support to be acidified. Then, the acid concentration of 0.5 M was selected to be treated in other clay samples. The specific surface area and total pore volume of all acid-activated clay samples were lower than those for the natural clay. The surfaces of acid-activated bentonite which obtained from SEM images were rougher than the surface of raw bentonite, and the morphology of acid-activated Thai clays insignificantly changed after treating.

The acid treatment generated catalytic activity for esterification of free fatty acids. The conversion levels are in range of 51.4% to 94.6%. The highest mono-glyceride yield and selectivity are 34.1% and 66.3% when using Bent 0.5 5.0 wt.%, 1:3 molar ratio of oleic acid/glycerol and reaction temperature at 160°C, 30 min.

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APPENDICES

1. Calculation of acid sites in catalysts

$$\text{Acid sites} = \frac{\text{mol NaOH}}{1000\ \text{mL NaOH}} \times \text{V mL NaOH} \times \frac{1\ \text{mol H}^+}{1\ \text{mol NaOH}} \times \frac{1000\ \text{mmol H}^+}{1\ \text{mol H}^+} \times \frac{1}{\text{g clay}}$$

2. Calculation of acidity in reaction mixture

$$\text{Acidity} = \frac{(282.47 \times \text{N} \times \text{V})}{\text{W}}$$

Where

N = Molar concentration of KOH solution

V = Volume of KOH solution employed for titration (mL)

W = Weight of sample (g)

3. Calculation of free fatty acid conversion

$$\%\ \text{Conversion} = \left(\frac{\text{A}_\text{i} - \text{A}_\text{t}}{\text{A}_\text{i}}\right) \times 100$$

Where

Ai = Initial acidity of oleic acid (mg/g sample)

At = Acidity at a time (mg/g sample)

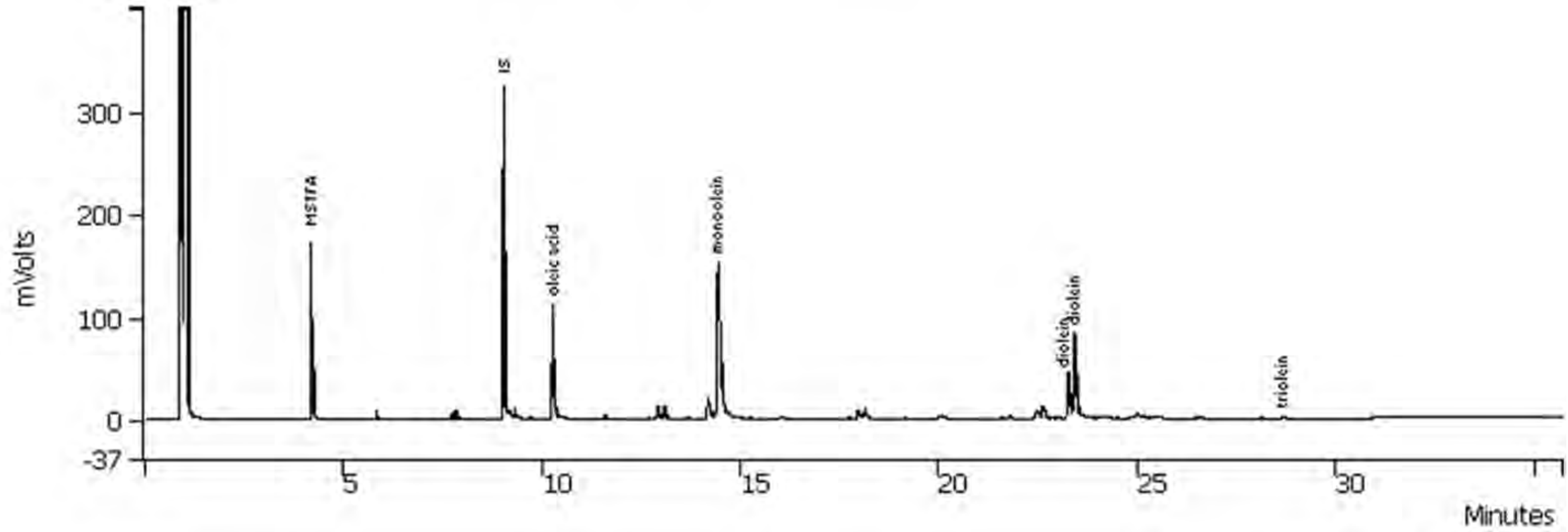

Figure A-1 GC chromatogram of mono-, di- and tri-olein product from esterification reaction.

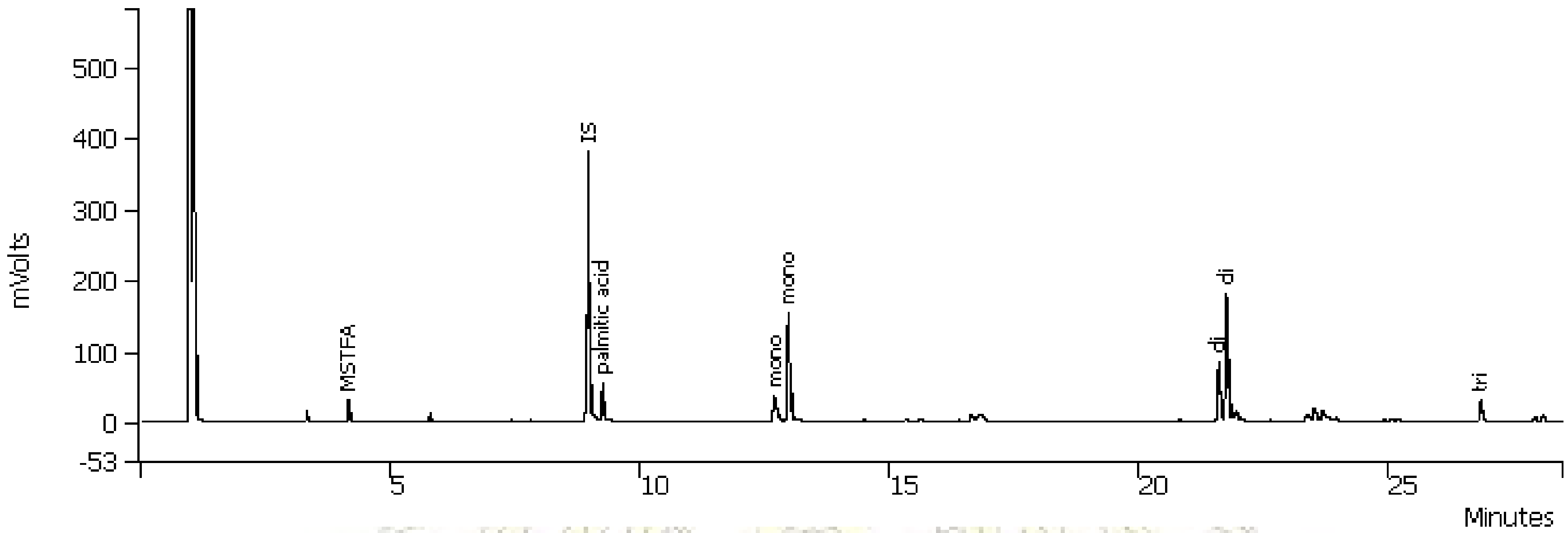

Figure A-2 GC chromatogram of mono-, di- and tri-palmitin product from esterification reaction.

4. Standard calibration curve

4.1 Monoolein calibration curve

The concentrations of monoolein were prepared as 0.078 M, 0.039 M, 0.020 M, 0.010 M and 0.005 M. The standard calibration curve of monoolein was shown in Figure A-2. The standard curve equation is expressed as following

$$y = 0.5436x - 0.0601$$

where y is area monoolein/IS ; area monoolein = Peak area of monoolein
area IS = Peak area of internal standard
x is weight monoolein/IS ; weight monoolein = Mass of monoolein (g)
weight IS = Mass of internal standard (g)

The correlation coefficient R^2 value for monoolein calibration curve is 0.9923

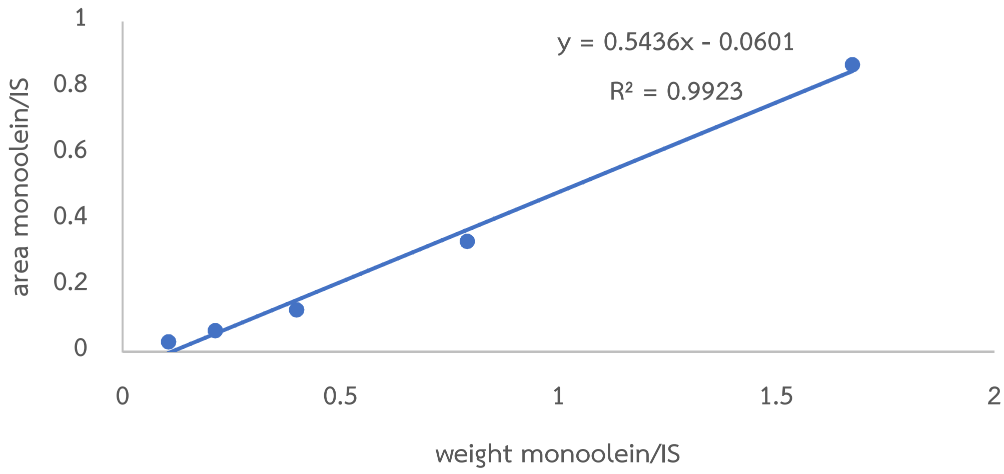

Figure A-3 Calibration curve of monoolein.

4.2 Diolein calibration curve

The concentrations of diolein were prepared as 0.0080 M, 0.0050 M, 0.0025 M, 0.0013 M and 0.0006 M. The standard calibration curve of diglyceride was shown in Figure A-3. The standard curve equation is expressed as following

$$y = 0.3342x - 0.0049$$

where y is area diolein/IS ; area diolein = Peak area of diolein

area IS = Peak area of internal standard

x is weight diolein/IS ; weight diolein = Mass of diolein (g)

weight IS = Mass of internal standard (g)

The correlation coefficient R^2 value for diolein calibration curve is 0.9357

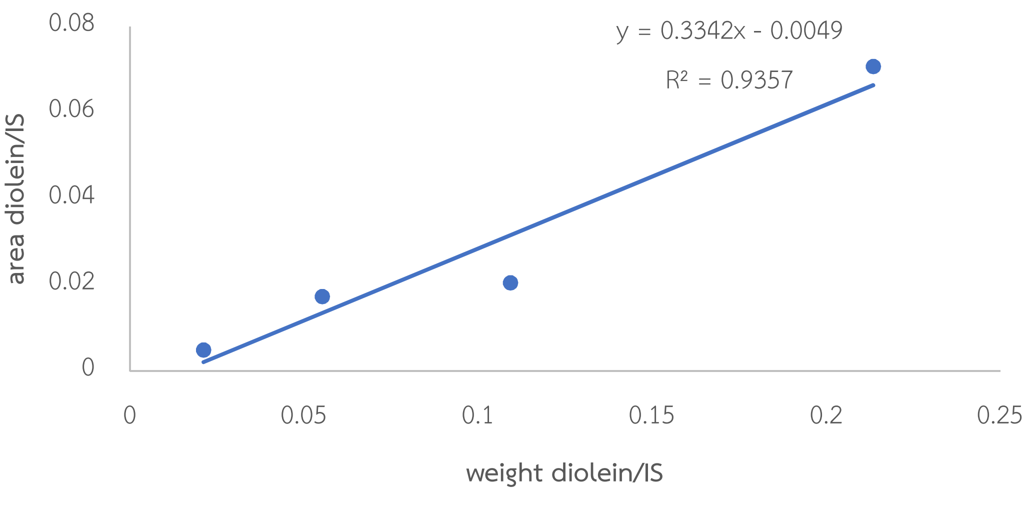

Figure A-4 Calibration curve of diolein

4.3 Triolein calibration curve

The concentrations of triolein were prepared as 0.078 M, 0.039 M, 0.020 M, 0.010 M and 0.005 M. The standard calibration curve of triolein was shown in Figure A-4. The standard curve equation is expressed as following

$$y = 0.1292x - 0.0016$$

where y is area triolein/IS ; area triolein = Peak area of triolein

area IS = Peak area of internal standard

x is weight triolein/IS ; weight triolein = Mass of triolein (g)

weight IS = Mass of internal standard (g)

The correlation coefficient R^2 value for triolein calibration curve is 0.9209

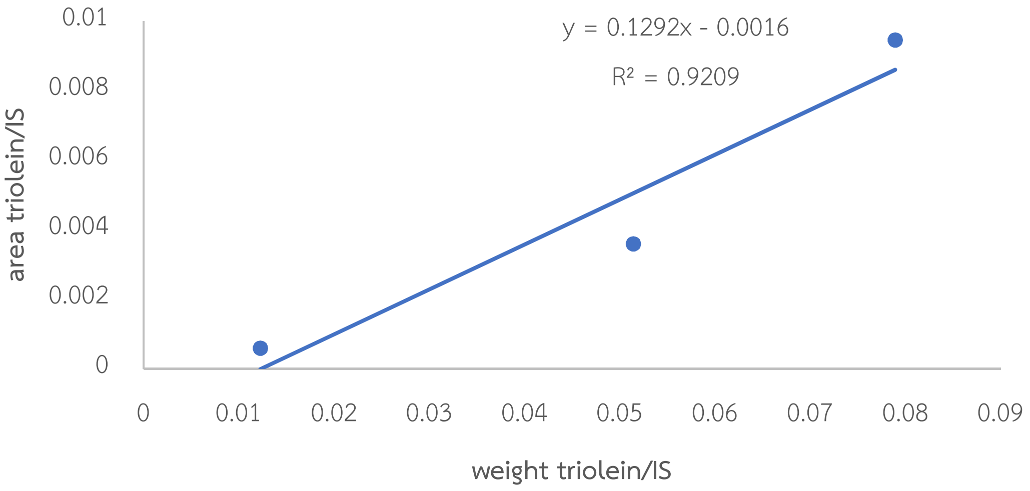

Figure A-5 Calibration curve of triolein

4.4 Monopalmitin calibration curve

The concentrations of monopalmitin were prepared as 0.084 M, 0.042 M, 0.021 M, 0.011 M and 0.005 M. The standard calibration curve of monopalmitin was shown in Figure A-5. The standard curve equation is expressed as following

$$y = 0.7616x - 0.069$$

where y is area monopalmitin/IS; area monopalmitin = Peak area of monopalmitin
area IS = Peak area of internal standard
x is weight monopalmitin/IS; weight monopalmitin = Mass of monopalmitin (g)
weight IS = Mass of internal standard (g)

The correlation coefficient R^2 value for monopalmitin calibration curve is 0.9964

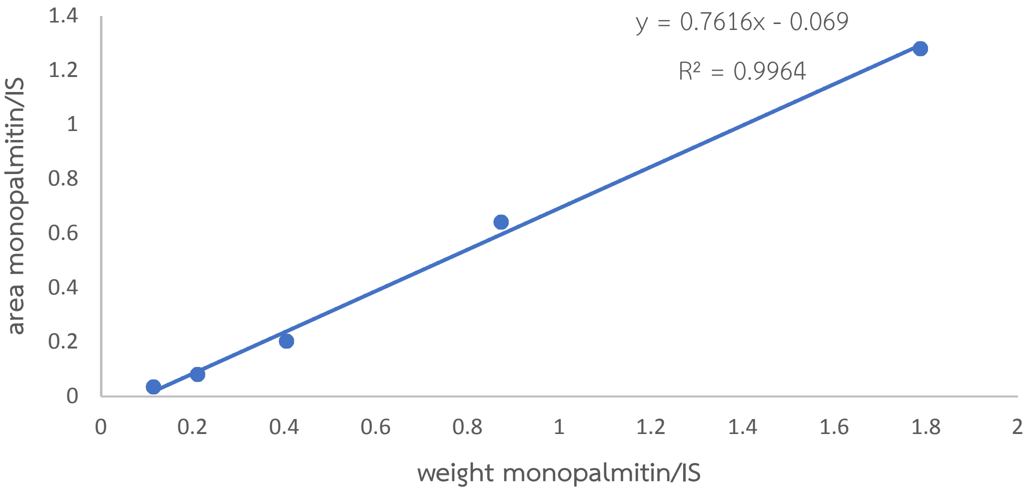

Figure A-6 Calibration curve of monopalmitin

5. Calculation of % glyceride yield

$$\%\ \text{Monoglyceride yield} = \frac{\text{Mole of monoolein}}{\text{Mole of starting oleic acid}} \times 100$$

$$\%\ \text{Diglyceride yield} = \frac{\text{Mole of diolein}}{\text{Mole of starting oleic acid}} \times 100$$

$$\%\ \text{Triglyceride yield} = \frac{\text{Mole of Trioein}}{\text{Mole of starting oleic acid}} \times 100$$

6. Calculation of % glyceride selectivity

$$\%\ \text{Monoglyceride selectivity} = \frac{\text{Monoglyceride yield}}{\text{Conversion}} \times 100$$

$$\%\ \text{Diglyceride selectivity} = \frac{\text{Diglyceride yield}}{\text{Conversion}} \times 100$$

$$\%\ \text{Triglyceride selectivity} = \frac{\text{Triglyceride yield}}{\text{Conversion}} \times 100$$

7. Esterification of glycerol and palmitic acid

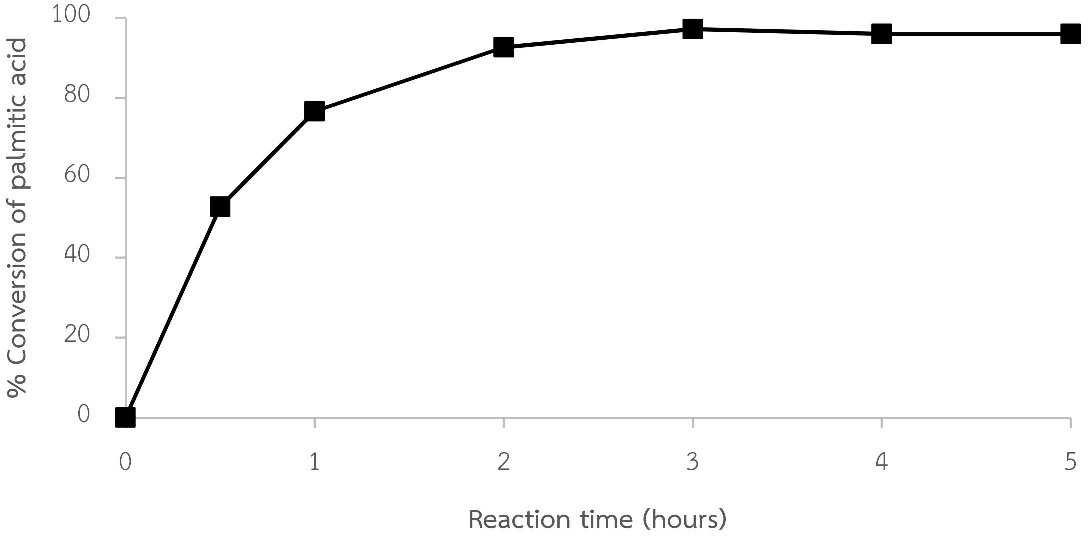

Figure A-7 Conversion of palmitic acid using 5.0 wt.% Bent 0.5 catalyst and a glycerol/palmitic acid molar ratio of 3:1 at 160°C.

Table A-1 Catalytic activity of acid-activated clays for the esterification of glycerol at a 3:1 glycerol: palmitic acid mole ratio and 5.0 wt% catalyst.

Catalyst	Reaction temperature	Reaction time	% Conversion	% Glyceride yields			% Glyceride selectivity		
				Mono-	*Di-	*Tri-	Mono-	*Di-	*Tri-
Bent 0.5	160°C	30 min	52.7	19.8	7.0	0.4	37.0	12.9	0.6
		1 h	76.6	21.9	11.3	2.9	28.4	14.6	3.9
		2 h	92.6	20.3	21.1	3.0	22.0	22.8	3.3
		3 h	97.2	14.1	20.3	4.5	14.4	20.8	4.7
		4 h	96.0	6.9	13.5	4.8	7.1	14.1	5.0
		5 h	96.0	3.5	10.9	5.7	3.6	11.3	5.9

*based on di- and tri-olein calibration curve

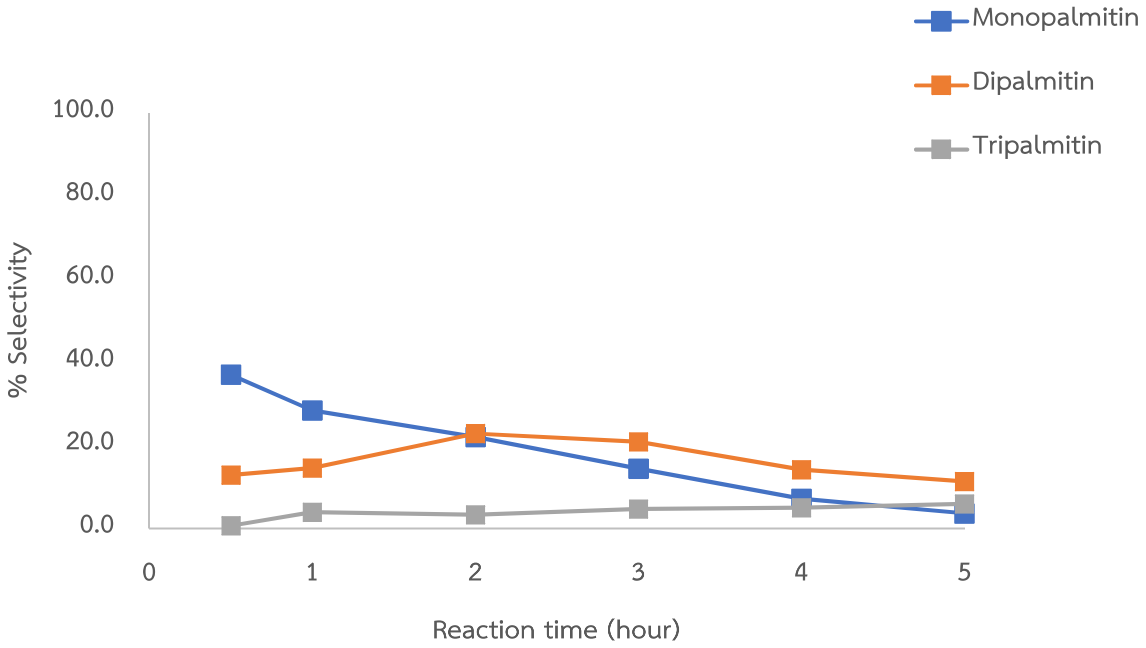

Figure A-8 Selectivity to glycerides using 5.0 wt.% catalyst and a glycerol/palmitic acid molar ratio of 3:1 at 160°C.

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