การเตรียมแคลเซียมออกไซด์ที่รองรับด้วยซิลิกาจากเถ้าแกลบเพื่อเป็นตัวเร่งปฏิกิริยา
สำหรับการผลิตไบโอดีเซล

นางสาวอภิชญา เที่ยงตรง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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PREPARATION OF CALCIUM OXIDE SUPPORTED RICE HUSK SILICA AS CATALYST

FOR BIODIESEL PRODUCTION

Miss Apichaya Thiangtrong

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science Program in Petrochemistry and Polymer Science

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Thesis Title	PREPARATION OF CALCIUM OXIDE SUPPORTED RICE HUSK SILICA AS CATALYST FOR BIODIESEL PRODUCTION
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อภิชญา เที่ยงตรง : การเตรียมแคลเซียมออกไซด์ที่รองรับด้วยซิลิกาจากเถ้าแกลบเพื่อเป็นตัวเร่ง ปฏิกิริยาสำหรับการผลิตไบโอดีเซล (PREPARATION OF CALCIUM OXIDE SUPPORTED RICE HUSK SILICA AS CATALYST FOR BIODIESEL PRODUCTION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.สมใจ เพ็งปรีชา, 63 หน้า.

งานวิจัยนี้มีวัตถุประสงค์เพื่อสังเคราะห์ตัวเร่งปฏิกิริยาแคลเซียมออกไซด์ที่รองรับด้วยซิลิกาจาก เถ้าแกลบด้วยวิธีอิมเพรกเนชันเพื่อใช้เป็นตัวเร่งปฏิกิริยาของแข็งชนิดเบสในการสังเคราะห์ไบโอดีเซลจาก ปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมันปาล์มกับเมทานอล โดยศึกษาปัจจัยในการเตรียมตัวเร่งปฏิกิริยา ได้แก่ อุณหภูมิที่ใช้ในการเผาตัวเร่งปฏิกิริยาและอัตราส่วนโดยน้ำหนักของแคลเซียมออกไซด์ต่อซิลิกา ตัวเร่ง ปฏิกิริยา CaO/SiO_2 ที่สังเคราะห์ได้จะถูกพิสูจน์ทราบเอกลักษณ์โดยอาศัยเทคนิคต่างๆได้แก่ เอกซเรย์ฟลูออ เรสเซนซ์ (XRF) การเลี้ยวเบนของรังสีเอกซ์ (XRD) การดูดกลืนรังสีในช่วงอินฟราเรด (FT-IR) การวัดการดูด ซับไนโตรเจน (BET) และหาค่าความเป็นเบสโดยการไทเทรชัน จากผลการทดลองพบว่า ตัวเร่งปฏิกิริยาที่มี แคลเซียมไนเตรต 30 เปอร์เซ็นต์โดยน้ำหนักต่อซิลิกา 5 เปอร์เซ็นต์โดยน้ำหนัก และทำการเผาที่อุณหภูมิ 700 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง เป็นตัวเร่งปฏิกิริยาที่มีความเหมาะสมและมีประสิทธิภาพมากที่สุด ซึ่งปฏิกิริยาทรานเอสเทอริฟิเคชันของน้ำมันปาล์มกับเมทานอลถูกศึกษาสำหรับการสังเคราะห์ไบโอดีเซล โดยการหาสภาวะที่เหมาะสมซึ่งประกอบด้วย อัตราส่วนโดยโมลของน้ำมันต่อแอลกอฮอล์, เวลาที่ใช้ในการ เกิดปฏิกิริยาและปริมาณของตัวเร่งปฏิกิริยาต่อน้ำมัน โดยผลการทดลองพบว่า ภาวะที่เหมาะสมที่สุดในการ เกิดปฏิกิริยาทรานส์เอสเทอริฟิเคชันเพื่อผลิตไบโอดีเซลคือ อัตราส่วนโดยโมลของน้ำมันต่อแอลกอฮอล์ 1:9, ปริมาณตัวเร่งปฏิกิริยา 3 เปอร์เซ็นต์โดยน้ำหนัก ที่อุณหภูมิ 65 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง ให้ผลได้ เมทิลเอสเทอร์สูงถึง 98.36 เปอร์เซ็นต์ ตัวเร่งปฏิกิริยาสามารถนำกลับมาใช้ใหม่ได้ถึง 4 รอบ โดยที่มีการ สูญเสียประสิทธิภาพของตัวเร่งปฏิกิริยาไปเพียงเล็กน้อย แสดงให้เห็นว่าตัวเร่งปฏิกิริยาแคลเซียมออกไซด์ที่ รองรับด้วยซิลิกาจากเถ้าแกลบนี้มีประสิทธิภาพสูงเหมาะสมที่จะนำไปใช้เป็นตัวเร่งปฏิกิริยาในการผลิตไบโอ ดีเซล

สาขาวิชา	ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์	ลายมือชื่อนิสิต ....
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5672135923 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: HETEROGENEOUS CATALYST / BIODIESEL PRODUCTION / SOLID BASE CATALYST

APICHAYA THIANGTRONG: PREPARATION OF CALCIUM OXIDE SUPPORTED RICE HUSK SILICA AS CATALYST FOR BIODIESEL PRODUCTION. ADVISOR: ASSOC. PROF. SOMCHAI PENGPRECHA, Ph.D., 63 pp.

This research aims to use calcium oxide supported on rice husk silica (CaO/SiO_2) as a solid base catalyst. The catalyst was prepared by impregnation method and used in transesterification reaction of palm oil as feedstock with methanol to produce biodiesel. The factors influencing the preparation of catalyst were studied including calcination temperature and the weight percentage of CaO. The synthesized CaO/SiO_2 catalyst was characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared (FT-IR), N_2 adsorption-desorption measurement techniques and the basicity of catalyst was determined by titration method. The results indicated that 30 wt.% of $Ca(NO_3)_2$ loaded on 5 wt.% of SiO_2, calcined at 700°C for 3 h, exhibited the most active catalyst. The transesterification of palm oil with methanol was studied for biodiesel synthesis. The effects of the mole ratio of methanol to oil, time of reaction, and mass of catalyst to oil were investigated to optimize the reaction condition. The results showed that by using 1:9 mole ratio of oil to methanol, 3 wt.% of catalyst based on oil weight at 65°C for 3 h of reaction time, 98.36% of methyl ester content was obtained. This catalyst could be reused up to 4 times with slightly loss in catalyst activity. As a result, the catalyst produced from calcium oxide supported on rice husk silica was proved to exhibit an excellent stability and a high activity for biodiesel production.

Field of Study: Petrochemistry and   Student's Signature ....
                  Polymer Science   Advisor's Signature ....

Academic Year: 2015

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จุหาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

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LIST OF ABBREVIATIONS

ASTM	American Standard Test and Method
°C	Degree Celsius
DI	Deionized
EN	European standard
g	Gram
h	Hour
kg	Kilogram
mg	Milligram
ml	Mililitre
M	Molar
ME	Methyl ester content
N	Normality
NMR	Nuclear Magnetic Resonance Spectroscopy
RHA	Rice husk ash
XRD	X-ray diffraction spectrophotometer
XRF	X-ray fluorescence spectrometer
wt.	Weight
wt.%	Percent Weight
δH	Chemical shift of ^{1}H NMR
% conversion	Percent Conversion

CHAPTER I

INTRODUCTION

Due to the rapid depletion of petroleum fuels, alternative fuels have recently received great attention. Biodiesel is one of alternative green fuel because of its non-toxicity, biodegradability, and renewability. It can be used directly or as diesel mixture in existing engines to provide excellent fuel characteristics such as high cetane number, elevated flash point and lower emission profile. [1]

Biodiesel including fatty acid methyl esters is produced from vegetable oils by transesterification of triglycerides with alcohols in the presence of a catalyst. In general, the biodiesel production is synthesized using a homogeneous base or acid catalyst. [2] Homogeneous basic catalysts such as sodium hydroxide and potassium hydroxide are widely employed in industrial biodiesel production because of the fast reaction rate under the mild reaction. [3] However, these catalysts have many drawbacks. Removal of the catalysts to purify the biodiesel is difficult and requires a large of water, therefore a massive amount of wastewater is produced. These catalysts are sensitive to water or free fatty acids (FFAs) in the feedstock to form soap, which reduces the efficiency of the catalyst and the biodiesel yield. [4]

Heterogeneous base catalysts have been widely investigated in order to resolve the problem with homogeneous basic catalysts. Heterogeneous basic catalysts have the advantage that they can be easily removed from the reaction. They can be reused for many reaction cycles, thus making it economical and environmentally preferable over the homogeneous catalyst. Several heterogeneous basic catalysts such as alkaline earth oxide, supported alkali and alkaline earth metals and basic zeolite. Among the heterogeneous basic catalysts, CaO is the most attractive one, not only has high alkalinity and activity but also does not insoluble in methanol, which is the ideal system of solid base catalyst for biodiesel production. CaO as a solid base catalyst has many advantages, such as relatively high basic strength, long catalyst lifetimes, low catalyst cost and less environmental impacts. [2] However, the specific surface area of CaO is usually small, also pure CaO is easy to form gels in methanol, so the activity of

CaO catalysts is affected. Supported base catalyst using CaO loaded on SiO_2 can be improved the stability and activity of the CaO solid base catalyst. [5]

Thailand is one of the largest rice producers in the world. A by-product of rice production is rice husk. The rice husk could be burned in power generation and its combustion creates rice husk ash (RHA). [6] RHA as biomass has a promising role with high silica content (87-99%) and available abundantly being a low-cost waste source as amorphous silica precursors. It is considered to be a support for heterogeneous catalyst due to its high surface area, which will provide sufficient surface area for any metal to disperse. [7]

In the present research, we have been using RHA as a low-cost material to prepare a solid base catalyst. RHA is used as a supporting material for CaO, which is considered as a strong base catalyst. The solid base catalyst is prepared using an impregnation method. Effects of various factors such as calcination temperature of the catalyst and weight percentage of CaO were studied to find suitable conditions for catalyst preparation. The catalytic performance was studied in the transesterification of palm oil with methanol under batch conditions. Moreover, the influences of reaction conditions on methyl ester content were studied to find suitable conditions.

1.1 Objectives of the research

1.1.1 To synthesize and characterize solid base catalyst calcium oxide supported on rice husk silica.

1.1.2 To study transesterification of palm oil with methanol over the solid base catalyst prepared from calcium oxide supported on rice husk silica.

CHAPTER II
THEORY AND LITERATURE REVIEWS

2.1 Biodiesel

Biodiesel including fatty acid methyl esters is produced from vegetable oils by transesterification of triglycerides with alcohols. Biodiesel has a potential an alternative fuel to conventional diesel fuel. Consequently, it can be used directly as fuel or blended with petroleum diesel and used in a diesel engine without modification. In addition, the several advantages of biodiesel over petroleum fuel are a high cetane number, high flash point, high lubricity, lower exhaust emissions of particulate matter and greenhouse gases. Biodiesel is good for the environment because it is non-toxic, biodegradable, renewable and exhibit low emission profile. [8]

Pure biodiesel fuel is designated as B100. A biodiesel blend is a mixture of pure biodiesel with conventional diesel. For example, B20 is derived from 80 vol.% petroleum diesel blended with 20 vol.% B100.

2.1.1 Properties and specification of biodiesel

Table 2.1 shows comparison of properties between diesel and biodiesel. As can be seen, the physicochemical properties of biodiesel are similar to diesel fuel. It confirms that biodiesel can use replacement of petroleum fuel.

In Thailand, the biodiesel properties are evaluated according to the standard issued by Department of Energy Business, Ministry of Energy, which is adopted from ASTM and EN standards. The standard specification for biodiesel in Thailand is listed in Table 2.2

Table 2.1 Comparison of diesel and biodiesel properties. [9]

Fuel Property	Diesel	Biodiesel
Fuel standard	ASTM D 975	ASTM D 6751
Composition	Hydrocarbon (C_{10}-C_{21})	Fatty acid alkyl ester (C_{12}-C_{22})
Kinetic viscosity range (mm^2/s, at 40°C)	1.3-4.1	1.9-6.0
Specific gravity (g/ml)	0.85	0.88
Flash point range (°C)	60-80	100-170
Cloud point range (°C)	-15 to 5	-3 to 12
Pour point range (°C)	-35 to -15	-15 to 10
Water (vol.%)	0.05 max	0.05 max
Carbon (wt.%)	87	77
Hydrogen (wt.%)	13	12
Oxygen (wt.%)	0	11
Sulfur (wt.%)	0.0015	0.0 to 0.0024
Cetane number	40-55	48-60

Table 2.2 Standard specification for biodiesel in Thailand. [10]

Property	Lower limit	Upper limit	Test method
Methyl ester (wt.%)	96.5	-	EN 14103
Density at 15°C (kg/m^3)	860	900	ASTM D 1298
Viscosity at 40°C (cSt)	3.5	5	ASTM D 445
Flash point (°C)	120	-	ASTM D 93
Sulfur (wt.%)	-	0.0010	ASTM D 2622
Carbon residue (wt.%)	-	0.30	ASTM D 4530
Cetane number	51	-	ASTM D 613
Sulfated ash (wt.%)	-	0.02	ASTM D 874
Water (wt.%)	-	0.050	ASTM D 2709
Total contaminate (wt.%)	-	00024	ASTM D 5452
Copper strip corrosion	-	No.1	ASTM D 130
Acid value (mg KOH/g)	-	0.50	ASTM D 664
Iodine value (g I_2/100 g)	-	120	EN 14111
Linolenic acid methyl ester (wt.%)	-	12	EN 14103
Monoglyceride (wt.%)	-	0.70	EN 14105
Diglyceride (wt.%)	-	0.20	EN 14105
Triglyceride (wt.%)	-	0.20	EN 1405
Free glycerin (wt.%)	-	0.02	EN 1405
Total glycerin (wt.%)	-	0.25	EN 14105
Group I metals (Na+K) (mg/kg)	-	5.0	EN 14108
Group II metals (Ca+Mg) (mg/kg)	-	5.0	pr EN 14538
Phosphorus (wt.%)	-	0.0010	pr EN 14538

2.2 Biodiesel production

2.2.1 Esterification reaction

Esterification is a reaction between carboxylic acid and alcohols in the presence of an acid catalyst to produce ester. The general equation for the esterification of carboxylic acid with alcohol is shown in Figure 2.1. [11]
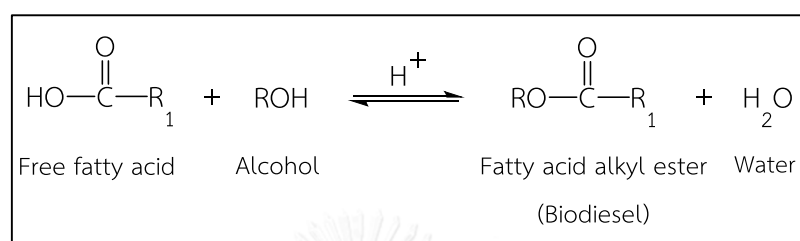
Figure 2.1 The simplified chemical reaction of esterification.

Acid catalysts, including hydrochloric acid, sulfuric acid, and phosphoric acid, are commonly used in the esterification. The high mole ratio of oil to methanol is required, usually ranging from 1:20 to 1:40. The esterification of FFAs with alcohol produces water as a by-product that must be removed because the acid catalyst is soluble, resulting in slower reaction rate.

2.2.2 Transesterification reaction

Transesterification is a reversible reaction between triglycerides and monohydric alcohols in the presence of a catalyst to produce mono-ester. Triglyceride is transformed to mono-ester and glycerol. The general equation for the transesterification of triglyceride with alcohol is shown in Figure 2.2. [12]
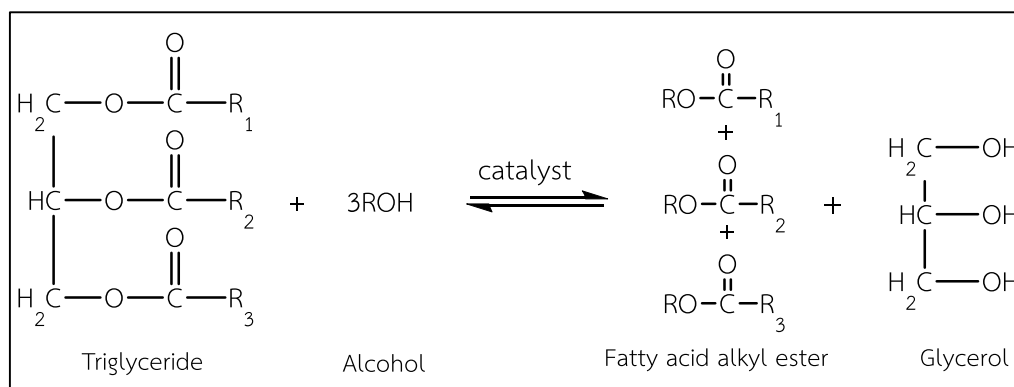
Figure 2.2 The simplified chemical reaction of transesterification.

Due to transesterification process being a reversible reaction, alcohol is generally used in excess to shift the reaction equilibrium to the product side. Stoichiometrically, three moles of alcohol are required to react with one mole of triglyceride for complete reaction. In practice, the high mole ratio of alcohol to triglyceride is important to shift the reaction equilibrium to achieve a maximum alkyl ester yield. Methanol and ethanol are commonly used in transesterification especially methanol because of its low cost, high reactivity and physicochemical properties (polar and shortest chain alcohol). It can easily react with triglyceride molecule. Furthermore, the catalyst such as NaOH can be easily dissolved in methanol much faster than the other alcohols. [13]

Transesterification involves their consecutive reversible reaction as shown in Figure 2.3. The first step; triglyceride reacts with alcohol to produce diglyceride and fatty acid alkyl ester. Then, diglyceride reacts with alcohol to produce monoglyceride and fatty acid alkyl esters. Finally, monoglyceride reacts with alcohol to form fatty acid methyl esters (FAME) and glycerol. For overall reaction, one molecule of triglyceride can produce three molecules of fatty acid. [14]
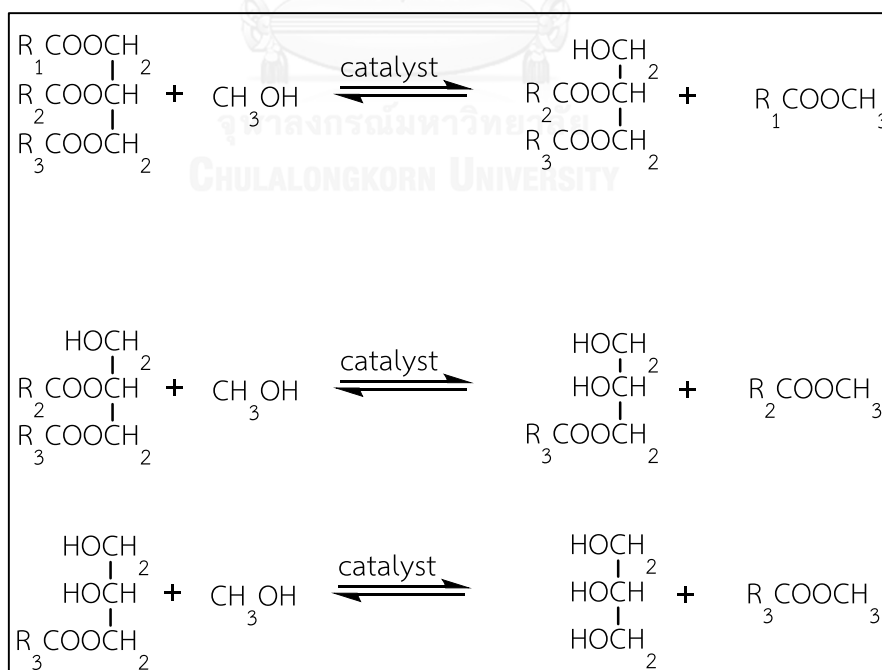
Figure 2.3 Three consecutive transesterifications of triglyceride.

There are numerous parameters that have an effect on transesterification such as reaction time, reaction temperature, mole ratio of oil to alcohol, the catalyst used (acid or base, homogeneous or heterogeneous) and catalyst loading.

2.2.3 Catalysis system for transesterification

2.2.3.1 Acid-catalyzed transesterification

The mechanism of acid catalyzed transesterification of triglycerides is shown in Figure 2.4. Firstly, the carbonyl group of triglyceride is protonated by an acid catalyst. Subsequently, the activated carbonyl group undergoes a nucleophilic attack by alcohol molecule to generate tetrahedral intermediate. Proton migration gives rise to a good leaving group with the assistance of solvent. Then, the carbonyl carbon-hydroxyl oxygen bond of tetrahedral intermediate cleaves yielding a protonated alkyl monoester and diglyceride molecule. After repeating twice, three molecules of alkyl monoester and one molecule of glycerol were produced and the catalyst was regenerated. [15]
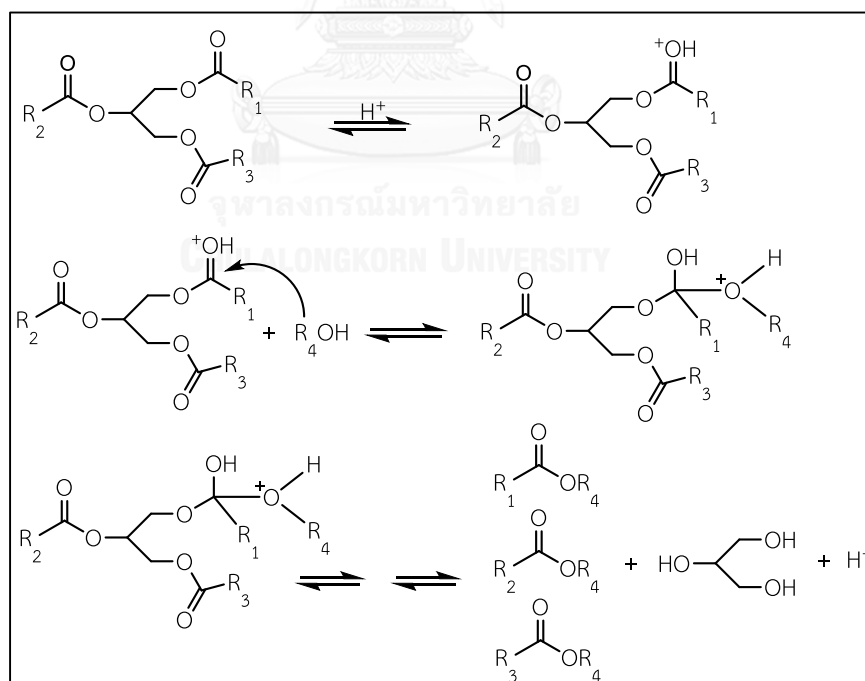
R_1, R_2, R_3: carbon chains of fatty acids

R_4: alkyl group of alcohol

Figure 2.4 Mechanism of transesterification of triglycerides catalyzed by acid.

2.2.3.2 Base-catalyzed transesterification

The mechanism of base catalyzed transesterification of triglycerides is shown in Figure 2.5. Firstly, the alkoxide ion (RO⁻) and protonated catalyst are generated by proton abstraction from alcohol with a basic catalyst. Secondly, alkoxide ion attacks carbonyl carbon of triglyceride, thereby, generating a tetrahedral intermediate. Then, the tetrahedral intermediate is rearranged to generate diglyceride ion and alkyl ester molecule. Lastly, the diglyceride ion reacts with the protonated base catalyst to generate a diglyceride molecule and restore the base catalyst to its original form. The regenerated catalyst is repeatedly used with another alcohol molecule for another catalytic cycle. [16]
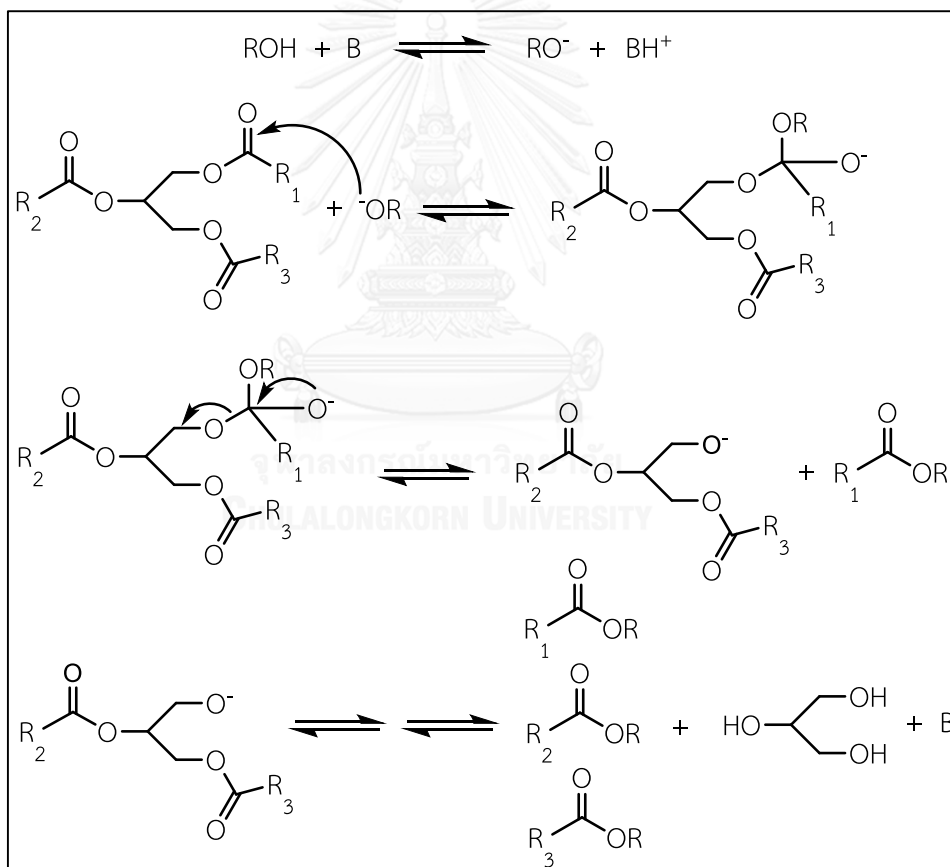
B: Base

R_1, R_2, R_3: carbon chains of fatty acids

R_4: alkyl group of alcohol

Figure 2.5 Mechanism of transesterification of triglycerides catalyzed by base.

2.3 Catalytic transesterification

2.3.1 Homogeneous catalyst

Homogeneous catalysts are present in the same phase as reactants and product. The homogeneous catalysts for biodiesel production can be acid catalysts (sulfuric acid, phosphoric acid) or base catalysts (sodium hydroxide, potassium hydroxide). The homogeneous base catalysts are more favored than the acid catalysts because they accelerate the reaction at a higher rate under mild conditions. Nevertheless, base catalysts are probably reacted with a free fatty acid, which produced soap formation. This undesirable saponification reduces the efficiency of the catalysts and the ester yield. [17]

2.3.2 Heterogeneous catalyst

Heterogeneous catalysts are present in a different phase of the reactants and products. The heterogeneous catalysts for biodiesel production can be solid acid catalysts (Amberlyst-15, sulfated zirconia and zeolites) or solid base catalysts (metal oxide, metallic salts, supported base catalyst and hydrotalcite). The heterogeneous catalysts can be easily separated from the reaction mixture and show easy regeneration. The cost of biodiesel could be reduced by using heterogeneous catalysts due to simplification of the separation and purification of products. Moreover, the heterogeneous catalysts are favored for biodiesel production. They can reduce side reaction such as saponification. [18]

2.4 Heterogeneous catalyst preparation

Heterogeneous catalysts are frequently defined as solid or mixtures of solids which accelerate a chemical reaction without themselves undergoing changes. The preparation of heterogeneous catalyst can be classified into two general methods such as i) bulk catalyst or supports and ii) Impregnated catalysts. On this basis the relative preparation methods are i) the catalytic active phase is generated as a new solid phase ii) the active phase is introduced or fixed on a pre-existing solid which depends on the support surface. Physical and chemical properties of the heterogeneous catalyst are

strongly affected by catalyst preparation. The properties are desired in the final composition. [19]

2.4.1 Bulk catalysts and support preparation

2.4.1.1 Precipitation

Precipitation is one of the general methods for catalyst preparation. It is used to prepare both single component catalysts and supports. Precipitation is the formation of a solid in a solution. The first step is mixing of solution or suspensions of materials, causing the precipitation of an amorphous or crystalline precipitate or gel. The formation of the precipitate from a homogeneous liquid phase may occur as a result of physical transformations (change of temperature or of solvent, solvent evaporation) but most often is intermediate by chemical processes (addition of bases or acids, use of complex forming agent).

It is generally desirable to precipitate the desired material in such a form. The counter ions of the precursor salts and precipitating agent can be occluded in the precipitate during the precipitation. It can easily be removed by a calcination step. The precipitation is induced by two methods such as physical means and the addition of a precipitating reagent. The physical means are cooling or evaporation of the solvent to attain supersaturation of the solution. The addition of a precipitating reagent, ions introduce into the system via this route also have to be considered. Favorable ions are carbonates nitrates or ammonium, which decompose to volatile products during calcination. The wet solid is converted to the finished catalyst by filtration, washing, drying, forming, calcination and activation. [20, 21]

2.4.1.2 Co-precipitation

Co-precipitation is the carrying down by a precipitate of substances normally soluble under the conditions employed that the synthesis of a multi-component system, the problems are even more complex. Co-precipitation is usually reserved for the preparation of multicomponent precipitates, which often are the precursors of the binary or multimetallic compound. The composition of the

precipitate depends on the difference in solubility between the components and the chemistry occurring during precipitation. [20, 21]

2.4.2 Supported catalyst preparation

2.4.2.1 Impregnation

Impregnation is the permanent solution to the porosity networks without impacting the functional or dimensional character of the supports. A certain volume of solution containing the metal precursor is contacted with the solid support, then it is aged, usually for a short time, dried and calcined. According to the volume of solution used, two types of impregnation can be distinguished: wet impregnation and incipient wetness impregnation.

In wet impregnation (also called soaking or dipping), an excess of solution is used. After a certain time, the solid is separated, and the excess solvent is then removed by drying. The composition of the batch solution will change, and release of debris can form a mud that makes it difficult to completely use the solution.

In incipient wetness impregnation is a general technique for the synthesis of heterogeneous catalysts. Typically, the active metal is dissolved in aqueous or organic solution. Then, the metal-containing solution is added to a catalyst support containing the same pore volume as the volume of the solution that added. The solution added in excess of the support pore volume is much slower because it caused the solution transport to change from a capillary action process to a diffusion process. Then, the catalyst is dried and calcined to drive off the volatile components to yield the deposition of metal on the surface of catalyst. The maximum loading is limited by the solubility of the precursor in the solution. The concentration profile of the impregnated compound depends on the mass transfer conditions within the pores during impregnation and drying. [19]

2.4.2.2 Ion exchange

Ion exchange is an exchange of ions between two electrolytes or an electrostatic interaction with the surface of a support by another ion species between an electrolyte solution and a complex. The supported catalyst has

importantly used an ability in ion exchanger (cation or anion). The esteemed ion exchangers are zeolites, clay, and montmorillonite. The support containing ions A is plunged ion into an excess volume (compared to the pore volume) of a solution containing ions B. Ions B slowly penetrate into the pore space of the support, while ions A pass into the solution. Until, the equilibrium is established corresponding to a given distribution of the two ions between the solid and the solution. [19]

2.4.2.3 Adsorption

Adsorption is used to describe all processes where ionic species from solution are attracted electrostatically by charged sites on a solid face. Often consideration is not given to the difference between true ion exchange processes and electrostatic adsorption on the charged surface of oxides. Catalyst systems, which need charge compensating ions are ideal materials for ion exchange (cationic clays, zeolites or layered double hydroxides). Instead most oxide supports, when placed in an aqueous solution, develop a pH-dependent surface charge. [19]

2.4.2.4 Dissolution-precipitation

Dissolution-precipitation method mainly composes two steps such as dissolved metal precursor and metal precipitated on the support. The metal precursor is dissolved in the acid solution for the metal ion. A supported metal is subsequently added to the slurry, which the metal ion is precipitated on a support material. Then, the catalyst is evaporated to dryness for removing excess water. Finally, it is calcined for generating new phases. Loading of metal precipitated on the support is determined by pH of the acid solution, the amount of metal precursor and the temperature during the dissolution. In some cases, a supporter is required, the corresponding metal precursor can be simultaneously added to the acid solution. [19]

2.4.3 Catalyst activation

After catalyst preparation, drying step the catalyst is subjected to drying step in the oven at 100°C overnight. Then, any undesirable materials such as a binder and organic material in the catalyst is burned out using muffle furnace. The catalyst is calcined for generating new phases at various temperatures. The temperature is very

important to generate crystallographic structure which should not high over that lead to sintering. [21]

2.5 Rice husk ash

Rice husk is an agriculture waste product as a by-product of the milling process. It is also abundantly available. Researchers, especially in rice producing countries, try to investigate the possibility to increase the rice husk value. This rice husk is mostly used as a fuel in the boiler for processing of paddy. Rice husk could be burned in power generation and its combustion creates rice husk ash (RHA). The composition of rice husk ash on a dry basis is shown in Table 2.3. [22-24]

Table 2.3 Composition of rice husk ash on dry basis [22]

Element	Mass Fraction (%)
Silica (SiO_2)	80-90
Alumina	1-2.5
Ferric oxide	0.5
Calcium oxide	1-2
Magnesium oxide	0.5-2.0
Sodium oxide	0.2-0.5
Potash	0.2
Loss on Ignition	10-20

From the Table 2.3, it is clear that silica is the major component in rice husk ash. This RHA contains silica content about 85-90%. According to the high amount of silica makes it an available material for use in the industrial application. The silica in the ash incurs structural transformations depended on burning conditions such as temperature and time. The amorphous silica is formed by combustion in the range of 500-700ºC but at higher temperature the crystalline is produced. Amorphous silica is commonly extracted from rice husk by acid leaching and followed by a carbon removing process.

The silica extraction process is simple and inexpensive, making it beneficial to use rice husk ash as a natural silica source instead of commercial silica. Amorphous silica is well known and commonly used as a support material due to its high porosity and surface area, which will provide sufficient surface area for any metal to disperse. Rice husk ash would be beneficial to the environment to recycle the waste to produce eco-material having a high-end value. These properties make the rice husk ash a valuable raw material for many industries.

2.6 Calcium oxide (CaO) as heterogeneous base catalyst

Calcium oxide (CaO) is one of the best choices for heterogeneous solid base catalyst due to its low cost, mild reaction condition, long lifetimes, high basicity and low solubility in methanol. Calcium oxide is usually produced by thermal decomposition of materials such as limestone or seashells and eggshells at high temperature. CaO is alkaline earth metal oxides that are formed out of ionic crystal and Lewis acidity of metal is very weak. Consequently, the conjugated oxygen anion shows the strong basic property. The mechanism of CaO as a solid base catalyst in transesterification is shown in Figure 2.6. Firstly, the solid base catalyst acted on the abstraction of a proton from methanol by the basic site of catalyst to form methoxide anion. Then, the methoxide anion attacks carbonyl carbon in a molecule of triglyceride to formed tetrahedral intermediate. Lastly, the tetrahedral intermediate rearranged to form diglyceride anion and a mole of methyl ester anion of diglyceride. The cycle continues until one molecule of triglyceride gives three molecules of alkyl monoester and one molecule of glycerol as the final products. [25]
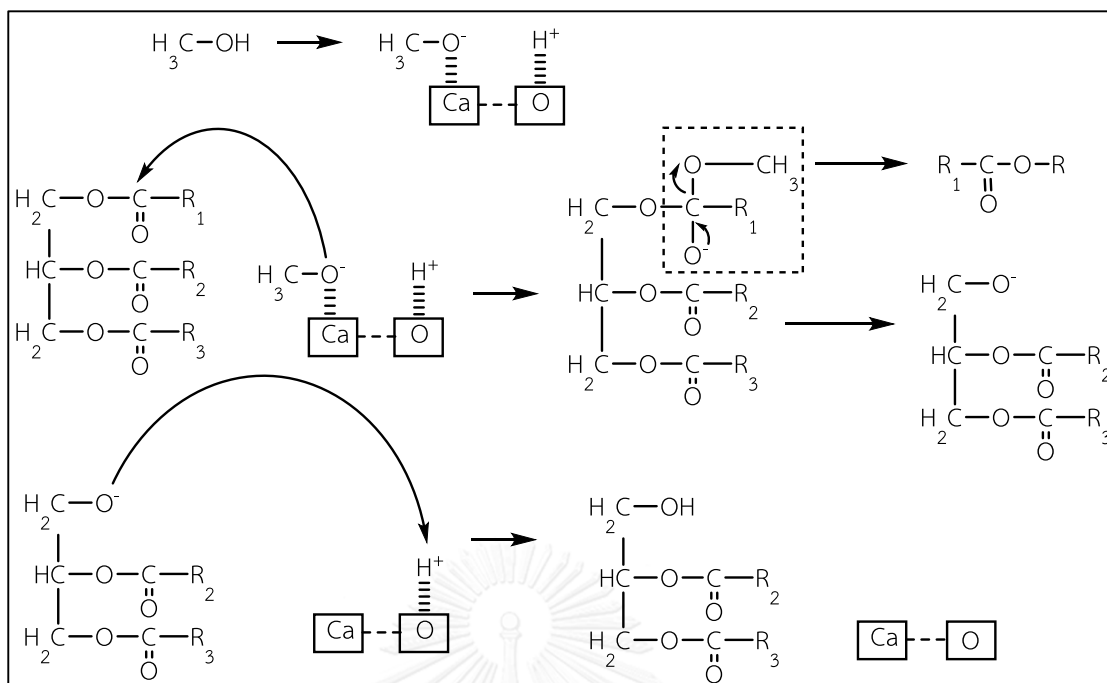
Figure 2.6 Mechanism of CaO-catalyzed transesterification. [26]

2.7 Literature reviews

In 2008, Kouzu *et al.* [26] studied different calcium-based catalysts for transesterification of edible soybean oil with refluxing methanol. The catalysts used were CaO, Ca(OH)$_2$, and CaCO$_3$. CaO was obtained after pulverized limestone (CaCO$_3$), moreover, Ca(OH)$_2$ was prepared by hydration of CaO. At 1 h of reaction time, the fatty acid methyl ester (FAME) yield of CaO, Ca(OH)$_2$, and CaCO$_3$ are 93%, 12%, and 0% respectively. As the result, CaO had higher activity. However, CaO was rapidly poisoned by moisture and carbon dioxide in the atmosphere.

In 2010, Ngamcharussrivichai *et al.* [27] prepared calcium oxide (CaO) catalyst from dolomite-calcite, cuttlebone, hydroxyapatite, and dicalcium phosphate via a thermal decomposition at high temperature. The transesterification of palm kernel oil (PKO) with methanol over the CaO was carried out by using 6 wt.% catalyst in oil to methanol mole ratio 1:30 at 60ºC for 3 h. At 3 h of reaction time, the FAME yield of CaO catalyst from dolomite-calcite, cuttlebone, hydroxyapatite and dicalcium phosphate are 98.6, 46.8, 24.1, 2.6 and 1.3 wt.% respectively. As the result, the dolomite calcined at 800 ºC was the most active catalyst and can be reused many times.

In 2009, Cho *et al.* [28] prepared calcium oxide (CaO) catalyst by calcining calcium precursor such as calcium acetate, -carbonate, -nitrate, -oxalate and -hydroxide. Calcium carbonate is the main source of CaO used in the industrial field. Calcium hydroxide is appropriate for preparation of highly pure CaO. Calcium nitrate and calcium acetate are convenient for preparation of supported CaO catalyst because of their great solubility in water. The precursors were transformed into CaO by calcination of different temperatures depending on the type of precursors. The calcination at an excessively high temperature caused a significant loss of the basic site. The transesterification of tributyrin with methanol over calcium oxide was carried out by using 0.1 wt.% catalyst in oil to methanol mole ratio 1:6 at 60°C for 2 h. As the result, calcium hydroxide calcined at 600-800°C showed the highest activity in the transesterification among the prepared catalyst. The CaO catalyst from the calcium hydroxide had largest surface area and strong basic site.

In 2008, Liu *et al*. [29] utilized calcium oxide (CaO) as a solid base catalyst for transesterification of soybean oil with methanol. The condition of transesterification was 1:12 mole ratio of oil to methanol, amount of catalyst of 8 wt.% and reaction temperature of 65°C. At 1.5 h of reaction, the biodiesel yield exceeded 95 wt.%. They revealed that the reaction rate is accelerated in the presence of water because CaO generated more methoxide anions, which are the true catalytic agent for transesterification. However, if too much water (more than 2.8 wt.%) was added to methanol, fatty acid methyl ester was hydrolyzed under basic conditions to generate a fatty acid that can react with CaO to form soap. The catalysis by CaO probably produces low fatty acid methyl ester yield which is usually ascribed to the formation of calcium methoxide ($Ca(OCH_3)_2$) on the surface of CaO. The active surface of CaO is easily chemisorbed by H_2O and CO_2 in the atmosphere. This research investigated the comparative activity of CaO with $K_2CO_3/\gamma Al_2O_3$ and $KF/\gamma Al_2O_3$ catalysts. Preparation of impregnated catalysts on alumina support was studied by impregnation method. The impregnated catalysts were calcined at 550 °C for 5 h. As the result, CaO can be reused for 20 cycles with the retention of biodiesel yield. However, the impregnated catalysts were not able to sustain activity and biodiesel yield after every use. Alkali metal

compounds dissolved in methanol; as a result, the active ingredients reduced and the biodiesel yield decreased in the repeated experiments.

In 2009, Kouzu *et al.* [30] investigated the leaching of solid base catalyst for transesterification of soybean oil with refluxing of methanol in the presence of calcium oxide. Calcium oxide is very active in a chemical reaction to produce biodiesel but the soluble substance was leached away from the solid catalyst during the reaction. In this study, the calcium contents of biodiesel and glycerol were 139 and 4602 ppm, respectively. This data indicated that the amount of the soluble substance corresponded to 10.5 wt.% of catalyst. Also, the reaction was catalyzed not only by basic sites on the surface of catalyst but also by the soluble substance. Calcium oxide was transformed into calcium diglyceroxide at the beginning of the reaction as many of the soluble substances derived from calcium diglyceroxide. On the other hand, calcium diglyceroxide was employed instead of calcium oxide; as a result, the reaction was catalyzed by only basic sites on the surface.

In 2009, Benjapornkulapong *et al.* [31] investigated the transesterification of palm kernel oil (PKO) and coconut oil (CCO), using Al_2O_3-supported alkali and alkali earth metal oxide as a heterogeneous catalyst. The catalyst was prepared by impregnation of alkali and alkali earth metal nitrate salts such as $LiNO_3$, $NaNO_3$, KNO_3, $Mg(NO_3)_2$ and $Ca(NO_3)_2$ into Al_2O_3 support to generate catalytic activities for transesterification. Among the catalysts, Al_2O_3 support loaded with $Ca(NO_3)_2$ and calcined at 450ºC was found to be the most suitable heterogeneous catalyst, which gave the highest methyl ester content of 94%. The suitable conditions for the transesterification of PKO and CCO with the methanol over $Ca(NO_3)_2/Al_2O_3$ catalyst are the methanol/oil mole ratio of 65, the temperature of 60ºC, the reaction time of 3 h, the catalyst amount of 10 wt.% and 15-20 wt.% for PKO and CCO respectively. They also compared catalytic activity of $Ca(NO_3)_2/Al_2O_3$, CaO, $Ca(OH)_2$ and $CaCO_3$ under the same reaction conditions and found that $Ca(NO_3)_2/Al_2O_3$ was much more active than bulk CaO. Small crystalline CaO particles formed through a suitable impregnation method may be more basic and active site than bulk CaO.

In 2014, Hindryawati *et al.* [7] investigated alkali metals (Li Na K) supported by rice husk silica as a solid base catalyst for transesterification. Alkali metals silicates (Li_2SiO_3, Na_2SO_3, and K_2SiO_3) were prepared by impregnation of alkali hydroxide on rice husk silica. The impregnated catalysts were calcined at 500ºC for 3h. The transesterification of used cooking oil with methanol over alkali metals silicates was carried out by using 3 wt.% catalyst in oil the methanol mole ratio 1:9 at 65ºC. At 1 h of reaction time, the FAME yield exceeded in the range of 96.5-98.2% for all series of catalyst. The catalyst is able to tolerant moisture and free fatty acid up to 1.75% and 1.25%, respectively. The catalyst was easily separated from the reaction mixture by filtration and could be reused for six times. Alkali metals silicates catalysts showed longer lasting activity than the traditional alkali catalysts.

CHAPTER III

EXPERIMENTAL

3.1 Materials and equipment

3.1.1 Raw materials

1. Rice husk ash biomass; power plant (Pijit province)

2. Silica-alumina catalyst support; Aldrich chemical company

3. Palm cooking oil; Market

3.1.2 Chemical reagents

1. 2-propanol (iso-propanol): analytical grade; Merck

2. Ammonium hydroxide: analytical grade; Merck

3. Benzoic acid: analytical grade; Merck

4. Bromothymol blue: analytical grade; Fluka chemie

5. Calcium nitrate tetrahydrate: analytical grade; Calo Erba

6. Chloroform-D: NMR spectroscopy grade; Merck

7. Deionized water (DI water)

8. Hexane: analytical grade; Lab-Scan

9. Methanol: analytical grade; Merck

10. Phenolphthalein indicator: analytical grade; Merck

11. Potassium hydroxide: analytical grade; Lab-Scan

12. Silica-alumina catalyst support: analytical grade; Aldrich chemical company

13. Sodium hydroxide: analytical grade; Merck

14. Sodium sulfate anhydrous: analytical grade; Merck

15. Sulfuric acid (96%): Carlo Erba

16. Toluene: analytical grade; Merck

3.1.3 Equipments

1. Surface area analyzer: Model BELSORP MIN, BEL

2. Furnace muffler (multiple furnace): Model L9/ 12/ P320, Nabertherm

3. Fourier Transform Infrared Spectrophotometer: Model Impact 410, Nicolet

4. NMR Spectrometer: Model Mercury (400MHz), Varian

5. Rotary evaporator: Model R-200, Buchi

6. X-Ray Fluorescence Spectrometer (XRF): Model ED-2000, Oxford

7. X-Ray Diffraction Spectrophotometer (XRD): Perkin Elmer

3.2 Catalyst preparation

3.2.1 Preparation of silica from rice husk ash

10 g of rice husk ash (RHA) were stirred in 80 mL of 2.5 N NaOH solution. Then, the mixture was refluxed for 3 h with stirring constantly. The solution was filtered and the filtrate was allowed to cool to room temperature. Next, the pH of the filtrate was adjusted to pH 2 using 5 N H_2SO_4 solution and adjusted back to pH 9 with 30% NH_4OH. The mixture was allowed to stand at room temperature for 3.5 h. Then, the mixture was filtrated and the residual was dried in an oven at 120°C for 12 h. Finally, the silica was ground and sieved through 100 mesh size sieve.

3.2.2 Preparation of supported catalyst

The base catalyst was prepared by the impregnation method, using CaO as an active component and RHA as support. Firstly aqueous solution of $Ca(NO_3)_2.4H_2O$ was prepared. Consequently, RHA was slowly added to the solution. The mixture was stirred at room temperature for 12 h. Lastly, the mixture was dried in an oven at 120°C overnight and then calcined at 500-900°C for 3 h.

3.3 Characterization of catalyst

3.3.1 Structure of catalyst

The structure of solid base catalyst was determined by X-ray diffraction spectrometer (XRD). The XRD patterns of the catalysts were obtained using Rigaku equipped with Cu Kα radiation. The sample was scanned over a 2θ range of 10°- 80° in step size of 0.02° at a scanning speed of 5°/min.

3.3.2 Functional group of catalyst

The functional groups of catalyst were identified by Fourier-transform infrared spectroscopy (FT-IR) technique. The samples were prepared into a KBr pellet. The infrared spectra were recorded in the range 400-4000 cm^{-1} in transmittance mode.

3.3.3 Elemental composition of catalyst

The elemental composition of solid base catalyst was determined by X-ray fluorescence spectrometer (XRF). The analysis was performed on X-ray fluorescence spectrometer at the Scientific and Technological Research Equipment Centre of Chulalongkorn University.

3.3.4 Surface area of catalyst

Specific surface area of catalyst was carried out by N$_2$ physisorption measurement at -196°C using BELSORP instrument. Surface area was calculated using the BET (Brunauer-Emmett-Teller) equation.

3.3.5 Basicity of catalyst

The basicity of catalyst was determined by titration method. In 250 mL of erlenmeyer flask, 0.05 g of catalyst was dissolved in 20 mL of distilled water. The solution was stirred for 1 h at room temperature and then filtered. After that, 1 mL of 1% bromothymol blue was added into the filtrate. The mixture was titrated with 0.2 M benzoic acid solution (in methanol) until the mixture changed from blue to yellow. The basicity of catalyst was determined by Equation 3.1. [32]

$$C(OH^-) = \frac{C(H^+) \times \Delta V}{m} \tag{3.1}$$

$C(OH^-)$	=	basicity of catalyst (mmol/g)
$C(H^+)$	=	concentration of the benzoic acid solution (mol/L)
ΔV	=	volume of titrant benzoic acid with sample (mL)
m	=	weight of catalyst (g)

3.4 Biodiesel production

The transesterification reaction of palm oil with methanol was performed in a 250 ml of round bottom flask equipped with a condenser, 1.0 g of CaO/SiO_2 catalyst was suspended in methanol, stirred continually for 30 min. Then, palm oil was added into the mixture under vigorous stirring and heated at constant temperature 65°C. The effects of mole ratio of oil to methanol (1:3-1:15), catalyst amount (1-5 wt.%) and reaction time (1-5 h) were investigated. After completion of the reaction, the catalyst was filtered by filter paper. The mixture was transferred to a separating funnel and 20 mL of hexane was added into the mixture. The mixture was purified by warm deionized water until the washing water became the clear solution. Finally, the mixture was dried over anhydrous Na_2SO_4 and concentrated by rotary evaporator. The percentage methyl ester content was determined by ^{1}H-NMR technique.

3.4.1 Influence of transesterification parameters of biodiesel using CaO/SiO_2 catalyst

3.4.1.1 Effect of reaction times on biodiesel production

The biodiesel was synthesized at various reaction times. The conditions of reaction times were studied at 1, 2, 3, 4 and 5 h, respectively. The products were analyzed by ^{1}H-NMR technique to investigate the optimum condition.

3.4.1.2 Effect of mole ratio of oil to methanol on biodiesel production

The biodiesel was synthesized at various mole ratios of oil to methanol. The conditions of mole ratios were studied at 1:3, 1:6, 1:9, 1:12 and 1:15, respectively. The products were analyzed by ^{1}H-NMR technique to investigate the optimum condition.

3.4.1.3 Effect of amounts of catalyst on biodiesel production

The biodiesel was synthesized at various amounts of CaO/SiO_2 catalyst. The conditions of amounts of catalyst were studied at 1, 2, 3, 4 and 5 wt.%, respectively. The products were analyzed by ^{1}H-NMR technique to investigate the optimum condition.

3.5 Reusability of catalyst

At the end of transesterification of palm oil with methanol, the catalyst was separated by filtration and washed with methanol. Then, it was calcined at 700°C for 3 h. The recovered catalyst was used for transesterification of palm oil with methanol to observe the remaining activity of catalyst. The product was analyzed by ^{1}H-NMR technique to investigate the activity of catalyst.

3.6 Comparison between CaO/SiO_2 and CaO/SiO_2-Al_2O_3 catalyst.

To compare the efficiency of the solid supported catalyst in biodiesel production, CaO/SiO_2, CaO/SiO_2-Al_2O_3 (SiO_2-Al_2O_3 is a commercial catalyst support) were studied. The experiment was carried out by following the method as describe in 3.4.1 with optimum conditions. The optimum conditions consist of reaction time, mole ratio of oil to methanol and amount of catalyst.

3.7 Characterization of biodiesel production

The optimum condition of biodiesel production was selected for determination of the properties of biodiesel. Reactant and product of transesterification of palm oil with methanol were analyzed by ^{1}H-NMR technique. The acid value was determined according to ASTM D 664.

3.7.1. Calculation of methyl esters product

The conversion of methyl esters from biodiesel production was analyzed in commercial chloroform-d (δ 7.6 ppm) at room temperature by ^{1}H-NMR technique. The peak area of methoxy and methylene protons were used to calculate the percentage of ester conversion by Equation 3.2. [33]

$$\% \text{ conversion} = \frac{2 \times I_{(-OCH_3)} \times 100}{3 \times I_{(-CH_2COO-)}} \tag{3.2}$$

$I_{(-OCH_3)}$ = integrated value of the protons of the methyl esters appearing at δ 3.7 ppm

$I_{(-CH_2COO-)}$ = integrated value of the methylene protons appearing at δ 2.3 ppm

3.7.2 Determination of acid value

ASTM D 664 is the standard test method for determination of the acid value. The acid value is used to quantify the amount of the acid remain in a sample of biodiesel, which measured by the milligrams of potassium hydroxide required to neutralize the free fatty acid.

According to the experiment, 2 g of biodiesel was dissolved in 25 ml of solvent. The solvent was prepared by 250 ml of toluene, 247.5 mL of isopropanol and 2.5 ml of deionized water. Then, 0.125 mL of 1% of phenolphthalein indicator was added into the mixture and titrated with 0.05 N potassium hydroxide solution (KOH) until the mixture became pale pink color. The acid value was determined by Equation 3.3. [34]

$$\text{Acid value} = \frac{(A-B) \times N \times 56.1}{W} \tag{3.3}$$

A = Volume of titrant KOH with sample (mL)

B = Volume of titrant KOH with blank (mL)

W = Weight of biodiesel (g)

N = Normality of KOH (mol/L)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation of catalyst

4.1.1 Effect of calcination temperature of catalyst

The XRD patterns of RHA and CaO/SiO_2 catalyst are shown in Figure 4.1. In the XRD pattern of RHA (Figure 4.1 a) shows the broad peak at 2θ ranging from 16° to 35° and the appearance of a diffuse maximum at $2\theta = 22.4°$ typical for amorphous silica. [35, 36] The XRD demonstrated that RHA can be a promising support material for calcium oxide. The amorphous phase of RHA was transformed to the CaO/SiO_2 after impregnation with $Ca(NO_3)_2.4H_2O$. The XRD pattern of CaO/SiO_2 catalyst (Figure 4.1 b) shows characteristic peaks of CaO at $2\theta = 33.4°$, 37.3°, 53.8°, 64.2°, 67.5° and SiO_2 at $2\theta = 26.8°$ (that is crystalline phase of silica).[37] In this XRD pattern, the characteristic diffraction peaks of $CaO-SiO_2$ also appeared $CaSiO_3$ at $2\theta = 39.2°$ and Ca_2SiO_4 at 2θ 35.1°. This CaO/SiO_2 catalyst could be considered to be formed by solid state reaction between CaO and SiO_2 support during the calcination process.
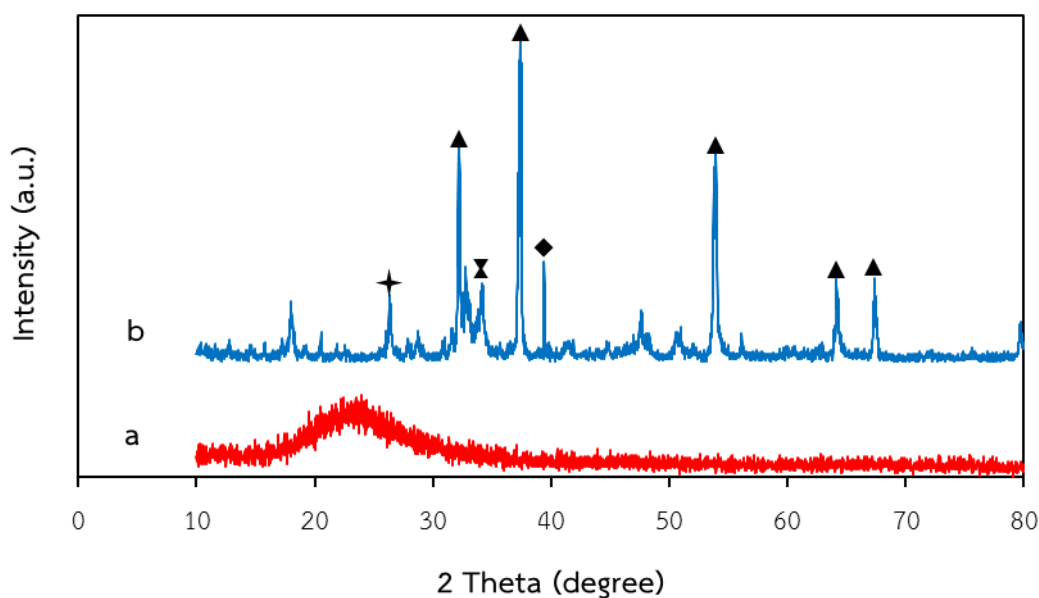
Figure 4. 1 The XRD patterns of RHA and prepared catalyst (CaO/SiO_2) (a) RHA, (b) CaO/SiO_2 (Symbol: ✛ = SiO_2, ▲ = CaO, ◆ = $CaSiO_3$, ✗ = Ca_2SiO_4

The XRD patterns for CaO/SiO_2 catalyst calcined at different temperature are shown in Figure 4.2. For the non-calcined sample, the major phases presenting in the catalyst were $Ca(NO_3)_2$ and SiO_2. The peak of CaO was observed when the catalyst was calcined at 500°C. However, the peak of $Ca(NO_3)_2$ was observed, it should be due to an incomplete decomposition of $Ca(NO_3)_2$ to CaO at 500°C. In the case, the diffraction peak attributed to $CaSiO_3$ could not be detected by XRD technique. This phenomenon shows that the compound of the solid catalyst is not decomposed on the surface of the catalyst if the calcination temperature is below 500°C. On calcination at 700°C, as shown in Figure 4.2 c, the characteristic diffraction peaks associated with SiO_2, CaO, $Ca(OH)_2$, $CaSiO_3$, Ca_2SiO_4 were detected respectively, demonstrating the load $Ca(NO_3)_2$ was decomposed because the characteristic peaks of $Ca(NO_3)_2$ disappeared on XRD pattern. With increasing the calcination temperature to 900°C (Figure 4.2 d), the main characteristic XRD peaks remained almost unchanged. Accordingly, the calcination temperature of 700°C is chosen as the optimal calcination temperature to transform the compound into calcium oxide as well as saves energy as compared to 900°C.
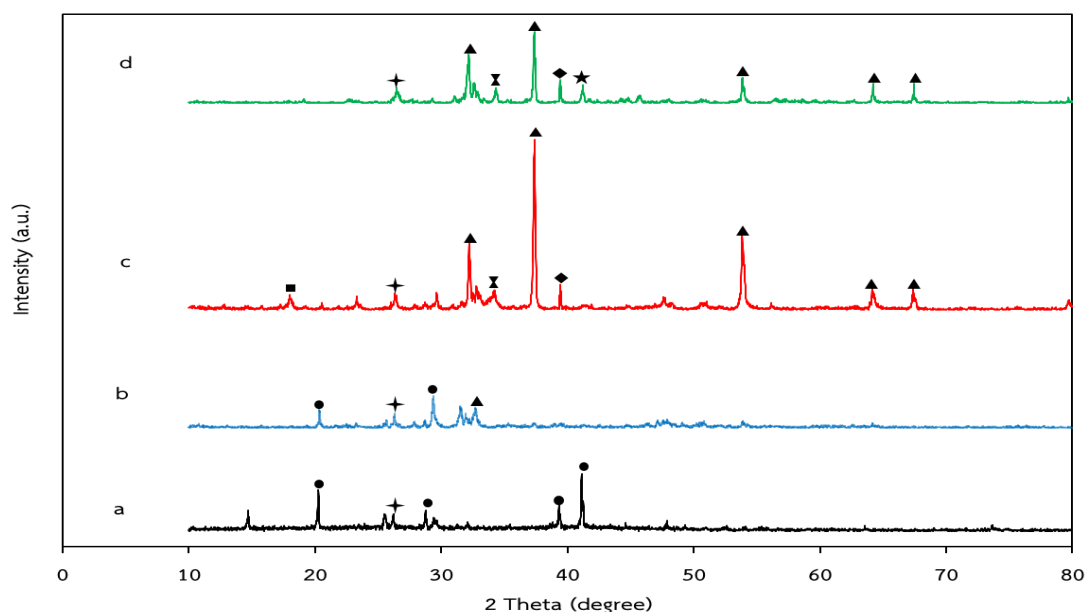
Figure 4. 2 The XRD patterns of CaO/SiO_2 catalyst calcined at different temperature (a) non-calcined, (b) 500°C, (c) 700°C and (d) 900°C (Symbol: ● = $Ca(NO_3)_2$, ✚ = SiO_2, ▲ = CaO, ■ = $Ca(OH)_2$, ◆ = $CaSiO_3$, ✗ = Ca_2SiO_4, ★ = Ca_3SiO_5

The FTIR spectrum of CaO/SiO$_2$ catalyst calcined at different temperature are shown in Figure 4.3. For the calcination temperature at 500°C (Figure 4.3 a), the absorption bands at 611 and 1100 cm^{-1} are assigned to the Si-O-Si bending and Si-O stretching, that indicate the appearance of SiO$_2$ in the RHA. The vibration bands at 1620 and 3650 cm^{-1} are assigned to the O–H stretching and the O–H bending vibration in Ca(OH)$_2$. The presence of Ca(OH)$_2$ should be due to the hydrolysis of CaO by moisture in the air during the sample preparation for the FT-IR analysis. After the calcination at 700°C and 900°C (Figure 4.5 b,c), the vibration band at about 991 cm^{-1} showed the presence of Si–O–Ca bond, which was an evidence for loading of CaO on RHA surface. This band was due to the formation of calcium silicate. Thus, FT-IR spectrum confirmed that Ca and Si oxides formed during the calcination procedure of impregnated Ca(NO$_3$)$_2$.4H$_2$O on SiO$_2$ at the temperature of 700°C in the muffle furnace.

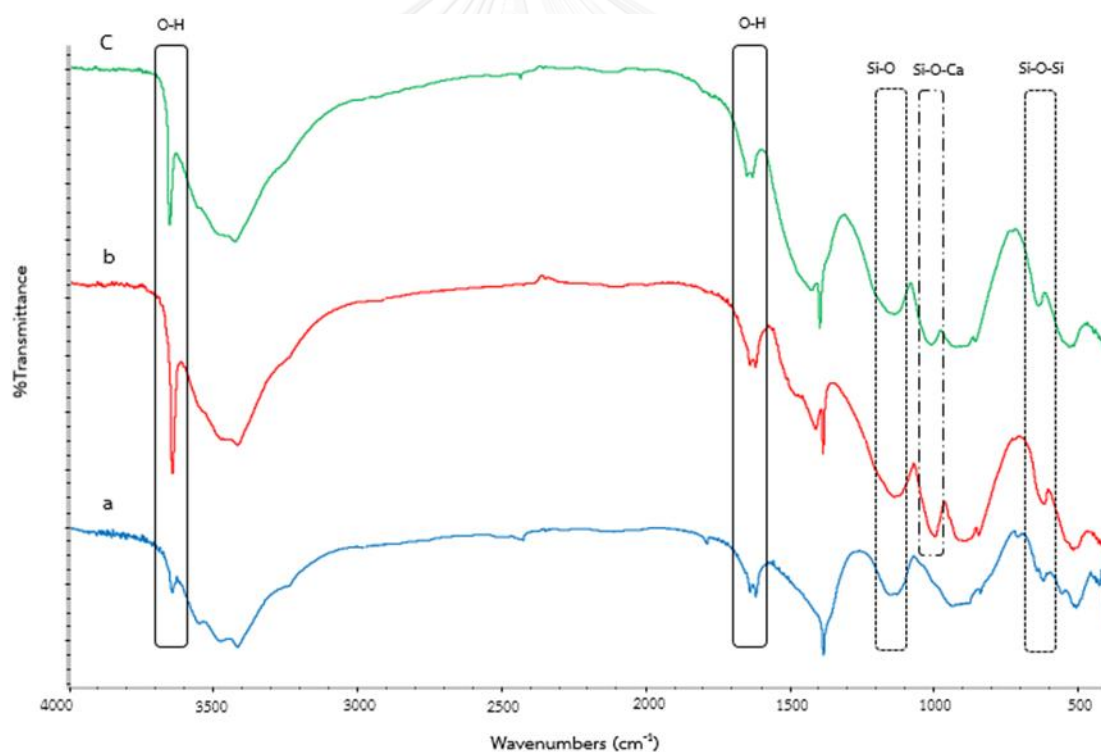**Figure 4.3** FT-IR spectrums of CaO/SiO$_2$ catalyst calcined at different temperature (a) 500°C, (b) 700°C and (c) 900°C

Table 4.1 Effect of calcination temperature of CaO/SiO_2 catalyst on the methyl ester content in transesterification of palm oil with methanol.

Catalyst	Calcination temperature (°C)	Methyl ester content (%)
$30wt.\%Ca(NO_3)_2/5wt.\%SiO_2$	none	0
	500	11.17
	700	97.55
	900	89.34

Effect of calcination temperature of CaO/SiO_2 catalyst on the transesterification of palm oil with methanol is summarized in Table 4.1. Before the calcination, the catalyst did not catalyze the transesterification. The methyl ester content was increased to 11.17% when increasing the calcination temperature of CaO/SiO_2 to 500°C. These results should be related to the increase in the amount of CaO. The methyl ester content was increased up to 97.55% when the calcination temperature of CaO/SiO_2 catalyst was performed at 700°C. Since 700°C, it was decomposed all of $Ca(NO)_3$ and $Ca(OH)_2$ to generate CaO phase. On calcination at 900°C, the methyl ester content reduced from 97.55 to 89.34%. The decrease in catalytic activity at the higher temperature resulted from the reduction of CaO species by a solid–solid impregnation and penetration of these species into the subsurface.[38] As the result, the calcination of impregnated $Ca(NO_3)_2.4H_2O$ on SiO_2 at 700°C provide the CaO/SiO_2 catalyst with high activity for transesterification reaction.

4.1.2 Effect of weight percentage of CaO/SiO$_2$

The effect of weight percentage of Ca(NO$_3$)$_2$ was investigated. The weight percentage of Ca(NO$_3$)$_2$ was varied from 10 wt.% to 40 wt.%.

The surface area and porosity of catalyst are determined by N$_2$ adsorption-desorption measurement. The specific surface area of catalyst was calculated using BET equation are given in Table 4.2.

Table 4.2 The surface area, pore volume and pore diameter of the prepared catalyst.

Catalyst	Surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
SiO$_2$	93.77	0.49	20.92
10wt.%Ca(NO$_3$)$_2$/5wt%SiO$_2$	8.38	0.07	29.15
20wt.%Ca(NO$_3$)$_2$/5wt%SiO$_2$	6.13	0.06	40.79
30wt.%Ca(NO$_3$)$_2$/5wt%SiO$_2$	4.81	0.04	45.98
40wt.%Ca(NO$_3$)$_2$/5wt%SiO$_2$	3.09	0.04	56.58

The surface area of the rice husk silica (SiO$_2$) was 93.77 m^2/g. Upon impregnation with CaO, the surface area of supported catalyst was reduced. The surface area of CaO/SiO$_2$ decreased with increasing CaO loading, which is indicated that the surface and pores of catalyst were covered by CaO on the SiO$_2$ surface during impregnation process. In general, the penetration of CaO into the pore of SiO$_2$ support could reduce the surface area of CaO/SiO$_2$.

Table 4.3 Basicity of prepared catalyst in various $Ca(NO_3)_2$ weight percentages.

Catalyst	Basicity (mmol/g)
$10wt.\%Ca(NO_3)_2/5wt\%SiO_2$	2.08
$20wt.\%Ca(NO_3)_2/5wt\%SiO_2$	4.05
$30wt.\%Ca(NO_3)_2/5wt\%SiO_2$	8.30
$40wt.\%Ca(NO_3)_2/5wt\%SiO_2$	8.87

Table 4.3 shows the total basicity of the catalyst by titration method. The total basicity of the catalyst increased from 2.08 to 4.05 mmol/g with the increase of $Ca(NO_3)_2$ weight percentage from 10 to 20 wt.%, then increased slightly from 8.30 to 8.87. mmol/g when the amount of $Ca(NO_3)_2$ increased from 30 to 40 wt.%. The basicity of the catalyst is promoted with increasing the amount of CaO loading, which is indicated that the basic sites of catalyst were increased by CaO.

Table 4.4 Effect of weight percentage of $Ca(NO_3)_2$ on the methyl ester content in transesterification of palm oil with methanol.

Catalyst	Basicity (mmol/g)	Methyl ester content (%)
$10wt.\%Ca(NO_3)_2/5wt\%SiO_2$	2.08	76.98
$20wt.\%Ca(NO_3)_2/5wt\%SiO_2$	4.05	85.56
$30wt.\%Ca(NO_3)_2/5wt\%SiO_2$	8.30	97.87
$40wt.\%Ca(NO_3)_2/5wt\%SiO_2$	8.87	98.39

Table 4.4 shows the effects of weight percentage of $Ca(NO_3)_2$ on the transesterification of palm oil with methanol in the range of 10-40 wt.%. It can be seen that, at the weight percentage $Ca(NO_3)_2$ of 10 %wt., the methyl ester content was achieved 76.98%. The $Ca(NO_3)_2$ loading of 10 wt.% did not provide enough active site (basic site) for transesterification due to its lower total basicity. The methyl ester

content was increased to 97.87% with increasing the weight percentage of $Ca(NO_3)_2$ to 30%. It should be related to the basicity of catalyst. The higher catalysts activity could have resulted from the higher basicity of the catalyst. The catalytic activity was increased with the amount of CaO loaded. This might be due to an increasing number of basic site. By further increasing the weight percentage of $Ca(NO_3)_2$ to 40%, the methyl ester content was slightly increased to 98.39%. These results suggested that to obtain the optimal value of the surface area and basicity, the weight percentage of $Ca(NO_3)_2$ should be 30wt.% for impregnating with SiO_2 to synthesis CaO/SiO_2 catalyst. As the result, the 30wt.%$Ca(NO_3)_2$/5wt.%SiO_2 was selected as a catalyst for further study in the transesterification of palm oil with methanol.

4.2 Biodiesel production

The effect of various parameters, such as reaction time, mole ratio of oil to methanol and the amount of catalyst, were studied in the reaction.

4.2.1 Effect of reaction time

This study investigated the effect of the reaction time for transesterification. The reaction time was varied in the range of 1 to 5 h. The reaction was carried out by 5 wt.% catalyst in mole ratio (oil to methanol) of 1:12 at $65^{o}C$. The methyl ester content with various reaction times is shown in Figure 4.4. The methyl ester content increased gradually from 66.80 to 99.35 % with increase in the reaction time from 1 to 5 h. In addition, the obtained equilibrium at variable time about 3 h. Thus, the appropriate reaction time is 3 h. under optimized reaction time.
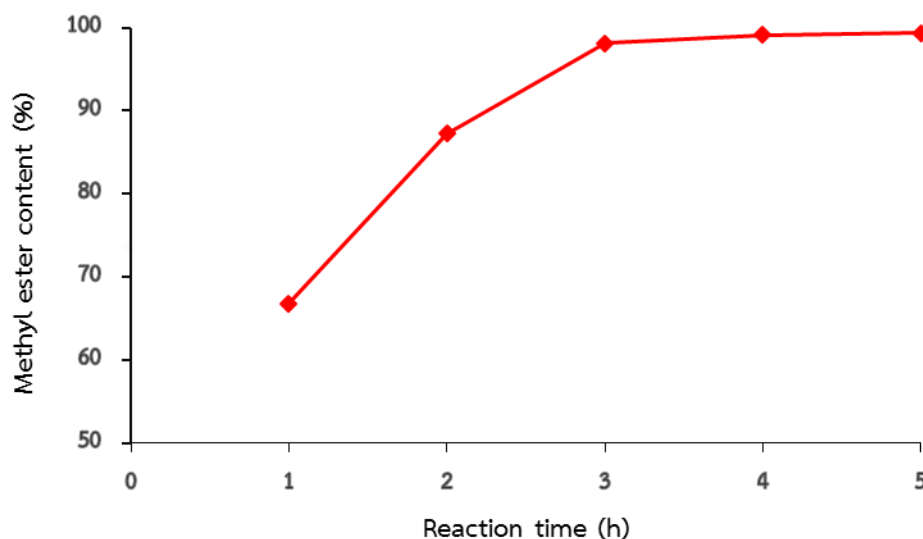
Figure 4.4 Effect of the reaction time on the methyl ester content at 65°C, with 1:12 mole ratio of oil to methanol and 5 wt.% catalyst.

4.2.2 Effect of mole ratio of oil to methanol

The mole ratio of oil to methanol is an important parameter in the transesterification reaction. From the reaction formula, the stoichiometric mole ratio of oil to methanol is 1:3. However, excess methanol can shift the equilibrium towards completion and produce more methyl ester as a product. The effect of mole ratios of oil to methanol on biodiesel production is shown in Figure 4.5. The result showed that the methyl ester content increased with increasing the mole ratio of oil to methanol. The highest methyl ester content was 97.82% at the mole ratio of oil to methanol of 1:9.
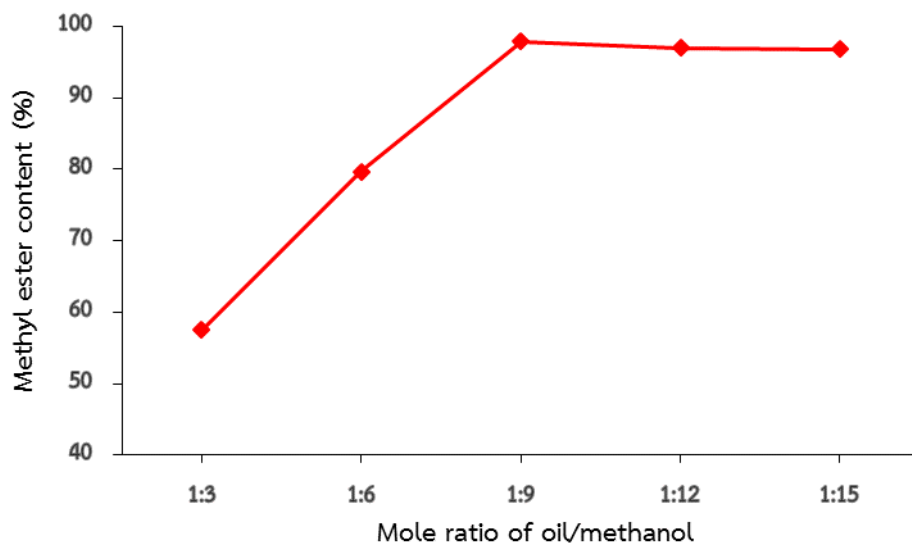
Figure 4.5 Effect of mole ratio of oil to methanol on the methyl ester content at 65°C, with 5 wt.% catalyst for 3 h.

4.2.3 Effect of the amount of catalyst

The influence of the amount of catalyst on biodiesel production was investigated at 1:9 mole ratio of oil to methanol at 65°C for 3 h. The amount of catalyst was varied from 1 to 5 wt.%. The effect of the amount of catalyst on biodiesel production is shown in Figure 4.7. The results showed that the methyl ester content increased from 46.92 to 98.36% with increasing the catalyst amount from 1 to 3 wt.%. By further increasing the catalyst amount to 3 to 5 wt.%, the methyl ester content was slightly increased to 98.43%. Therefore, the optimum amount of catalyst was 3 wt.%. It can be concluded that 98.36% methyl ester content was achieved using 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65°C for 3 h.
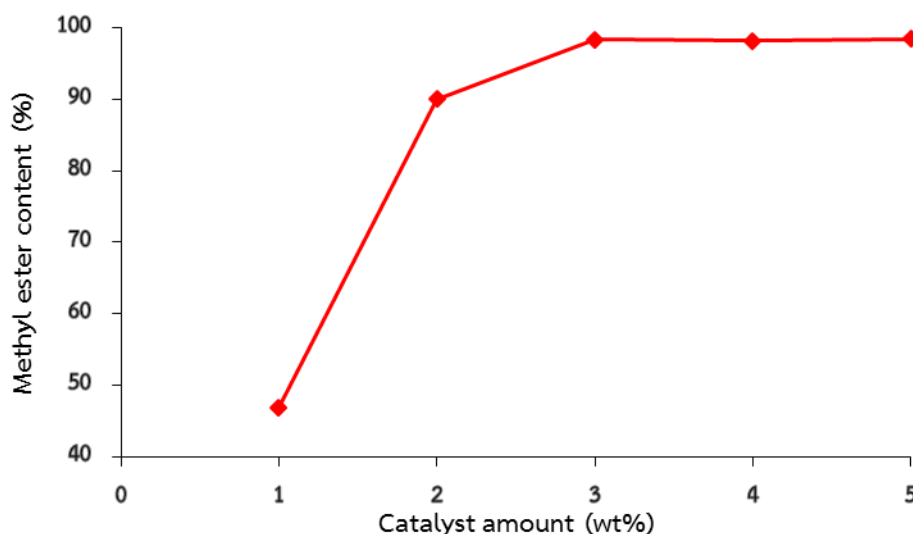
Figure 4.6 Effect of the amount of catalyst on the methyl ester content at 65°C, with 1:9 mole ratio of oil to methanol for 3 h.

4.2.4 Reusability of catalyst

Reusability is one of the most important features of a solid catalyst. In order to study the reusability of catalyst, the catalyst was separated from the reaction by filtration and was washed with methanol. The catalyst was calcined at 700ºC for 3h and reused for transesterification of palm oil with methanol under the reaction condition as 3 wt.% catalyst, 1:9 mole ratio of oil to methanol at 65ºC for 3 h. Figure 4.8. showed that the methyl ester content remains more than 85.79% within 4 cycles (after 4 cycles, the methyl ester content dropped to 70.64%). The decrease in activity of the catalyst might be due to the deactivation of CaO/SiO$_2$ catalyst which is leaching of CaO in the reaction and glycerol, fatty acid or glycerine covering the surface of catalyst that makes the active site was deactivated. They were also considered as the reason for the activity of catalyst loss.
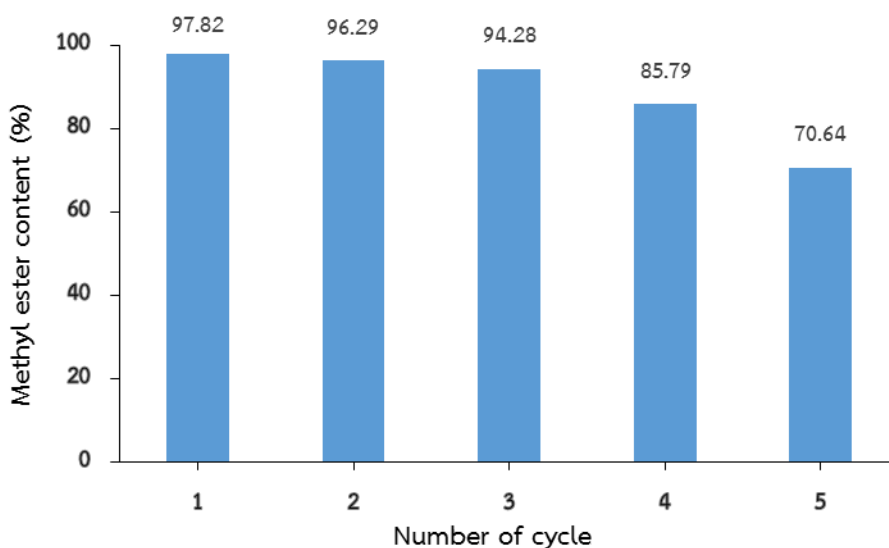
Figure 4.7 Reusability of the CaO/SiO$_2$ catalyst on the methyl ester content at 65°C, with 1:9 mole ratio of oil to methanol and 3 wt.% catalyst for 3 h.

The XRD patterns of fresh CaO/SiO$_2$ catalyst and CaO/SiO$_2$ catalyst after 4 cycles are shown in Figure 4.8. Besides, CaO/SiO$_2$ catalyst after 4 cycles, the main characteristic XRD peaks remained almost unchanged. However, the peak intensity of CaO decreased gradually. This might be due to CaO leaching into the reaction.

In addition, the fresh CaO/SiO$_2$ catalyst and CaO/SiO$_2$ catalyst after 4 cycles were measured by XRF analysis to evaluate the calcium oxide content of the catalyst. Table 4.5 showed the amount of CaO for the fresh catalyst decreased significantly with subsequent reaction cycles, becoming lower than 58.5% after the 4 cycles. Additionally, the decrease of the catalytic activity might be due to the deactivation of the CaO/SiO$_2$ catalyst during the repeated experiments which are not only the CaO leaching from this support, but the calcination at high temperature for many times can also cause another form of active site.
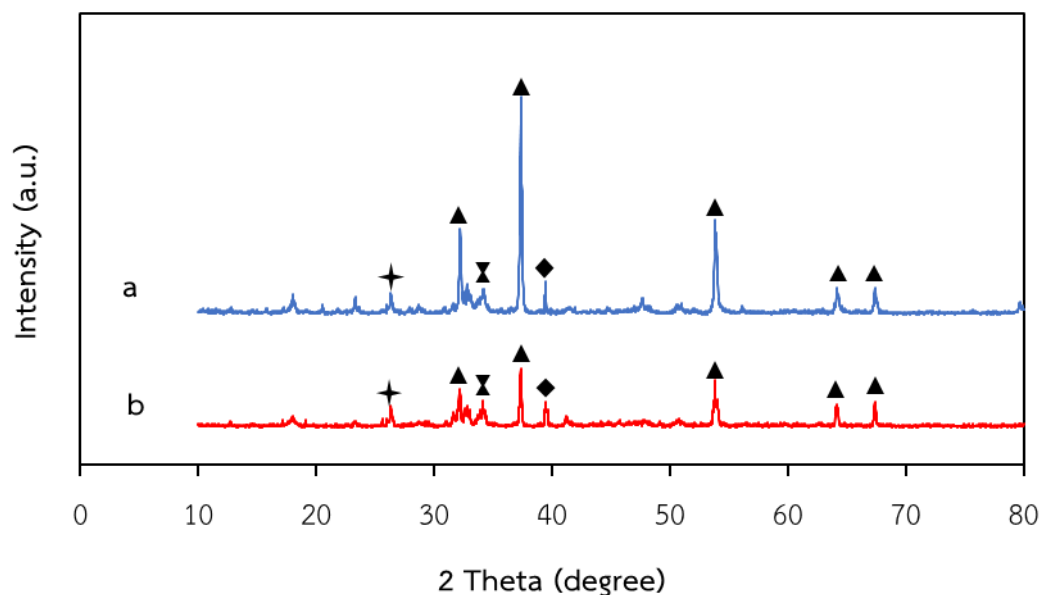
Figure 4.8 The XRD patterns of prepared CaO/SiO$_2$ catalyst (a) fresh CaO/SiO$_2$ catalyst, (b) CaO/SiO$_2$ catalyst after 4 cycles (Symbol: ✚ = SiO$_2$, ▲ = CaO, ◆ = CaSiO$_3$, ✗ = Ca$_2$SiO$_4$

Table 4.5 The amount of calcium oxide and basicity of fresh CaO/SiO$_2$ catalyst and CaO/SiO$_2$ catalyst after 4 cycles.

Catalyst	CaO (%)	Basicity (mmol/g)	Methyl ester content (%)
fresh CaO/SiO$_2$	64.0	8.30	98.36
4 cycles CaO/SiO$_2$	58.5	3.96	85.79

4.2.5 Comparison with other catalysts

To compare the efficiency of the solid supported catalyst in biodiesel production, CaO/SiO$_2$, CaO/SiO$_2$-Al$_2$O$_3$ (SiO$_2$-Al$_2$O$_3$) is a commercial catalyst support) were studied at a 1:9 mole ratio of oil to methanol, 3 wt.% of catalyst for 3 h of reaction time at 65°C. The methyl ester content with different solid support catalyst are shown in Table 4.6. The results show that CaO/SiO$_2$ gave the higher methyl ester content (98.36%) than CaO/SiO$_2$-Al$_2$O$_3$ (87.18%). It might be due to CaO/SiO$_2$ had higher

basicity and basic site than CaO/SiO_2-Al_2O_3. As a result, the CaO/SiO_2 catalyst was more active than CaO/SiO_2-Al_2O_3 catalyst.

The XRD patterns of CaO/SiO_2 catalyst and CaO/SiO_2-Al_2O_3 catalyst are shown in Figure 4.9. For CaO/SiO_2-Al_2O_3 catalyst, the main characteristic XRD peaks were also similar to CaO/SiO_2 catalyst which indicated that Al_2O_3 did not react with CaO. However, the peak intensity of CaO decreased gradually. This might be due to the amount of CaO was lower than CaO/SiO_2 catalyst. The surface of SiO_2 was shielded by Al_2O_3 causing the interaction between CaO and SiO_2 is low, therefore the amount of CaO in CaO/SiO_2-Al_2O_3 was decreased. As a result, the basic site of CaO/SiO_2-Al_2O_3 was decreased by Al_2O_3. Since Al_2O_3 had an impact on the catalytic activity of CaO/SiO_2-Al_2O_3 catalyst.

Table 4. 6 Comparison of CaO/SiO_2 and CaO/SiO_2-Al_2O_3 catalyst.

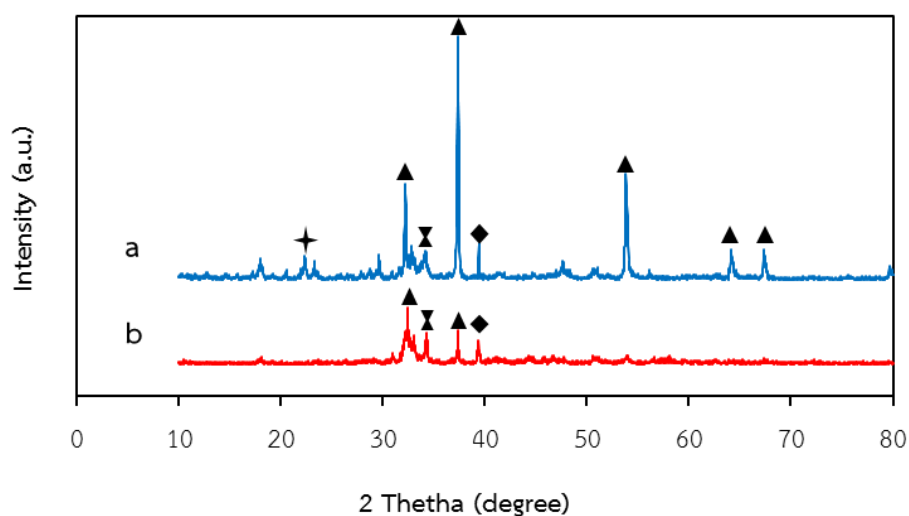| Catalyst	Surface area (m^2/g)	Basicity (mmol/g)	Methyl ester content (%)
30wt.%CaO/5wt%SiO_2	4.81	8.30	98.36
30wt.%CaO/5wt%SiO_2-Al_2O_3	4.53	4.06	87.18

Figure 4.9 The XRD patterns of different solid support catalyst (a) CaO/SiO_2 catalyst, (b) CaO/SiO_2-Al_2O_3 (Symbol:✚ = SiO_2, ▲ = CaO, ◆ = $CaSiO_3$,✖ = Ca_2SiO_4

4.3 Properties of biodiesel

The properties of biodiesel such as ester content and acid value were determined according to ASTM standard in Table 4.7. The ester content of commercial biodiesel should be higher than 96.5wt%. Furthermore, the acid value standard is less than 0.50 mg KOH/g.

Table 4.7 Specification for quality of biodiesel

Property	Method	Specification	Result
Acid value (mg KOH/g)	ASTM D 664	< 0.5	0.43
Ester content (wt.%)	EN 14103-11	> 96.5	98.36

From Table 4.7, the acid value of methyl ester was analyzed according to ASTM standard. The standard acid value of commercial biodiesel is 0.5 mg KOH/g. The result of acid value of methyl ester was 0.43 mg KOH/g, which in the range of commercial biodiesel. Besides, the percentage of ester content was 98.36%, which corresponded with the ester content of commercial biodiesel (higher than 96.5 wt%.) As a result, fatty acid methyl ester synthesized via CaO/SiO_2 catalyst is appropriate for use as biodiesel fuel.

CHAPTER V

CONCLUSION

5.1 Synthesis of solid base catalyst (CaO/SiO$_2$)

The calcium oxide supported on rice husk silica was prepared by impregnation method. The reaction condition was 30 wt.% of calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$.4H$_2$O) per 5 wt.% of SiO$_2$ (from RHA) and 12 h of reaction time. After that, the mixture was dried in an oven at 120°C on overnight. Then the solid was calcined at 700°C for 3 h to form CaO/SiO$_2$ catalyst. Under the batch condition, the surface area of catalyst was 4.81 m^2/g and its basicity was 8.30 mmol/g. As the result, the obtained CaO/SiO$_2$ can be used as a solid base catalyst for biodiesel synthesis.

5.2 Biodiesel synthesis

This part of work focuses on the parameters of reaction that affect the optimum conditions for biodiesel synthesis using the solid base catalyst as calcium oxide support on rice husk silica (CaO/SiO$_2$). The various parameters, including reaction time, mole ratio of oil to methanol and the amount of catalyst were determined. Catalytic performance of (CaO/SiO$_2$) catalyst was compared with CaO/SiO$_2$-Al$_2$O$_3$ catalyst in the transesterification of palm oil with methanol.

The optimum condition for biodiesel synthesis with calcium oxide support on rice husk silica catalyst (CaO/SiO$_2$) was 1:9 mole ratio of oil to methanol, 3 wt.% of catalyst for 3 h of reaction time at 65°C. This method is indicated that the methyl ester content was increased up to 98.36%. This catalyst could be reused up to 4 times with a little loss in its catalyst activity. Comparison between CaO/SiO$_2$ and CaO/SiO$_2$-Al$_2$O$_3$ the results show that CaO/SiO$_2$ is more active than CaO/SiO$_2$-Al$_2$O$_3$. Accordingly, this solid base catalyst was proved to exhibit an excellent stability, and a high activity for an achievement in the transesterification reaction.

5.3 Suggestions

1. To gain higher reusability, the support should be altered into another type such as zeolite in order to enhance an interaction between active site and support.

2. The optimum condition should be studied about calcination temperature in order to prevent deactivation at high temperature.

REFERENCES

[1]   Xie, W. and Zhao, L. Production of biodiesel by transesterification of soybean oil using calcium supported tin oxides as heterogeneous catalysts. Energy Conversion and Management 76 (2013): 55-62.

[2]   Wu, H., Zhang, J., Wei, Q., Zheng, J., and Zhang, J. Transesterification of soybean oil to biodiesel using zeolite supported CaO as strong base catalysts. Fuel Processing Technology 109 (2013): 13-18.

[3]   Xie, W. and Zhao, L. Heterogeneous CaO–MoO$_3$–SBA-15 catalysts for biodiesel production from soybean oil. Energy Conversion and Management 79 (2014): 34-42.

[4]   Chen, C.L., Huang, C.C., Tran, D.T., and Chang, J.S. Biodiesel synthesis via heterogeneous catalysis using modified strontium oxides as the catalysts. Bioresour Technol 113 (2012): 8-13.

[5]   Sun, H., Duan, J., Chen, P., Lou, H., and Zheng, X. Room temperature transesterification of soybean oil to biodiesel catalyzed by rod-like Ca$_x$SiO$_{x+2}$ solid base. Catalysis Communications 12(11) (2011): 1005-1008.

[6]   Thuadaij, N. and Nuntiya, A. Preparation of Nanosilica Powder from Rice Husk Ash by Precipitation Method. Chiang Mai J. Sci. 35(1) (2008): 206-211.

[7]   Hindryawati, N., Maniam, G.P., Karim, M.R., and Chong, K.F. Transesterification of used cooking oil over alkali metal (Li, Na, K) supported rice husk silica as potential solid base catalyst. Engineering Science and Technology, an International Journal 17(2) (2014): 95-103.

[8]   Lin, C., Lin, H., and Hung, L. Fuel structure and properties of biodiesel produced by the peroxidation process. Fuel 85(12-13) (2006): 1743-1749.

[9]   Joshi, R.M. and Pegg, M.J. Flow properties of biodiesel fuel blends at low temperatures. Fuel 86(1-2) (2007): 143-151.

[10]   กรมธุรกิจพลังงาน. ประกาศกรมธุรกิจพลังงาน เรื่อง กำหนดลักษณะและคุณภาพของไบโอดีเซลประเภทเมทิลเอสเตอร์ของกรดไขมัน พ.ศ. 2556. กรมธุรกิจพลังงาน (2556): 15-17.

[11]   Singh, S.P. and Singh, D. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. <u>Renewable and Sustainable Energy Reviews</u> 14(1) (2010): 200-216.

[12]   Leung, D.Y.C., Wu, X., and Leung, M.K.H. A review on biodiesel production using catalyzed transesterification. <u>Applied Energy</u> 87(4) (2010): 1083-1095.

[13]   Demirbas, A. Progress and recent trends in biodiesel fuels. <u>Energy Conversion and Management</u> 50(1) (2009): 14-34.

[14]   Canakci, H.S.M. Effects of Different Alcohol and Catalyst Usage on Biodiesel Production from Different Vegetable Oils. <u>Energy & Fuels</u> 22 (2008): 2713–2719.

[15]   Helwani, Z., Othman, M.R., Aziz, N., Kim, J., and Fernando, W.J.N. Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review. <u>Applied Catalysis A: General</u> 363(1-2) (2009): 1-10.

[16]   Ulf Schuchardta, R.S., Rogério Matheus Vargas. Transesterification of Vegetable Oils: a Review. <u>J. Braz. Chem. Soc.</u> 9(1) (1998): 199-210.

[17]   Kulkarni, M.G. and Dalai, A.K. Waste Cooking Oils An Economical Source for Biodiesel: A Review. <u>Ind. Eng. Chem. Res.</u> 45 (2006): 2901-2913.

[18]   Semwal, S., Arora, A.K., Badoni, R.P., and Tuli, D.K. Biodiesel production using heterogeneous catalysts. <u>Bioresour Technol</u> 102(3) (2011): 2151-61.

[19]   Campanati, M., Fornasari, G., and Vaccari, A. Fundamentals in the preparation of heterogeneous catalysts. <u>Catalysis Today</u> 77(4) (2003): 299-314.

[20]   Schwarz, J.A., Contescu, C., and Contescu, A. Methods for Preparation of Catalytic Materials. <u>Chemical Reviews</u> 95(3) (1995): 477-510.

[21]   G. Ertl, H.K., J. Weitkamp. <u>Preparation of Solid Catalysts</u>. 1999, Wiley VCH: NewYork.

[22]   Balakrishnan, S. <u>Rice husk ash silica as a support material for iron and ruthenium based heterogeneous catalyst</u>. Master of Science, Department of Chemical Sciences Sains Malaysia University, 2006.

[23]   Ajay Kumar, K.M., Devendra Kumar, Om Parkash. Properties and Industrial
       Applications of Rice husk:A review. International Journal of Emerging
       Technology and Advanced Engineering 2(10) (2012): 86-90.

[24]   A.D. Onojah, N.A.A., C. Mbakaan. Rice husk ash refractory: The temperature
       dependent crystalline phase aspects. IJRRAS 15(2) (2013): 246-248.

[25]   Kouzu, M. and Hidaka, J.-s. Transesterification of vegetable oil into biodiesel
       catalyzed by CaO: A review. Fuel 93 (2012): 1-12.

[26]   Kouzu, M., Kasuno, T., Tajika, M., Sugimoto, Y., Yamanaka, S., and Hidaka, J.
       Calcium oxide as a solid base catalyst for transesterification of soybean oil
       and its application to biodiesel production. Fuel 87(12) (2008): 2798-2806.

[27]   Ngamcharussrivichai, C., Nunthasanti, P., Tanachai, S., and Bunyakiat, K.
       Biodiesel production through transesterification over natural calciums. Fuel
       Processing Technology 91(11) (2010): 1409-1415.

[28]   Cho, Y.B., Seo, G., and Chang, D.R. Transesterification of tributyrin with
       methanol over calcium oxide catalysts prepared from various precursors. Fuel
       Processing Technology 90(10) (2009): 1252-1258.

[29]   Liu, X., He, H., Wang, Y., Zhu, S., and Piao, X. Transesterification of soybean oil
       to biodiesel using CaO as a solid base catalyst. Fuel 87(2) (2008): 216-221.

[30]   Kouzu, M., Yamanaka, S.-y., Hidaka, J.-s., and Tsunomori, M. Heterogeneous
       catalysis of calcium oxide used for transesterification of soybean oil with
       refluxing methanol. Applied Catalysis A: General 355(1-2) (2009): 94-99.

[31]   Benjapornkulaphong, S., Ngamcharussrivichai, C., and Bunyakiat, K. Al_2O_3-
       supported alkali and alkali earth metal oxides for transesterification of palm
       kernel oil and coconut oil. Chemical Engineering Journal 145(3) (2009): 468-
       474.

[32]   Liu, T., Li, Z., Li, W., Shi, C., and Wang, Y. Preparation and characterization of
       biomass carbon-based solid acid catalyst for the esterification of oleic acid
       with methanol. Bioresour Technol 133 (2013): 618-21.

[33]   Naureen, R., Tariq, M., Yusoff, I., Chowdhury, A.J., and Ashraf, M.A. Synthesis,
       spectroscopic and chromatographic studies of sunflower oil biodiesel using
       optimized base catalyzed methanolysis. Saudi J Biol Sci 22(3) (2015): 332-9.

[34]   Method, A.S.T.a. <u>American Standard Test and Method</u> 2010, July 2010. 1-7.

[35]   Mansha, M., Javed, S.H., Kazmi, M., and Feroze, N. Study of Rice Husk Ash as Potential Source of Acid Resistance Calcium Silicate. <u>Advances in Chemical Engineering and Science</u> 1(03) (2011): 147-153.

[36]   Kalapathy, U., Proctor, A., and Shultz, J. A simple method for production of pure silica from rice hull ash. <u>Bioresource Technology</u> 73 (2000): 257-262.

[37]   Saengprachum, N. <u>Glycerin, mono-, di-glycerine removal from crude biodiesel using silica from rice husk ash and silica alumina adsorbents.</u> Doctor's Thesis, Philosophy Program in Environmental Management Chulalongkorn University, 2013.

[38]   Ho, W.W., Ng, H.K., and Gan, S. Development and characterisation of novel heterogeneous palm oil mill boiler ash-based catalysts for biodiesel production. <u>Bioresource Technology</u> 125 (2012): 158-64.

APPENDIX

Appendix A: ^{1}H-NMR Spectrum of palm biodiesel
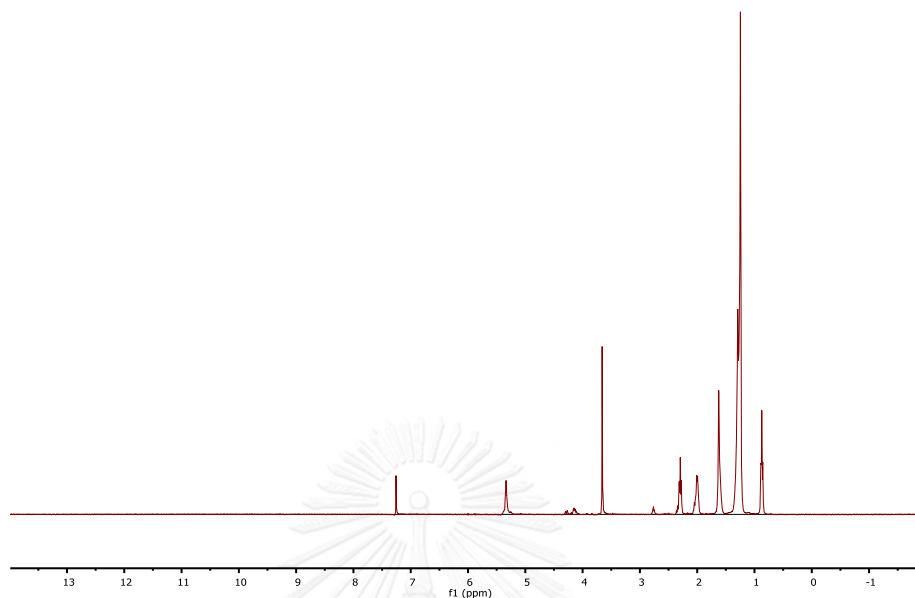
Figure A-1 ^{1}H-NMR spectrum of biodiesel at 1:12 mole ratio of oil to methanol, 5 wt.% catalyst at 65°C for 1 h. (CDCl$_3$, 400MHz)
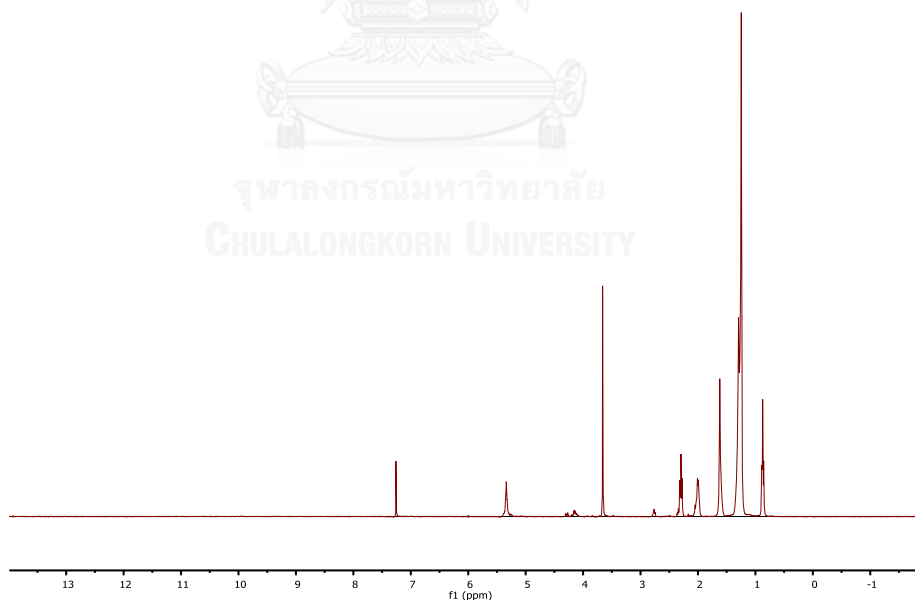
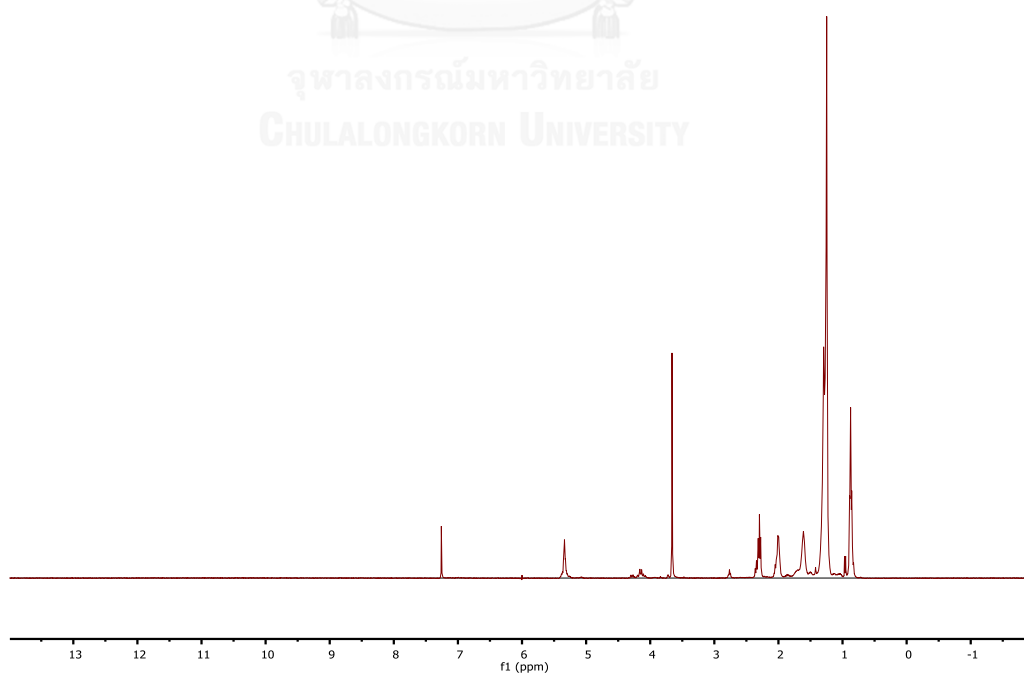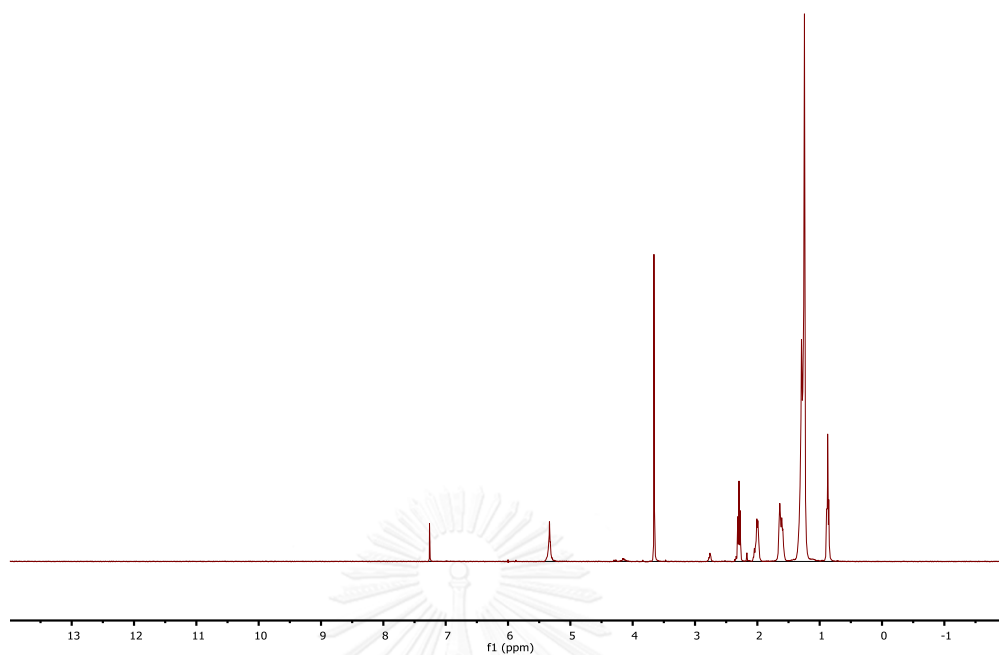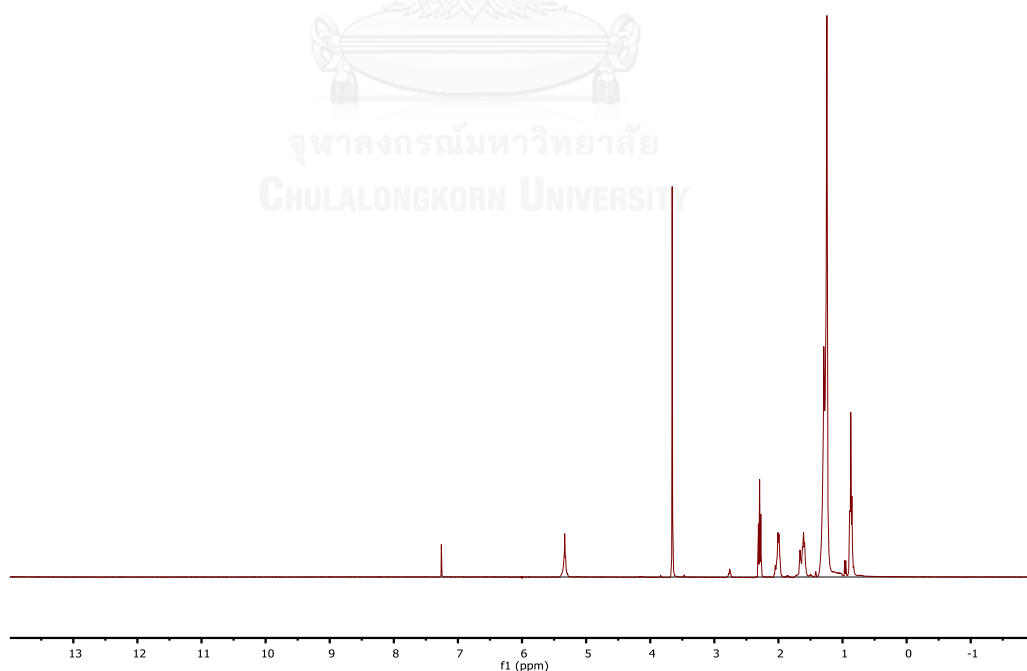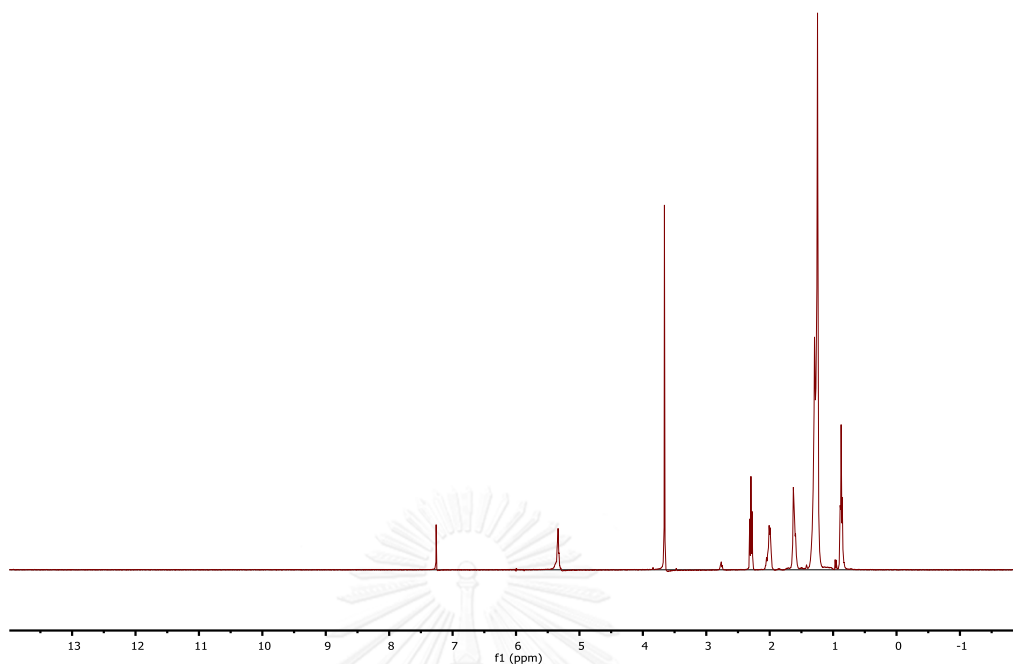**Figure A-2** ^{1}H-NMR spectrum of biodiesel at 1:12 mole ratio of oil to methanol, 5 wt.% catalyst at 65°C for 2 h. (CDCl$_3$, 400MHz)
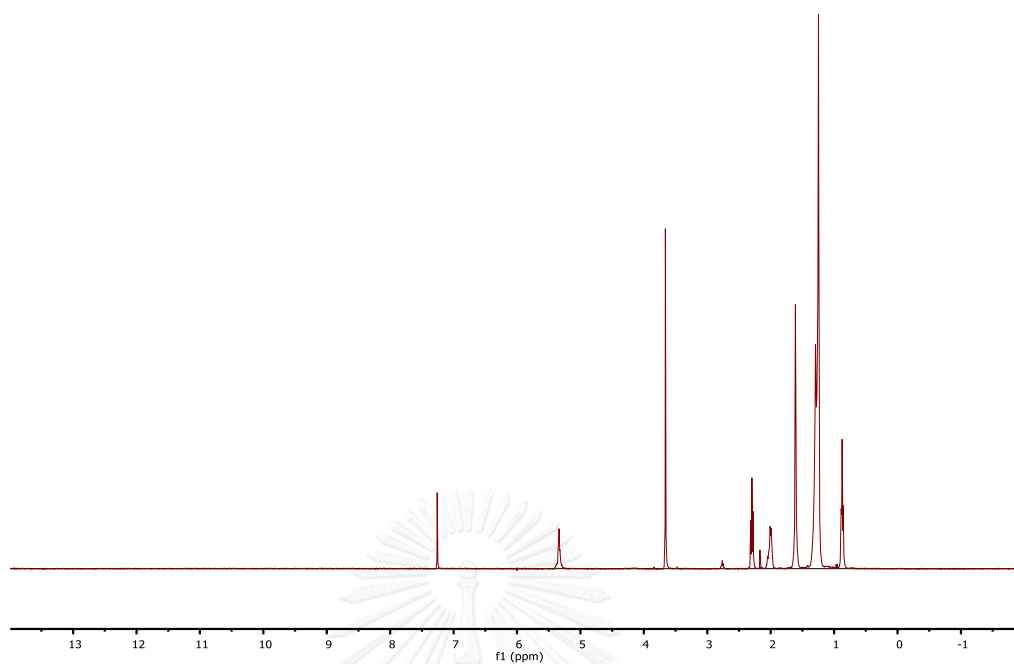
Figure A-3 ^{1}H-NMR spectrum of biodiesel at 1:12 mole ratio of oil to methanol, 5 wt.% catalyst at 65°C for 3 h. (CDCl₃, 400MHz)
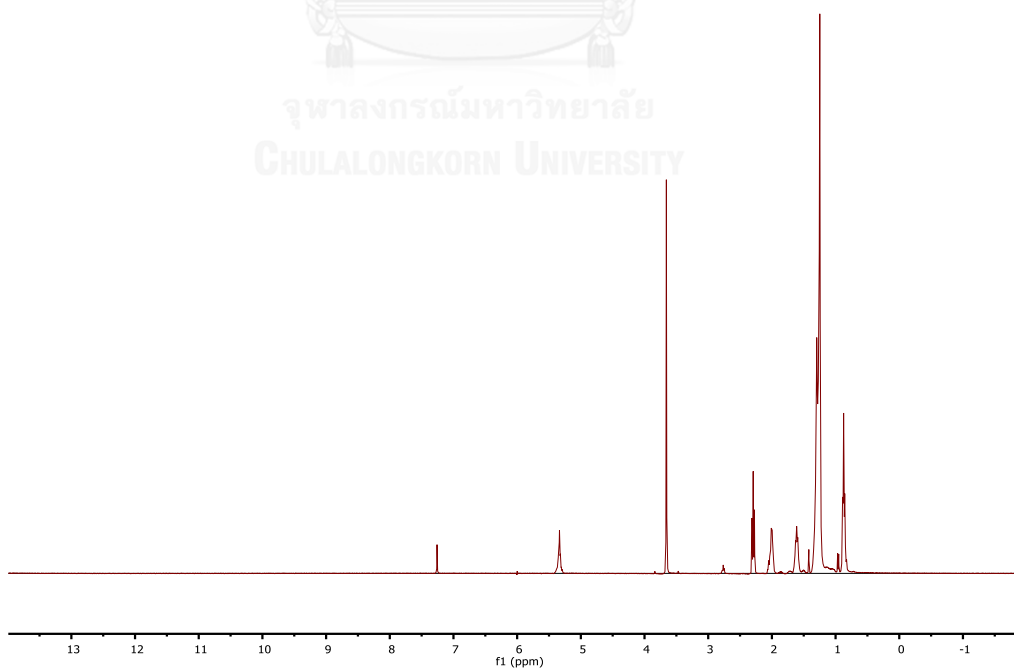
Figure A-4 ^{1}H-NMR spectrum of biodiesel at 1:12 mole ratio of oil to methanol, 5 wt.% catalyst at 65°C for 4 h. (CDCl₃, 400MHz)
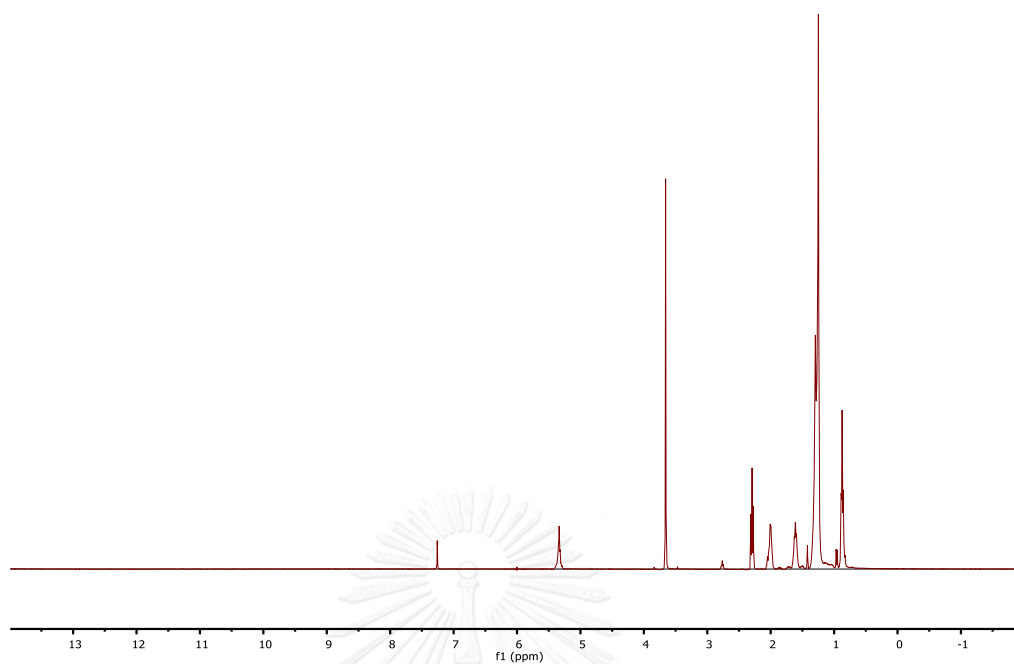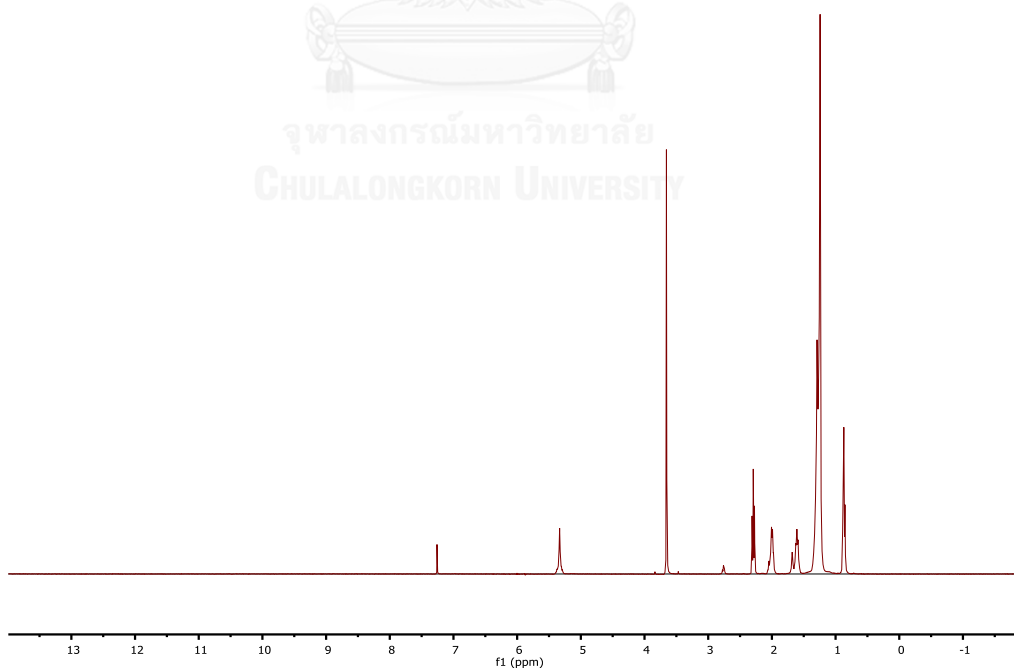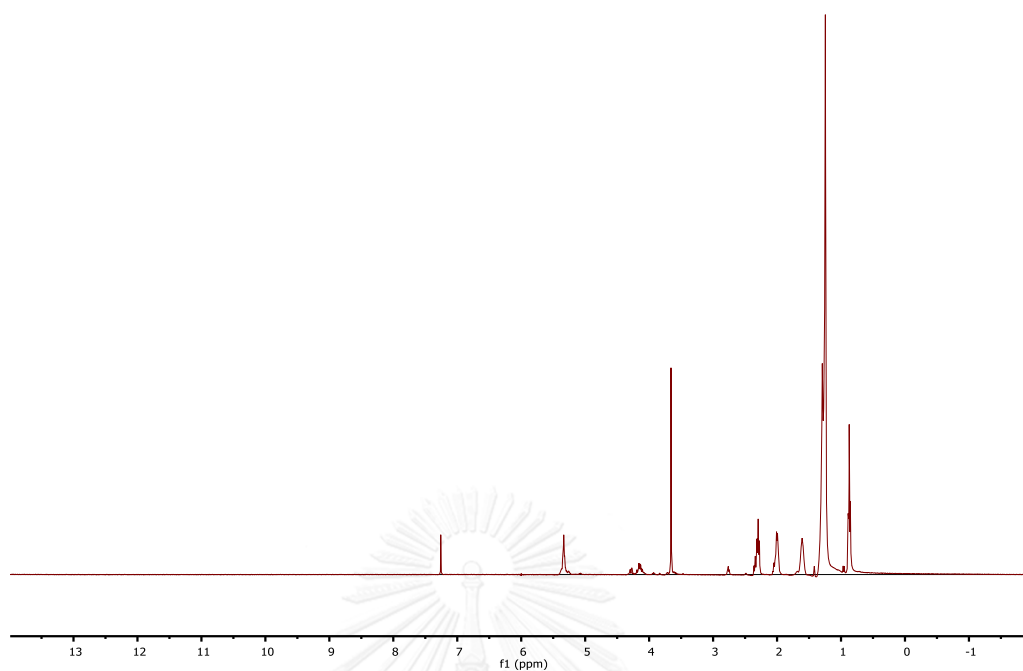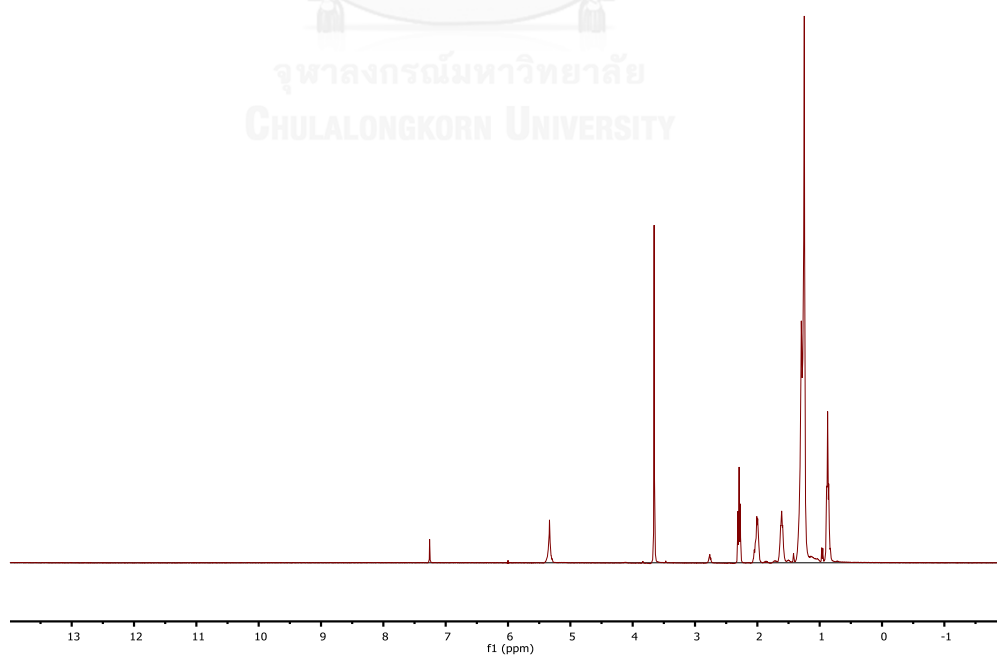
Figure A-5 ^{1}H-NMR spectrum of biodiesel at 1:12 mole ratio of oil to methanol, 5 wt.% catalyst at 65°C, for 5 h. (CDCl$_3$, 400MHz)

Figure A-6 ^{1}H-NMR spectrum of biodiesel at 1:3 mole ratio of oil to methanol, 5 wt.% catalyst at 65°C for 3 h. (CDCl$_3$, 400MHz)

Figure A-7 ^{1}H-NMR spectrum of biodiesel at 1:6 mole ratio of oil to methanol, 5 wt.% catalyst at 65°C for 3 h. (CDCl$_3$, 400MHz)

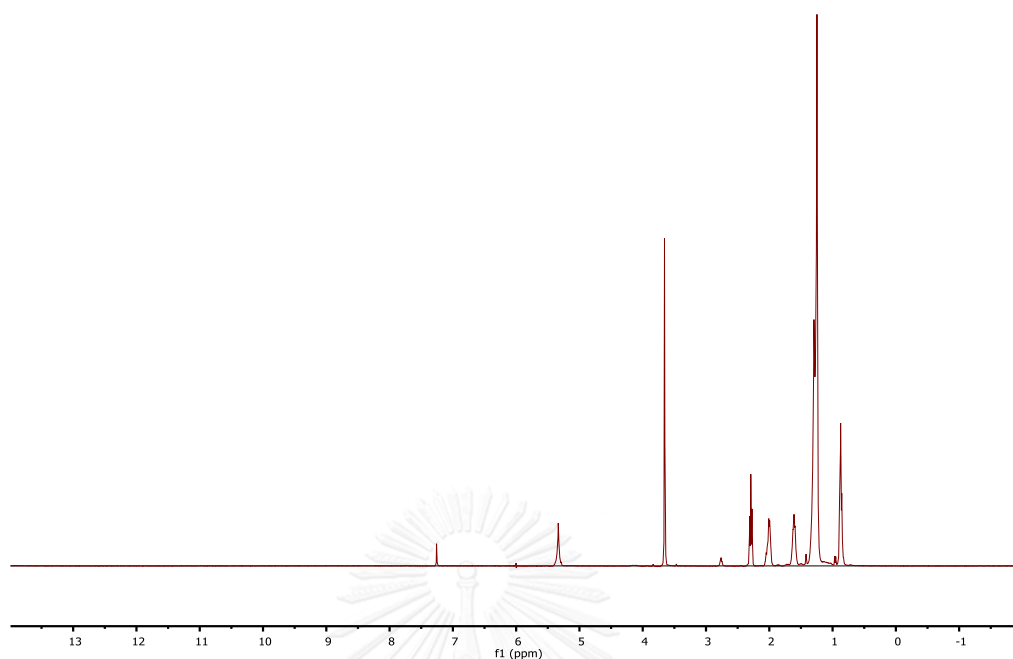**Figure A-8** ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 5 wt.% catalyst at 65°C for 3 h. (CDCl$_3$, 400MHz)
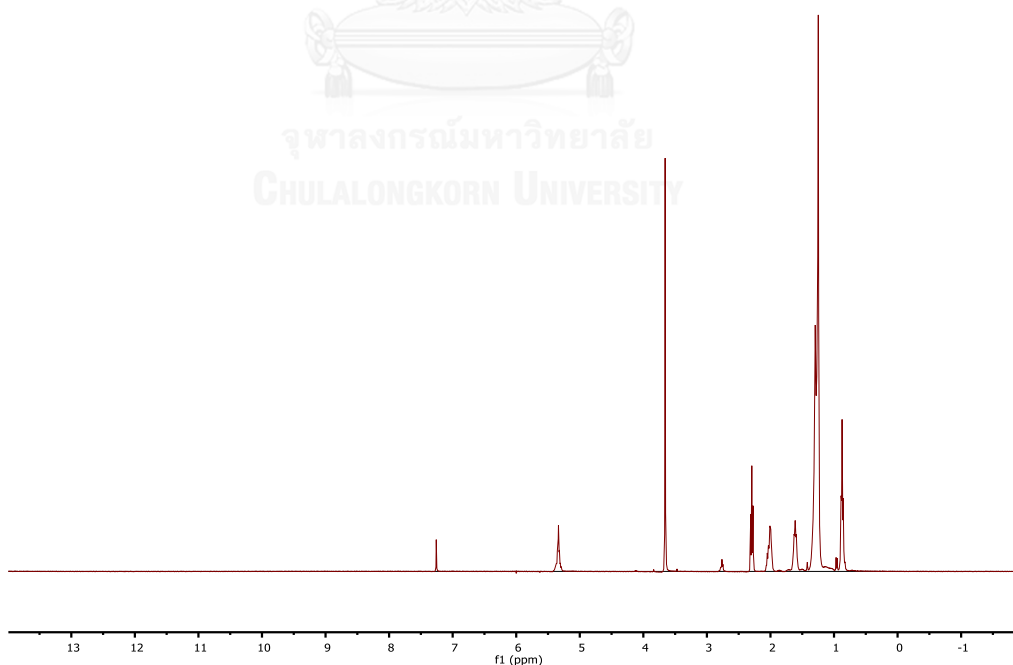
Figure A-9 ^{1}H-NMR spectrum of biodiesel at 1:12 mole ratio of oil to methanol, 5 wt.% catalyst at 65°C for 3 h. (CDCl₃, 400MHz)

Figure A-10 ^{1}H-NMR spectrum of biodiesel at 1:15 mole ratio of oil to methanol, 5 wt.% catalyst at 65°C for 3 h. (CDCl₃, 400MHz)

Figure A-11 ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 1 wt.% catalyst at 65°C for 3 h. (CDCl₃, 400MHz)

Figure A-12 ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 2 wt.% catalyst at 65°C for 3 h. (CDCl₃, 400MHz)
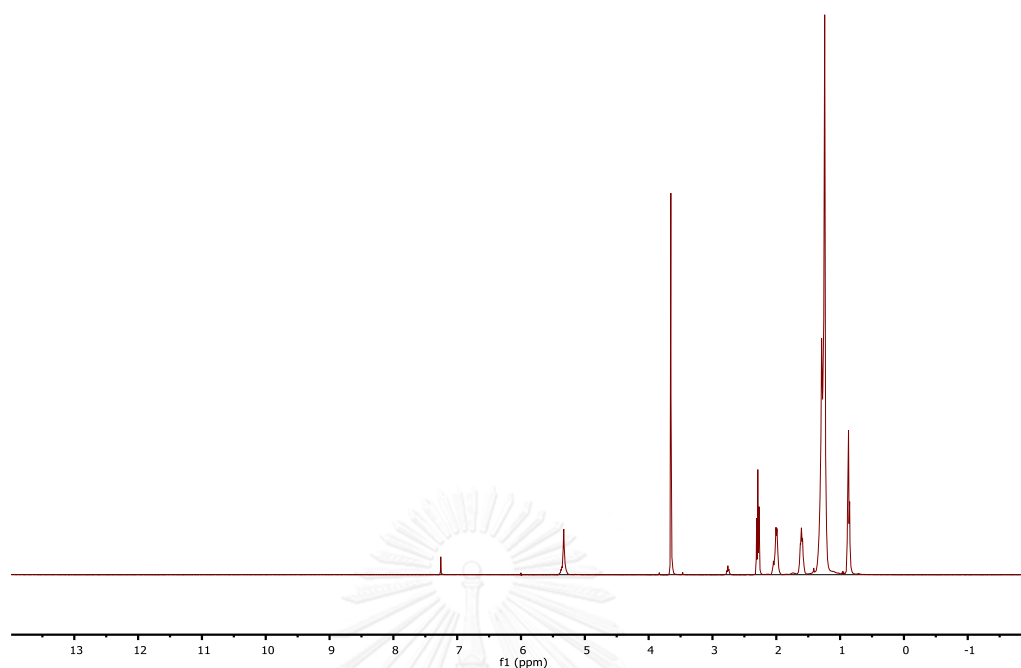
Figure A-13 ¹H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65°C for 3 h. (CDCl₃, 400MHz)
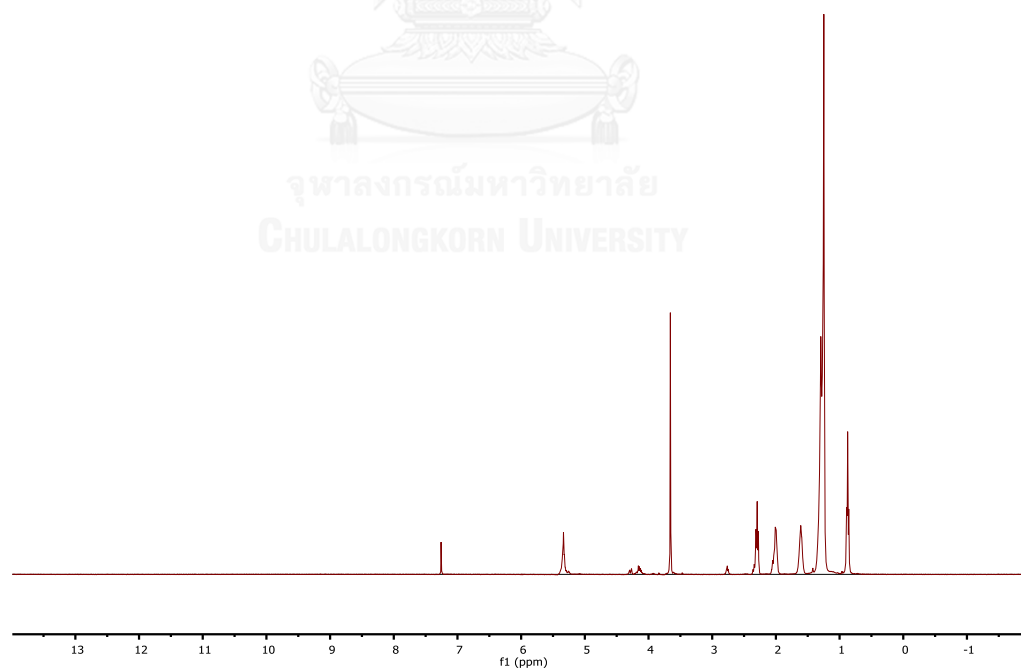

Figure A-14 ¹H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 4 wt.% catalyst at 65°C for 3 h. (CDCl₃, 400MHz)

Figure A-15 ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 5 wt.% catalyst at 65ºC for 3 h. (CDCl$_3$, 400MHz)

Figure A-16 ^{1}H-NMR spectrum of biodiesel at 1:9 mole of palm oil to methanol, 3 wt.% catalyst at 65ºC for 3 h. (catalyst: 10wt.%CaO/5wt%SiO$_2$) (CDCl$_3$, 400MHz)
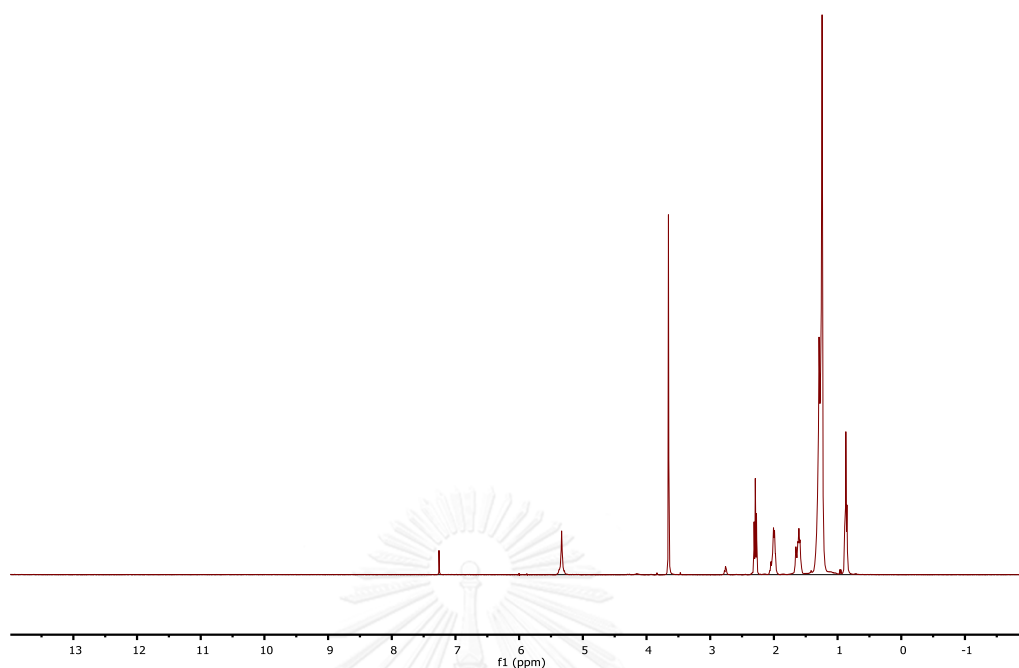
Figure A-17 ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65ºC for 3 h. (catalyst: 20wt.%CaO/5wt%SiO$_2$) (CDCl$_3$, 400MHz)
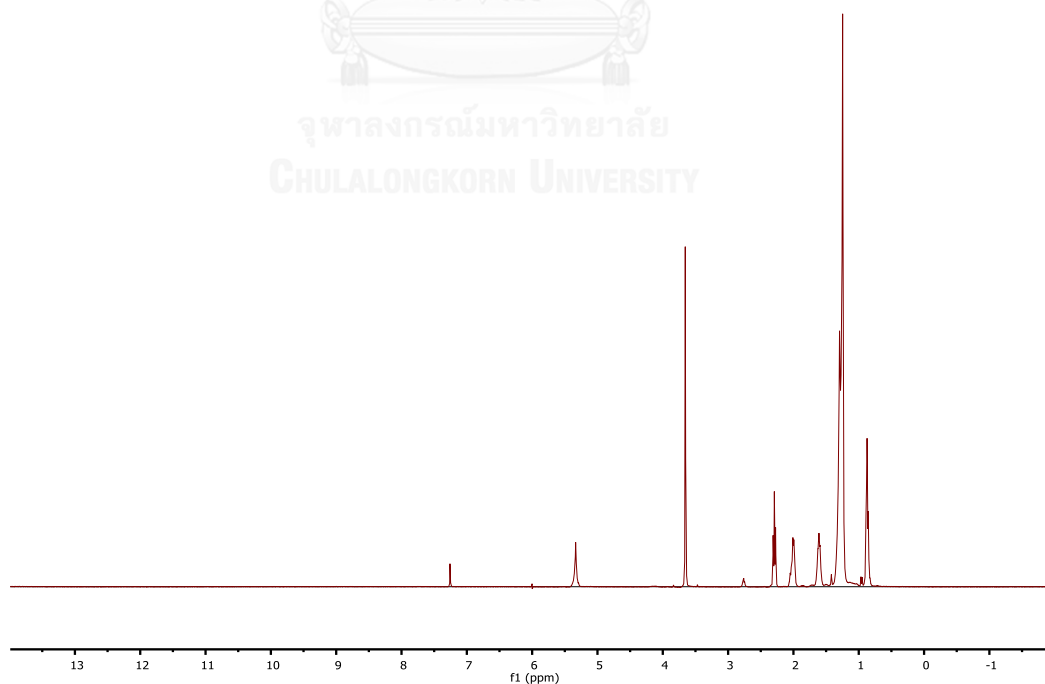

Figure A-18 ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65ºC for 3 h. (catalyst: 30wt.%CaO/5wt%SiO$_2$) (CDCl$_3$, 400MHz)

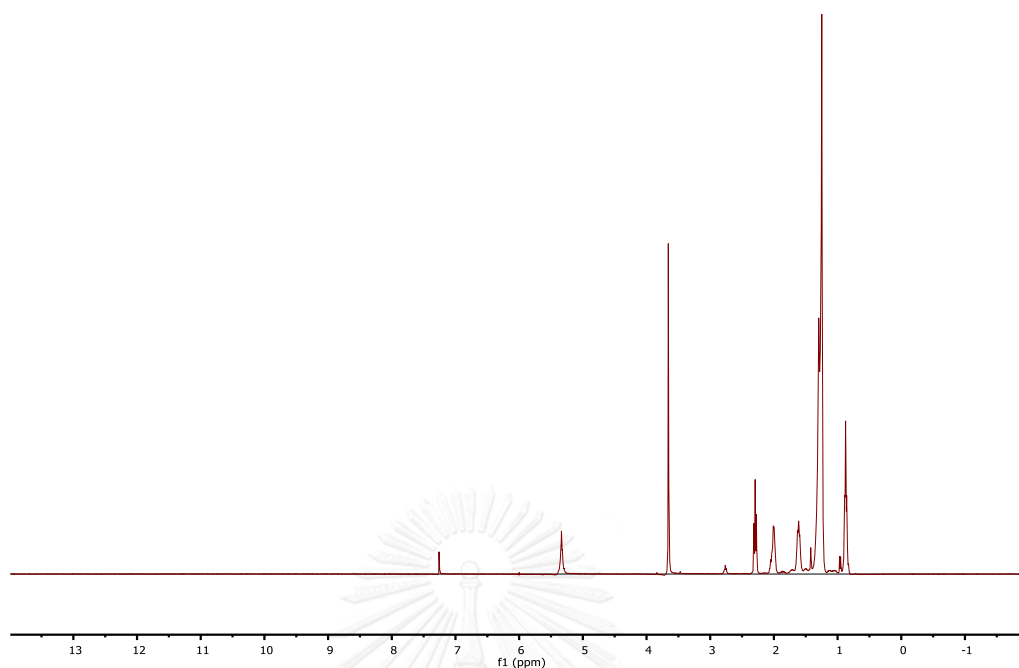**Figure A-19** ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65°C for 3 h. (catalyst: 40wt.%CaO/5wt%SiO$_2$) (CDCl$_3$, 400MHz)
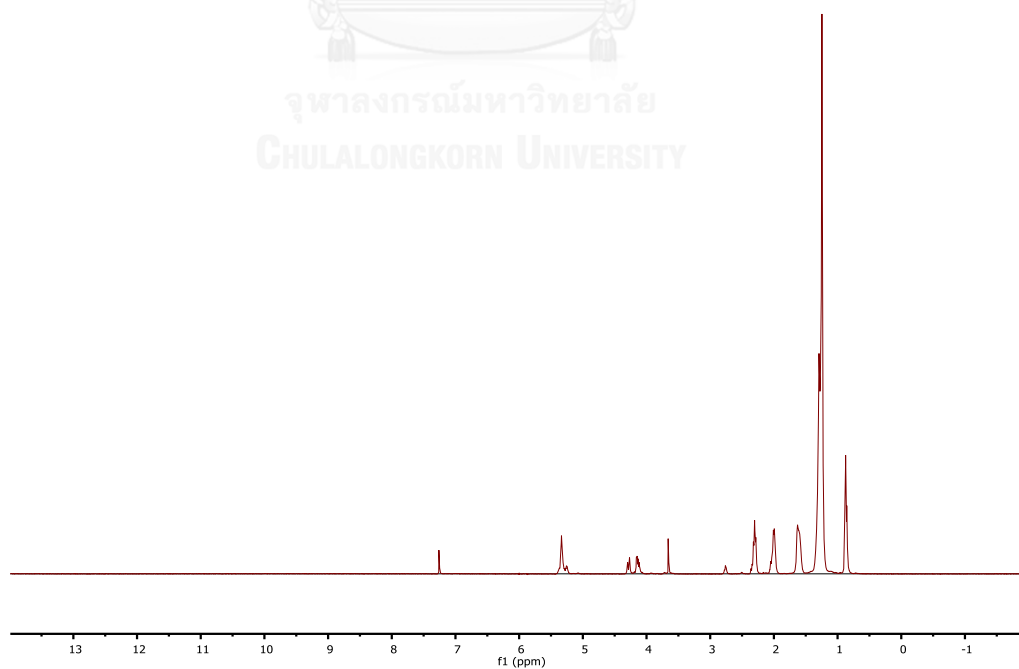

Figure A-20 ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65°C for 3 h. (catalyst calcined at 500°C) (CDCl$_3$, 400MHz)

Figure A-21 ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65°C for 3 h. (catalyst calcined at 700°C) (CDCl₃, 400MHz)

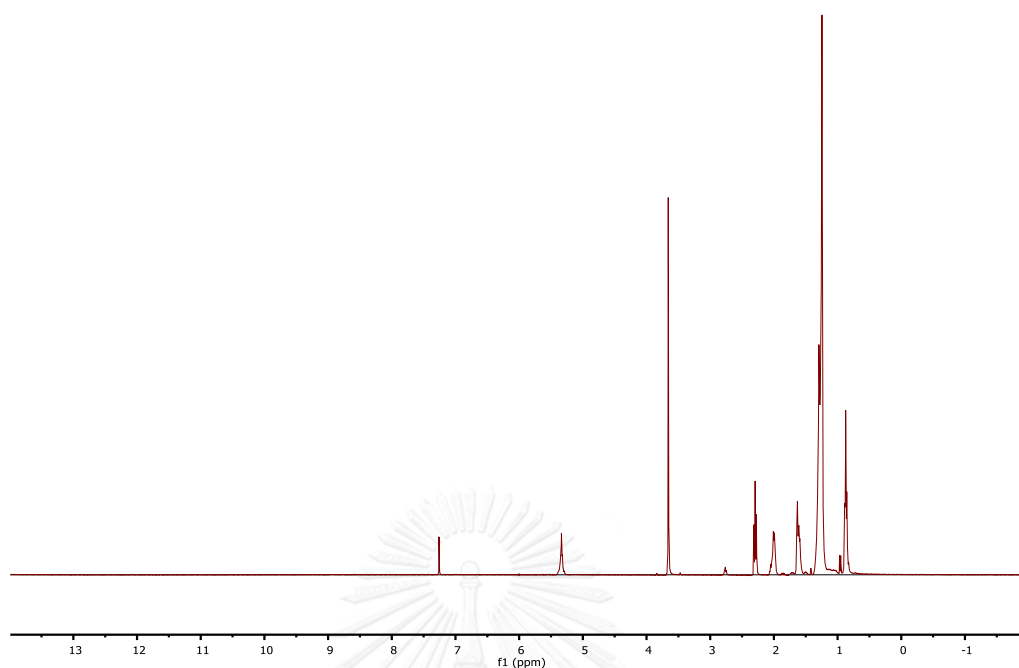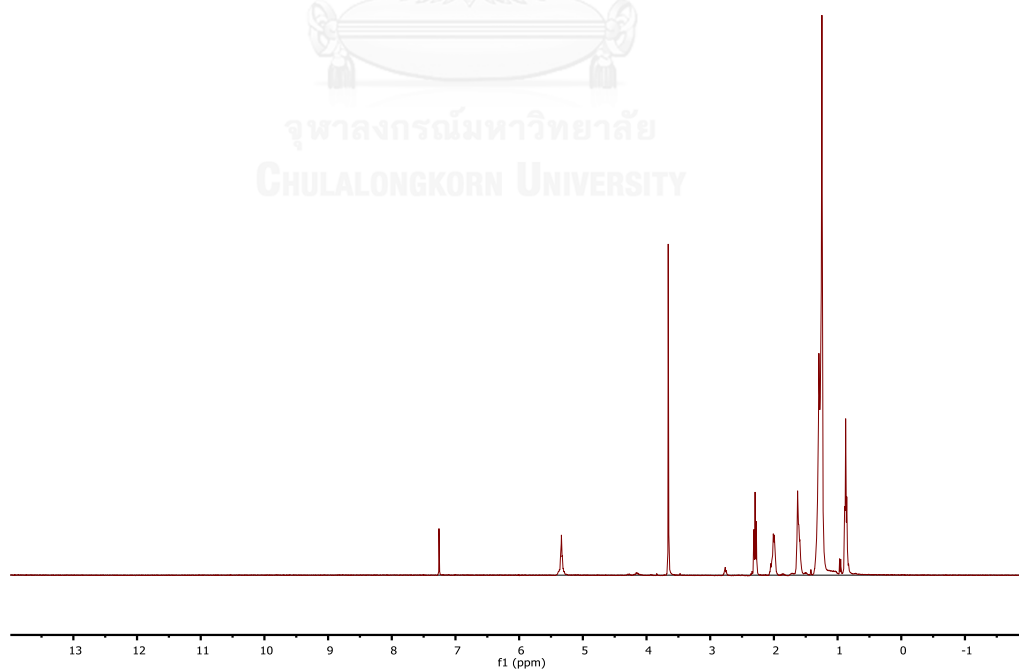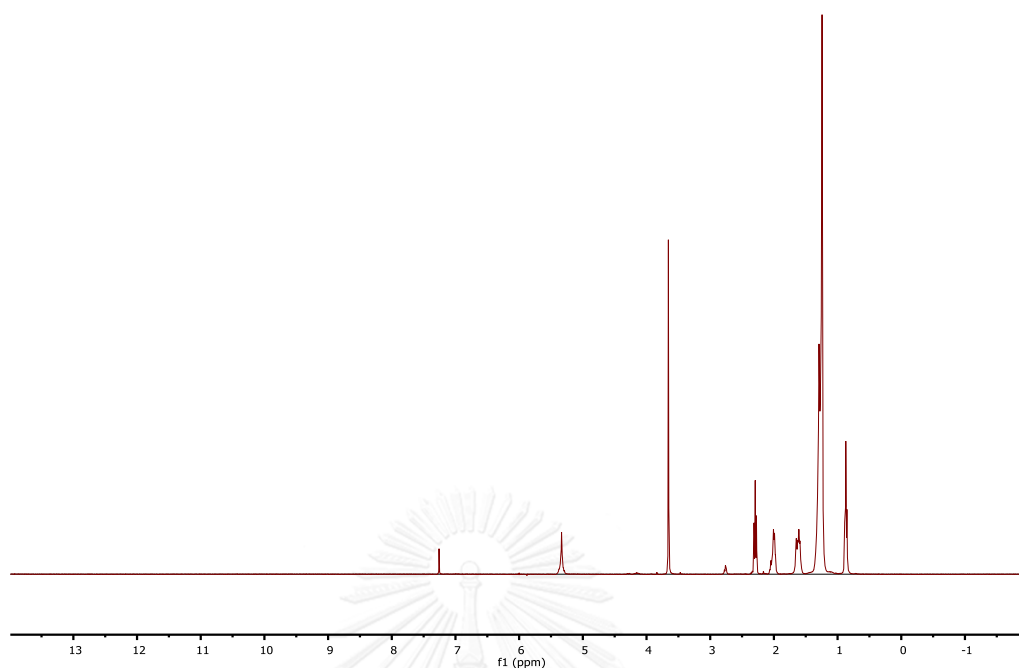**Figure A-22** ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65°C for 3 h. (catalyst calcined at 900°C) (CDCl₃, 400MHz)

Figure A-23 ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65°C for 3 h. (catalyst: CaO/SiO$_2$-Al2O$_3$) (CDCl$_3$, 400MHz)

Figure A-24 ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65°C for 3 h. (catalyst: reuse1) (CDCl$_3$, 400MHz)

Figure A-25 ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65°C for 3 h. (catalyst: reuse2) (CDCl$_3$, 400MHz)

Figure A-26 ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65°C for 3 h. (catalyst: reuse3) (CDCl$_3$, 400MHz)

Figure A-27 ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65°C for 3 h. (catalyst: reuse4) (CDCl$_3$, 400MHz)
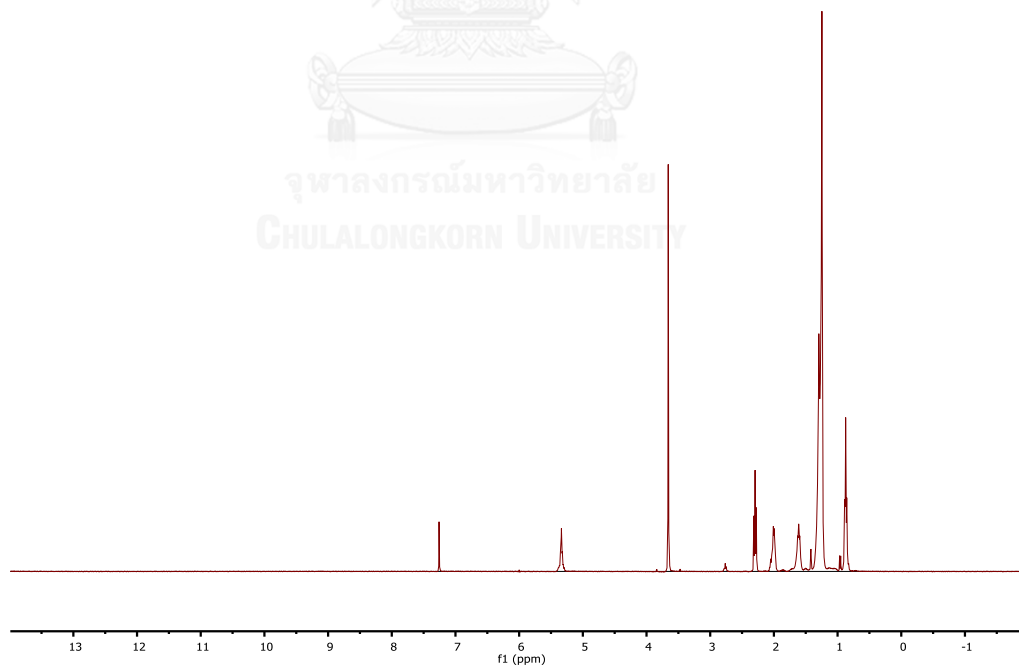

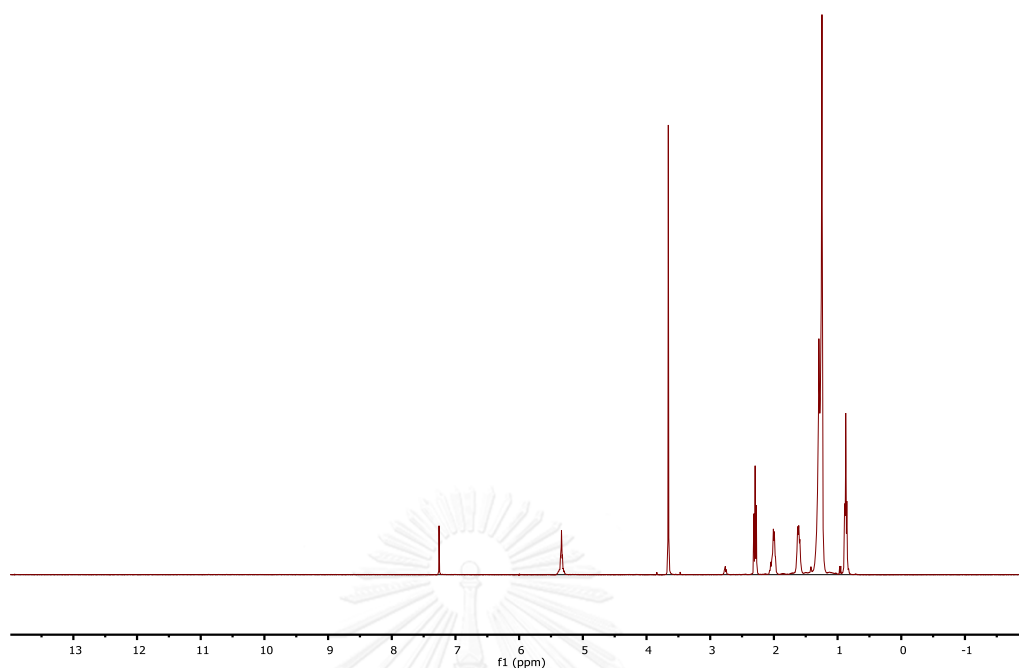**Figure A-28** ^{1}H-NMR spectrum of biodiesel at 1:9 mole ratio of oil to methanol, 3 wt.% catalyst at 65°C for 3 h. (catalyst: reuse5) (CDCl$_3$, 400MHz)

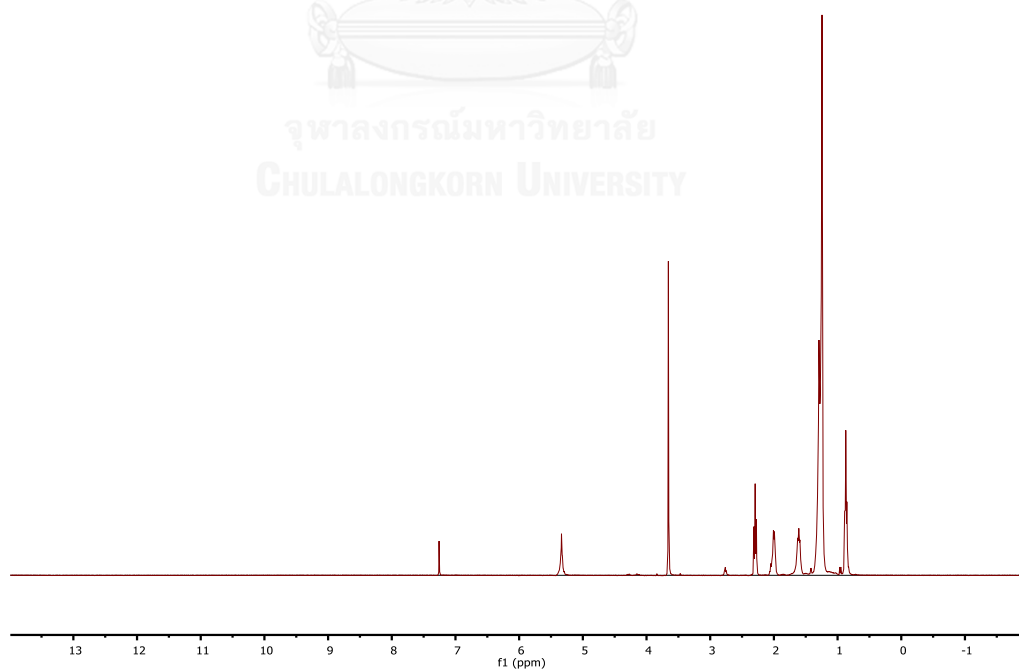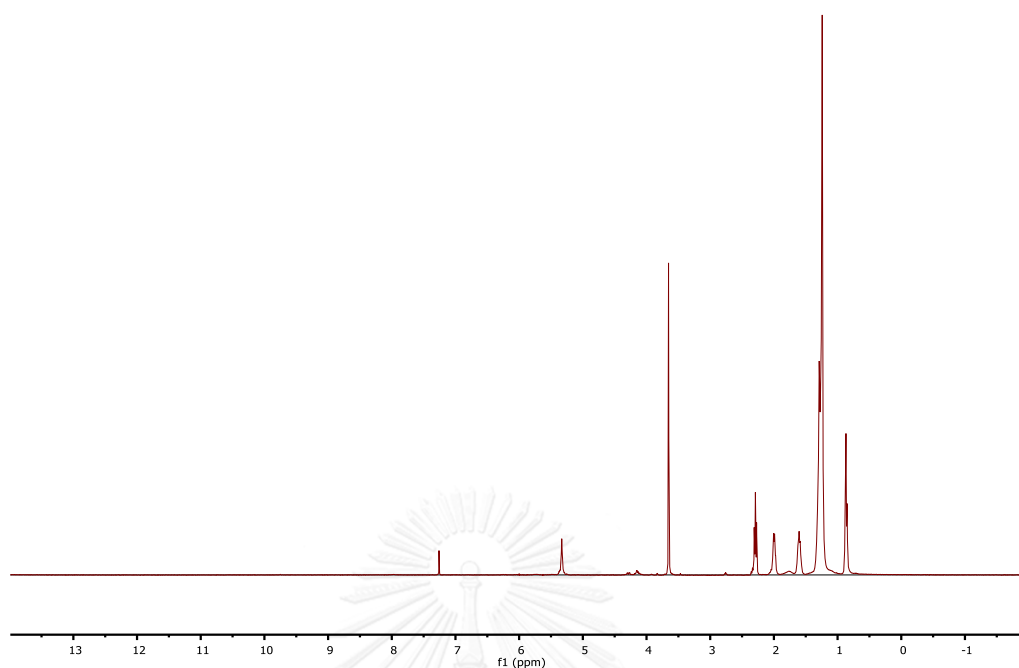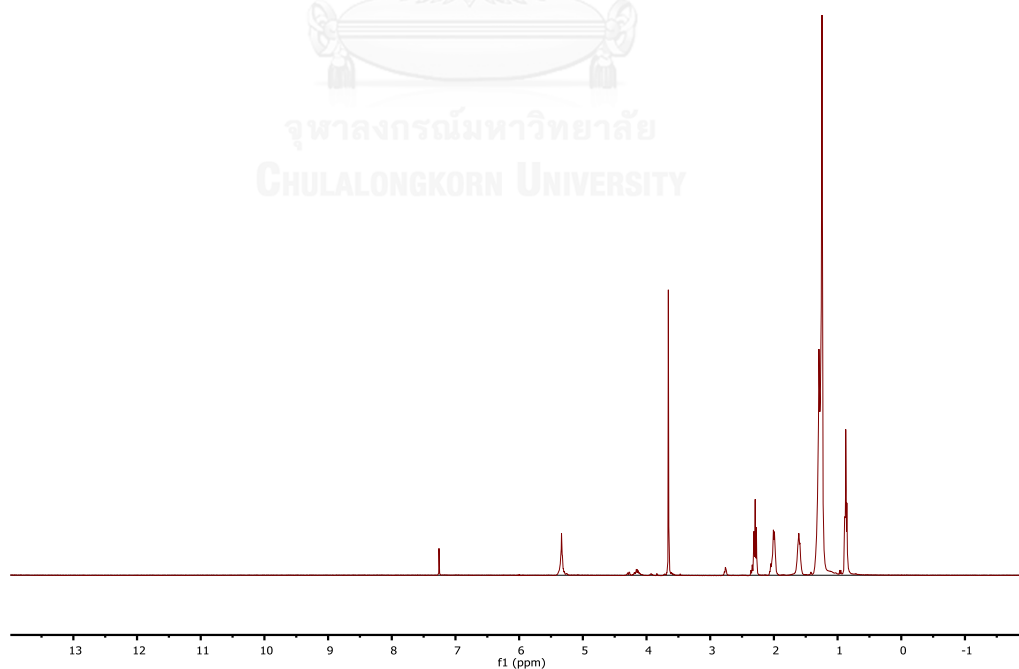**Appendix B: Biodiesel production.**

Table B-1 The percent conversion of methyl ester at various reaction times.

Time (h.)	% Conversion			
	First	Second	Third	Average
1	66.05	67.52	66.83	66.80
2	86.67	87.92	87.09	87.23
3	98.78	97.94	97.55	98.09
4	99.03	99.57	98.69	99.10
5	99.15	99.12	99.78	99.35

Table B-2 The percent conversion of methyl ester at various mole ratios of oil to methanol.

Oil:Methanol	% Conversion			
	First	Second	Third	Average
1:3	55.95	57.84	58.61	57.47
1:6	80.69	78.83	79.67	79.67
1:9	98.20	97.44	97.82	97.82
1:12	97.16	97.94	97.55	97.55
1:15	97.27	96.24	98.36	97.29

Table B-3 The percent conversion of methyl ester at various the amount of catalyst.

wt.% catalyst	% Conversion			
	First	Second	Third	Average
1	47.09	46.52	47.16	46.92
2	96.14	82.9	91.05	90.03
3	99.81	97.48	97.78	98.36
4	98.75	98.27	97.46	98.16
5	97.59	99.01	98.68	98.43

Table B-4 The percent conversion of methyl ester for reusability.

Reuse	% Conversion			
	First	Second	Third	Average
1	97.69	97.47	98.31	97.82
2	94.18	98.04	96.67	96.29
3	91.56	96.99	94.29	94.28
4	86.22	84.69	86.47	85.79
5	71.68	69.73	70.51	70.64

Table B-5 The basicity of catalyst at various the weight percentage of CaO.

Catalyst	Basicity (mmol/g)			
	First	Second	Third	Average
10wt.%CaO/5wt%SiO$_2$	1.54	2.35	2.36	2.08
20wt.%CaO/5wt%SiO$_2$	3.97	4.25	3.90	4.05
30wt.%CaO/5wt%SiO$_2$	7.20	8.88	8.70	8.30
40wt.%CaO/5wt%SiO$_2$	9.11	9.27	8.24	8.87

Table B-6 Acid value of palm biodiesel.

$$\text{Acid value} = \frac{(A-B) \times N \times 56.1}{W}$$

Sample	Wt. of sample (g)	Titrant vol. of sample, A (ml)	Titrant vol. of blank, B (ml)	Acid value (mg KOH/g)
Palm biodiesel (1)	2.0178	0.42	0.10	0.44
Palm biodiesel (2)	2.0062	0.40	0.10	0.42
Average				0.43

*N = 0.05

VITA

Miss Apichaya Thiangtrong was born on 25th October, 1990 in Prachuapkhirikhan, Thailand. She graduated from Prachuapwittayalai School, Prachuapkhirikhan in 2009. She received a Bachelor degree of Science in Chemistry, Chulalongkorn University in 2012. She continued her Master degree in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2013 and graduated in 2016.

Presentation

9-11 February 2016 Poster presentation " Preparation of calcium oxide supported rice husk silica as catalyst for biodiesel production" The 2016 Pure and Applied Chemistry International Conference (PACCON 2016) at Bangkok International Trade & Exhibition Centre (BITECH), Bangkok, Thailand.