รายงานการวิจัยฉบับสมบูรณ์

ปัจจัยของตัวรองรับที่มีผลต่อปฏิกิริยาไฮโดรจีเนชันแบบบางส่วนของเมทิลเอสเทอร์ชนิดไม่อิ่มตัวเชิงซ้อนเพื่อปรับปรุงคุณภาพน้ำมันไบโอดีเซล

Effect of Type of Support on Partial Hydrogenation of Poly-unsaturated Fatty Acid Methyl Esters for Biodiesel Upgrading

นางสาวณัฐธิดา นุ่มวงศ์

ได้รับทุนสนับสนุนงานวิจัยจากงบประมาณเงินรายได้ ประจำปีงบประมาณ พ.ศ. 2560
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สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

ชื่อโครงการ ปัจจัยของตัวรองรับที่มีผลต่อปฏิกิริยาไฮโดรจีเนชันแบบบางส่วนของเมทิลเอสเทอร์ชนิดไม่อิ่มตัวเชิงซ้อนเพื่อปรับปรุงคุณภาพน้ำมันไบโอดีเซล

แหล่งเงิน แหล่งเงินรายได้

ประจำปีงบประมาณ 2560 จำนวนที่ได้รับการสนับสนุน 50,000.00 บาท

ชื่อ-สกุล หัวหน้าโครงการ และผู้ร่วมโครงการวิจัย พร้อมระบุ หน่วยงานต้นสังกัด

ดร. ณัฐธิดา นุ่มวงศ์ ภาควิชาเคมี คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

บทคัดย่อ

งานวิจัยนี้ได้ทำการพัฒนาความเสถียรต่อการออกซิเดชันของน้ำมันไบโอดีเซลในเตาปฏิกรณ์แบบกะด้วยปฏิกิริยาไฮโดรจีเนชันแบบบางส่วนของเมทิลเอสเทอร์ชนิดไม่อิ่มตัวเชิงซ้อน โดยใช้ตัวเร่งปฏิกิริยา Pd บนตัวรองรับอะลูมินา (Al_2O_3) ซิลิกา (SiO_2) และ MCM-41 เพื่อศึกษาผลของตัวรองรับต่อความสามารถในการทำปฏิกิริยาไฮโดรจีเนชันแบบบางส่วน ผลการทดลองพบว่าพื้นที่ผิวของตัวรองรับส่งผลอย่างมากต่อความสามารถในการเกิดปฏิกิริยา โดยที่ตัวเร่งปฏิกิริยา 0.5 wt.% Pd/MCM-41 ให้ความจำเพาะต่อสารประกอบ cis-C18:1 สูงที่สุด เนื่องจากอนุภาคของ Pd บนตัวรองรับ MCM-41 นี้มีขนาดเล็กและมีการกระจายตัวบนตัวรองรับที่ดี ด้วยขนาดอนุภาคของ Pd ที่เล็กนั้นทำให้การดูดซับของสารประกอบ C18:1 บนพื้นผิวของ Pd ลดลง ส่งผลให้สารประกอบ cis-C18:1 ไม่สามารถเกิดปฏิกิริยาไฮโดรจีเนชันและจัดเรียงตัวใหม่เป็นสารประกอบ trans-C18:1 ได้

คำสำคัญ: ความเสถียรต่อการออกซิเดชัน น้ำมันไบโอดีเซล ปฏิกิริยาไฮโดรจีเนชันแบบบางส่วน ตัวเร่งปฏิกิริยา Pd

Research Title: Effect of type of support on partial hydrogenation of polyunsaturated fatty acid methyl esters for biodiesel upgrading

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Faculty: Science **Department:** Chemistry

Abstract

In this study, the improvement of soybean biodiesel oxidative stability by partial hydrogenation of polyunsaturated fatty acid methyl ester (FAMEs) was investigated in a batch reactor. The Pd supported on: alumina (Al_2O_3), silica (SiO_2), and MCM-41 were used as catalysts. The effect of Pd support on selective partial hydrogenation activity was studied. The result showed that surface area of support had a significant effect on the partial hydrogenation activity. The 0.5 wt.% Pd/MCM-41 exhibited the highest selectivity of cis-C18:1 due to smaller Pd particle size and higher Pd dispersion on the high surface MCM-41 support. Again, small Pd particle size provided limited surface for the adsorption of C18:1 and hence low possibility in hydrogenation and isomerization of cis-C18:1 to C18:0 and trans-C18:1, respectively.

Keywords: biodiesel, cold flow properties, partial hydrogenation, Pd catalysts, oxidative stability

กิตติกรรมประกาศ

โครงการวิจัยนี้สามารถสำเร็จลุล่วงได้เป็นอย่างดี โดยได้รับทุนสนับสนุนการวิจัยจากสถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง งบประมาณเงินรายได้ ประจำปีงบประมาณ พ.ศ. 2560 และความอนุเคราะห์เครื่องมือในการทดลองจาก ศาสตราจารย์ ดร. อาภาณี เหลืองนฤมิตชัย วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย

ณัฐธิดา นุ่มวงศ์

สารบัญ

สารบัญ (ต่อ)

สารบัญตาราง

ตารางที่ **หน้า**

สารบัญภาพ

ภาพที่ **หน้า**

Chapter 1

Introduction

1.1 Motivation

At the present, there are an increasing demand of fossil fuel. Therefore, many researchers are thinking about alternative energy, such as fuel from biomass, fuel from the water, and fuel from hydrogen, etc.

Biodiesel is one of an alternatived energy or fatty acid methyl esters (FAMEs) alternatively used as diesel fuel. It is produced from renewable resources, such as vegetable oil, animal fat, or algae. The reaction between triglyceride, the main component in vegetable oil with alcohol is called transesterification reaction. Methanol is commonly used in this reaction because of its low price and availability. The major product and by-product is fatty acid methyl ester and glycerol, respectively.

Biodiesel is biodegradable, environmentally friendly, renewability, non-toxic, low emission profiles, and higher cetane number as compared to petroleum based diesel. However, the direct use of biodiesel in diesel engine can lead to many problems such as the composition of diesel engine, which is made from rubber, may be dissolved in biodiesel [1,2].

Generally, biodiesel consists of saturated, mono-unsaturated, di-unsaturated, and tri-unsaturated FAMEs. The FAMEs composition depends on type of starting vegetable oil, which provides the differences in chemical and physical properties of biodiesel fuels [3]. The unsaturated contents have strong effect on the quality of biodiesel especially oxidative stability. The higher number of unsaturated composition the lower the oxidative stability. In contrast, the higher the saturated fatty acid composition, the worse the cold flow properties becomes [4]. Therefore, we need to optimize between the oxidative stability and cold flow properties by increasing the amount of methyl oleate (C18:1) and methyl palmitoleate (C16:1). Thus, partial hydrogenation of polyunsaturated FAMEs (C18:2 and C18:3) to monounsaturated FAMEs (C18:1) is a promising way to improve the oxidative stability and the cold flow properties of biodiesel [5].

In this research, biodiesel was synthesized from soybean oil, which contains high amount of polyunsaturated fatty acids. The quality of soybean oil derived biodiesel was improved by partial hydrogenation reaction using supported Pd catalysts in batch reactor. The effect of supports: α-Al_2O_3, SiO_2, and MCM-41 on the catalytic activity was studied. In addition, the effect of Pd particle size was also investigated to improve selectivity towards *cis*-isomer.

1.2 Objectives

1) To improve the oxidative stability of soybean oil derived-biodiesel by partial hydrogenation using supported Pd catalysts.
2) To understand the effect of support: α-Al_2O_3, SiO_2, and MCM-41 on partial hydrogenation activity and *cis-trans* isomerization selectivity of catalysts.

1.3 Scope of study

The scopes of this project are as follows:

1) Biodiesel synthesis by transesterification of soybean oil.
2) Catalyst preparation by incipient wetness impregnation of palladium on supports: α-Al_2O_3, SiO_2, and MCM-41.
3) Characterization of catalysts by X-Ray Diffraction Spectroscopy (XRD), Temperature Programmed Reduction (TPR), Nitrogen Adsorption, and Thermogravimetric Analysis (TGA)
4) Partial hydrogenation reaction of polyunsaturated FAMEs in batch reactor.
5) Analysis of biodiesel feed and products by Gas Chromatography with Flame Ionization Detector (GC-FID): HP-88 Column
6) Biodiesel feed and product properties testing especially oxidative stability and cold flow properties.

1.4 Expected results

It is expected that this study could provide the techniques and catalysts for improving properties of biodiesel, such as oxidative stability, pour point, and cloud point. Moreover, the knowledge obtained from this study can be applied in diesel and biodiesel field.

Chapter 2

Theory and Literature Reviews

2.1 VEGETABLE OIL

A vegetable oil is a triglyceride, which is extracted from various parts of plants. Normally, oils are liquid at room temperature, fats are solid and a dense brittle fat is called wax. Although many parts of plants may yield oil, in commercial practice, oil is extracted primarily from seeds of oilseed plants. In addition, there are several types of vegetable oils, such as coconut oil, corn oil, cottonseed oil, olive oil, rapeseed oil, etc. Uses of vegetable oil such as, prevent sticky lids, treat the hair, clean the pearls, remove paint from hands, etc. [6].

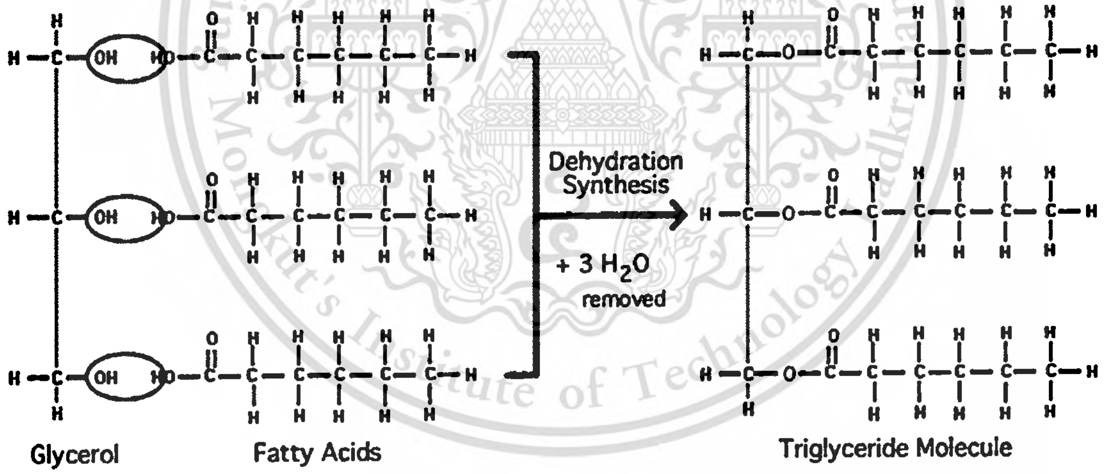


Figure 2.1 Formation of triglyceride [7].

As shown in Figure 2.1, a triglyceride is an ester, which is formed by combining glycerol with three fatty acid molecules. A glycerol molecule has three hydroxyl (-OH) groups. Each fatty acid has carboxyl (-COOH) group [8]. This reaction transforms the hydroxyl group and hydrogen atom of fatty acid into the water. Dehydration of glycerol and three fatty acids produces triglyceride, and three water molecules are removed. The fatty acid, which become triglyceride, may be the same type or different type of fatty acid. In addition, fatty acids vary in their carbon chain length and the number of double bonds. Therefore, this reason leads to the different characteristics of vegetable oil.

The common fatty acids found in vegetable oils are palmitic, stearic, oleic, linoleic and linolenic [9]. In addition, the fatty acid is a carboxylic acid, which have aliphatic type long carbon chain. This long carbon chain is either saturated or unsaturated fatty acid. However, the fatty acid has at least eight carbon atoms. Most naturally occurring fatty acids have a chain of an even number of carbon atoms, from 12 to 28 [10]. Names and descriptions of some common fatty acids are shown in Table 2.1. Fatty acid compositions of vegetable oils are shown in Table 2.2. Properties of vegetable oils are shown in Table 2.3.

Table 2.1 Chemical names and descriptions of some common fatty acids [11].

Chemical Names and Descriptions of some Common Fatty Acids				
Common Name	Carbon Atoms	Double Bonds	Scientific Name	Source
Butyric Acid	4	0	butanoic acid	butterfat
Caproic Acid	6	0	hexanoic acid	butterfat
Caprylic Acid	8	0	octanoic acid	coconut oil
Capric Acid	10	0	decanoic acid	coconut oil
Lauric Acid	12	0	dodecanoic acid	coconut oil
Myristic Acid	14	0	tetradecanoic acid	palm kernel oil
Palmitic Acid	16	0	hexadecanoic acid	palm oil
Palmitoleic Acid	16	1	9-hexadecanoic acid	animal fats
Stearic Acid	18	0	octadecanoic acid	animal fats
Oleic Acid	18	1	9-octadecanoic acid	olive oil
Ricinoleic Acid	18	1	12-hydroxyl-9-octadecenoic acid	castor oil
Vaccenic Acid	18	1	11-octadecenoic acid	butterfat
Linoleic Acid	18	2	9,12-octadecadienoic acid	grape seed oil
Alpha-Linolenic Acid	18	3	9,12,15-octadecatrienoic acid	flaxseed (linseed) oil
Gamma-Linoleic Acid	18	3	6,9,12-octadecadienoic acid	borage oil

Table 2.2 Fatty acid compositions of vegetable oils [12].

Vegetable oil	Fatty acid composition (% weight)								
	16:1	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.60	0.48
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00
Crambe	20.7	0.70	2.09	0.80	1.12	18.86	58.51	9.00	6.85
Peanut	11.38	2.39	1.32	2052	1.23	48.28	0.00	31.95	0.93
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.4	0.00	22.30	8.23
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00
Castor	0.00	0.00	0.00	0.00	0.00	87.0	0.00	0.00	11.2
Palm	10.2	3.7	0.00	0.00	0.00	22.8	0.00	53.7	8.6

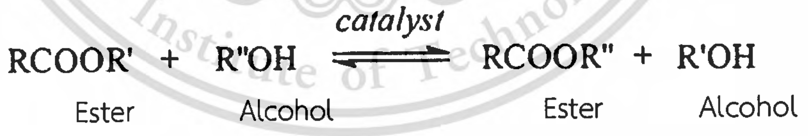
Table 2.3 Properties of vegetable oils [13].

Vegetables	Kinematic viscosity at 40°C (cSt)	Flash point (°C) (ASTM, 1995a)	Specific gravity (ASTM, 1995c)	Iodine value (mg KOH g^{-1}) (AOAC,1	Saponification value (mg KOH g^{-1}) (AOAC,1997)	Acid value (mg KOH g^{-1})	Ash content (%) (ASTM, 1995b)
Soybeans	32.60	254	0.9138	112.5	189-195	-	<0.010
Tobacco	27.70	220	0.9175	135.0	193	-	0.008
Rapeseed	37.00	246	0.9115	130.0	168-181	-	0.054
Parinari (ASH)	25.74	228	0.8390	80.7	118	2.620	0.006
Parinari (NHS)	46.85	234	0.8970	168.5	246	2.244	0.038
European standard for automotive diesel fuel	2-4.50	56 (min)	0.820-0.845	120.0	-	/	0.010 (max)

2.2 TRANSESTERIFICATION OF VEGETABLE OIL

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety [28]. A general equation of transesterification reaction is shown in Figure 2.2. The transesterification is an equilibrium reaction, and the transformation occurs essentially by mixing the reactants [14]. This reaction is often catalyzed by the addition of an acid or base catalyst [15]. The catalyst is usually used to improve the reaction rate and yield. In addition, the presence of a catalyst, which is typically a strong acid or base acceralates considerably the adjustment of the equilibrium [14].

The alcohols, which are used in transesterification reaction are methanol, ethanol, propanol, buthanol and amyl alcohol. However, methanol and ethanol are most frequently used, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol) [9]. The alcohol/vegetable oil molar ratio is one of the main factors that influences the transesterification. However, an excess of the alcohol favors the formation of the products. Therefore, the ideal alcohol/oil ratio has to be established empirically, considering each individual process [14].



$$\underset{\text{Ester}}{RCOOR'} + \underset{\text{Alcohol}}{R''OH} \xrightleftharpoons{\textit{catalyst}} \underset{\text{Ester}}{RCOOR''} + \underset{\text{Alcohol}}{R'OH}$$

Figure 2.2 General equation of a transesterification reaction [14].

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base producing a mixture of fatty acids alkyl esters (FAAEs) and glycerol as shown in Figure 2.3. The overall process is a reversible reaction, in which diglycerides and monoglycerides are formed as intermediates. The stoichiometric reaction requires 1 mole of a triglyceride and 3 moles of alcohol.

However, the excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed [14].

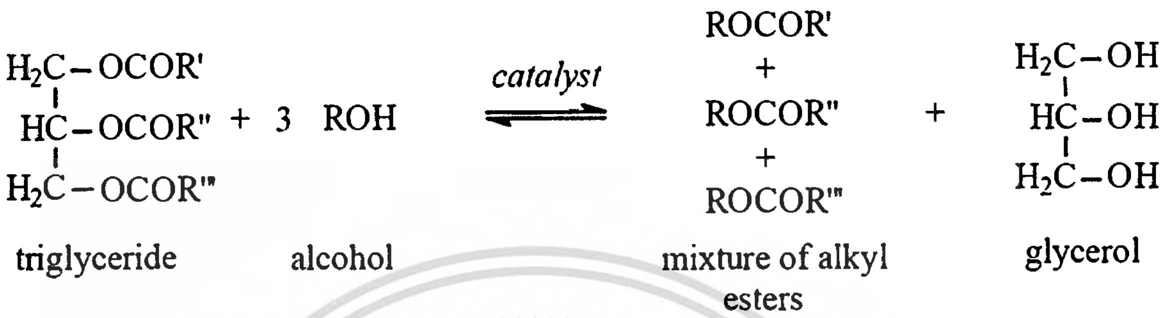


Figure 2.3 Transesterification of vegetable oils [14].

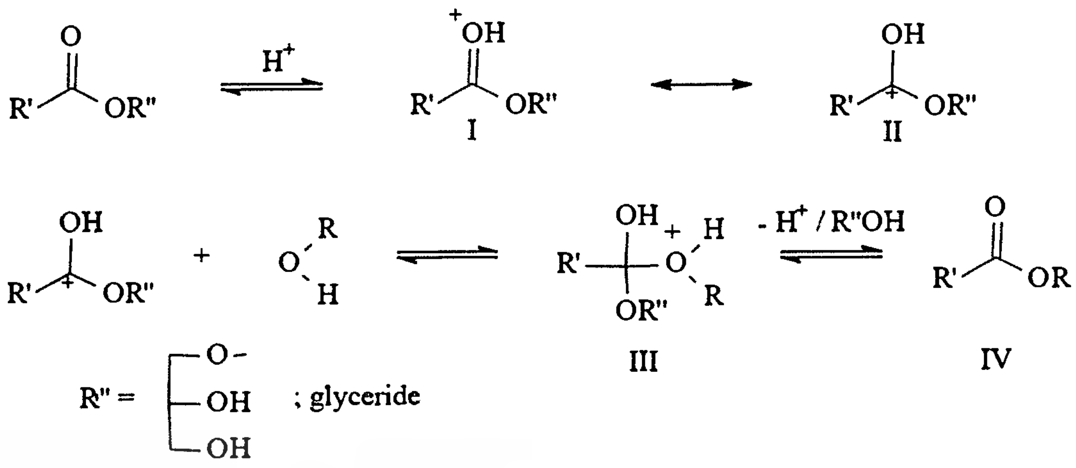
Transesterification is the most popular way to transform vegetable oils or animal fats into biofuels. This reaction can be catalyzed by acid or base catalysts. However, base catalysts provide higher reaction rates, whereas acid catalysts are preferred when significant amounts of impurities are present in the reactants [16]. The catalyst in transesterification can be divided in two types; homogeneous and heterogeneous catalyst. At the present, homogeneous catalyst is commonly used in commercial biodiesel production because it provides high conversion and short reaction time. Catalysts in transesterification are as follows:

1. Homogeneous Catalyst

The homogeneous catalyst can be divided in two types as follows:

1.1 Homogeneous Acid Catalyst

The transesterification process is catalyzed by Bronsted acids, especially by sulfonic and sulfuric acid [14]. These catalysts provide very high yields in alkyl esters, but acid-catalyst reaction requires higher temperature and pressure as well as higher amount of alcohol. In addition, the reaction rate is very slow, and it takes more than 3 h. The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 2.4.



R' = carbon chain of the fatty acid
R = alkyl group of the alcohol

Figure 2.4 The pathway of the acid-catalyzed transesterification of vegetable oils [14].

Figure 2.4 is the mechanism for monoglyceride. However, it can be extended to diglycerides and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation (II). After a nucleophilic attack of the alcohol, it produces the tetrahedral intermediate (III), which eliminates glycerol to form the new ester (IV), and to regenerate the catalyst H^+. In addition, carboxylic acids can be formed by reaction of the carbocation (II) with water present in the reaction mixture. Therefore, it should avoid the competitive formation of carboxylic acids, which reduce the yields of alkyl esters [14].

1.2 Homogeneous Base Catalyst

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. In addition, alkaline catalysts are less corrosives than acidic compounds. Therefore, the industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates [14]. The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Figure 2.5.

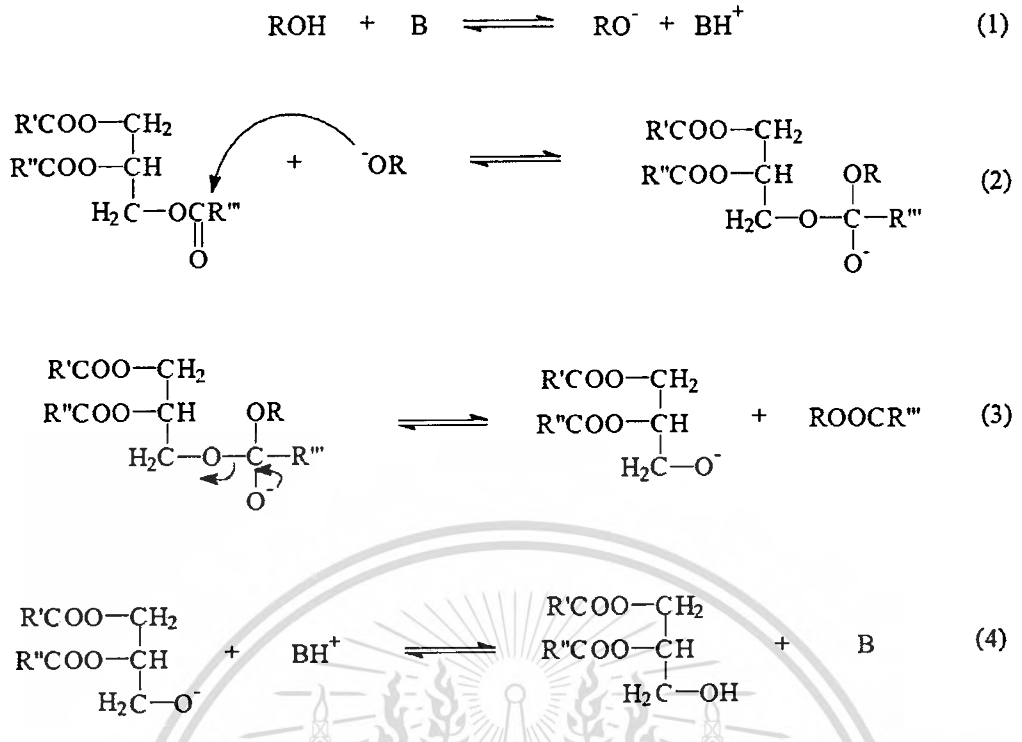


Figure 2.5 The mechanism of the base-catalyzed transesterification of vegetable oils [14].

As shown in Figure 2.5, the first step (Eq. 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, therefore regenerating the active species (Eq. 4), which is able to react with a second molecule of the alcohol. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol [14].

2. Heterogeneous Catalyst

At the present, the heterogeneous catalyst is widely used as a catalyst for transesterification because it is easily to separate the catalyst from the products. In addition, the heterogeneous catalyst provides high yield of biodiesel and no waste from washing step.

2.3 BIODIESEL

At the present, the diesel fuel is gradually consumed by many people in the world, and this problem may be soon the crisis. Therefore, many researchers are thinking about alternative and renewable energy. The alternative energy encompasses all energy that do not consume fossil fuel. It is widely available and environment friendly, such as wind energy, solar energy, nuclear energy, etc [17]. Biodiesel is one of alternative energy. It is an alternative diesel fuel, which has similar combustion properties as petroleum diesel fuel.

Biodiesel is monoalkyl esters of long chain fatty acids derived from renewable feedstock, such as vegetable oils or animal fats. Biodiesel is usually produced by transesterification reaction of triglyceride, which is the main component in oils with a low molecular weight alcohol and called fatty acid alkyl esters (FAAEs) [9]. There are many advantages of biodiesel. For example, it causes less pollution than petroleum diesel, it has a high cetane number of above 100, compared to only 40 for petroleum diesel fuel, it is biodegradable and non-toxic. Although there are a lot of advantages, biodiesel presents some drawbacks. For example, it is not suitable for use in low temperatures, it causes to clog in engine because the dirt of biodiesel is collected in fuel filter, it can harm rubber hoses in some engines [18]. The use of biodiesel can extend the life of diesel engines because it is more lubricating and power output is relatively unaffected by biodiesel.

The properties of biodiesel and diesel fuel are compared and shown in Table2.4. In this table, biodiesel specifications and test methods are according to American Society for Testing and Materials (ASTM). In addition, there are some properties of biodiesel, such as oxidative stability and cold flow properties. These properties strongly depend on the natural characteristics of the starting vegetable oil. Different types of vegetable oil have different chemical structures: chain length, branching of the chain, and especially degree of unsaturated compounds [19]. Biodiesel produced from vegetable oil, which contains high amount of saturated fatty acid has better oxidative stability. However, the higher amount of saturated fatty acid provides the worse cold flow properties [9]. Therefore, a promising way, which solve this problem is partial hydrogenation. The main objective of partial hydrogenation is to saturate the polyunsaturated FAMEs (C18:3 and C18:2) to the monounsaturated

(C18:1), in order to obtain biodiesel product with relatively high oxidative stability and good cold flow properties [9].

Table 2.4 Properties of biodiesel [20].

Test Property	ASTM Method no.	#2 Ref Diesel fuel	Methyl Soyate (Biodiesel)
Viscosity @ 40 °C (cSt)	D-445	2.39	4.08
Specific gravity @ 15.6 °C	-	0.847	0.884
Higher heating value (MJ/KG)	D-240	45.2	39.8
Cetane no.	D-613	45.8	46.2
Distillation 90% °C	D-86	296	342
Pour point (°C)	D-97	-23	-1
Cloud point (°C)	D-2500	-19	2
Flash point (°C)	D-93	78	141
Sulfer (%mass)	D-129	0.25	0.01
Corrosion	D-130	1-a	1-a
Ash (%mass)	D-482	0.025	<0.01
Color (ASTM color code)	D-1500	L2.0	L2.0

2.4 Heterogeneous catalyst for partial hydrogenation of polyunsaturated FAMEs

In general, the catalyst employed in the partial hydrogenation of polyunsaturated FAMEs is the catalyst for hydrogenation of fats and oils such as Ni, Cu, and noble metals. The catalyst used in commercial hydrogenation of fats and oils is usually Ni catalyst supported on silica or alumina [9]. Nickel (Ni) is used as a catalyst due to its low cost. However, it requires a higher reaction temperature and gives lower activity as compared to the other noble metals. Instead of using Ni, many researchers report that the most common noble metals such as platinum (Pt) and palladium (Pd) have been used in several reactions, including partial hydrogenation [19]. The different metals exhibit different catalytic activity as well as cis–trans isomerization selectivity. Therefore, the type of metal has considerable influence on the hydrogenation of vegetable oil [21].

Many researchers have been studied the effect of supports especially its acidity. Materials usually used as a catalyst support are: carbon, silica, alumina, and zeolite. However, silica (SiO_2) seems to be the most popular one. There are many advantages of SiO_2 such as: greater specific surface area and pore volume, which simplifies the adsorption and dispersion of the noble metal via impregnation method [19]. Due to the difference in nature and structure of each support, the type of support is believed to affect catalytic activity and selectivity of the catalyst. In addition, the same support with different pore size also affects the rate and selectivity of the reaction [22]. There are several studies, which have been done on the hydrogenation of vegetable oil to increase its shelf life by improving its oxidative and thermal stability.

In 2012, Bruno S. Souza and co-workers [23] studied the catalytic activity of highly active supported palladium (Pd) nanoparticles in imidazolium-based ionic liquid in partial hydrogenation of biodiesel. However, the drawback commonly observed on hydrogenating partially polyunsaturated olefins is the conversion of cis- into the more thermodynamically favored trans-double bonds. In the case of biodiesel, the side isomerization of oleic into elaidic chains (18 carbons with one trans-double bond) is particularly undesirable due to the lower crystallization point of the trans-isomers when compared with those of cis, which also compromises the cold flow properties of the fuel

In order to increase formation of the cis-monounsaturated FAMEs, they further investigated the effects of temperature and pressure on the hydrogenation of biodiesel. According to the result of their study, at 27°C and 10 atm of hydrogen, at 27°C and 30 atm of hydrogen, at 27°C and 75 atm of hydrogen, at 27°C and 110 atm of hydrogen using their catalyst leads to a high content of cis-C18:1 and low content of trans-C18:1 [23].

In 2014, Hajime Iida and co-workers [24] studied the effect of support materials on trans-fatty acid levels by hydrogenation of soybean oil using different supports and platinum (Pt) as a metal. The supports are: activated carbon, ZrO_2, Al_2O_3, SiO_2 (Q-6, MCM-41, SBA-15), TiO_2, CeO_2, MgO, $BaSO_4$, CaO, and MoO_3. In general, the chemical and physical properties of the hydrogenated oils are influenced by the degree of unsaturation and the cis–trans isomerization of fatty acids. The aim of their work is to reduce trans-fatty acid (TFA) formation during hydrogenation because it leads to increase risk of coronary heart disease (CHD). However, it has not been possible to produce partially hydrogenated oils with low TFA levels. According to the result of their study, there was a linear relationship between the catalytic activity and Pt dispersion of the catalysts. The Pt/$BaSO_4$ catalyst was the most effective for the reduction of trans-fatty acid and additional saturated fatty acid (ASFA) levels in hydrogenated oils at iodine value (IV) = 70 among the examined platinum catalysts [24].

In 2015, Chachchaya Thunyaratchatanon and co-workers [19] studied catalytic upgrading of soybean oil methyl esters by partial hydrogenation using Pd catalysts. The aim of their work was to upgrade oxidative stability of biodiesel by partial hydrogenation using different metals: Ni, Pd, and Pt on SiO_2 (Q30) support. Each catalyst has different characteristics in catalytic activity, selectivity, and trans-isomerization. They found that three metal types: Ni, Pd, and Pt, exhibited good partial hydrogenation of soybean oil based-biodiesel. Among the catalysts studied, Pd/SiO_2 presented the highest activity as evaluated by turnover frequency (TOF) of C18:2 conversion, while Ni/SiO_2 showed the lowest activity. The order of catalytic activity was as follows: Pd/SiO_2 > Pt/SiO_2 > Ni/SiO_2. In addition, oxidative stability of the feed biodiesel was 1.4 h since it had a large amount of polyunsaturated FAMEs. According to biodiesel standards, this feed biodiesel was below the minimum specified limit of ASTM D6751 (>3 h) and EN 14214 (>6 h), which would be considered as a low quality biodiesel. After partial hydrogenation, oxidative stability significantly increased when using Pd/SiO_2 (30.4 h) followed by Pt/SiO_2 (5 h), and Ni/SiO_2 (3.6 h), leading to an increase in the storage duration of biodiesel [19].

Chapter 3

Experimental

3.1 Chemical reagents

1. Cetyltrimethyl ammonium bromide [$C_{19}H_{33}(CH_3)_3NBr$], 99%, Acros Organic
2. 2. Sodium hydroxide anhydrous pellets ($NaOH$), 98%, Carlo Erbar
3. Fumed silica (SiO_2), Chemical Village
4. Soybean oil, Thai Vegetable Oil
5. Methanol (CH_3OH), Analytical grade, Fisher Chemical
6. *n*-Hexane (C_6H_{14})
7. Magnesium sulfate anhydrous ($MgSO_4$), Technical grade, Panreac
8. Potassium hydroxide (KOH), Analytical Reagent grade, Lab-Scan
9. Palladium (II) acetate [$Pd(CH_3COO)_2$], 98%, Aldrich
10. Pd/Al_2O_3 commercial catalyst, SCG Chemicals
11. Distilled water
12. Deionized water
13. Air, High purity (99.99%), Praxair
14. Hydrogen gas, High purity (99.99%), Praxair

3.2 Apparatus and instruments

1. 500 mL three-necked round-bottomed flask
2. Magnetic stirrer
3. Hot plate and stirrer
4. Magnetic bar
5. Thermometer
6. Condenser
7. Separatory funnel
8. Laboratory glassware
9. Laboratory plastic ware
10. Oven

11. 100 mL teflon-lined stainless steel autoclave
12. Centrifuge
13. pH-indicator strips
14. Glove box
15. Buchner funnel, Buchner flask, and vacuum pump
16. Tube furnace with programmable temperature controller
17. Batch reactor for catalytic testing
18. Gas Chromatograph with Flame Ionization Detector (GC-FID)
19. X-ray Powder Diffractometer (National Metal and Materials Technology, MTEC)
20. Thermogravimetric analyzer (Parkin-Elmer, Scientific Instrument Service Centre, KMITL)
21. N_2-Adsorption (Quantachrome Autosorb-1, Analytical and Testing Service Center, The Petroleum and Petrochemical College)
22. Temperature Program Reduction (Faculty of Science, KMITL)

3.3 EXPERIMENTAL PROCEDURE

3.3.1 Support and catalyst preparation

3.3.1.1 Synthesis of MCM-41 silica support

Mesoporous MCM-41 silica was synthesized from a gel having the following molar composition: 1.0 SiO_2: 0.15 CTAB: 0.17 Na_2O: 120 H_2O [1]. In a typical procedure Fumed silica, SiO_2 was dissolved in deionized water and NaOH at room temperature. Then, CTAB (cetyltrimethyammonium bromide) was added. The mixture as stirred at a rate of 500 rpm for 4 h at room temperature. The resulting gel was introduced into a teflon-lined stainless steel autoclave and was heated at 100°C for 48 h. After that, the precipitate was then washed with deionized water using centrifuge at 5,000 rpm for 10 min until the pH was 7 and dried in an oven at 90°C overnight. Finally, the organic material was removed by calcination in a horizontal tube furnace under a flow of air (60 mL/min) at 550°C for 6 h with a heating rate of 1°C/min.

3.3.1.2 Preparation of supported Pd catalysts

The 0.5 wt.% Pd supported on different type of supports (SiO_2 and MCM-41) were prepared by incipient wetness impregnation using palladium (II) acetate [$Pd(CH_3COO)_2$] solution as a metal precursor. After that, the impregnated catalyst was dried in an oven at 90°C for 12 h and calcined in a horizontal tube furnace under 60 mL/min of an oxygen stream at 400°C for 2 h with a heating rate of 1°C/min. Finally, the catalyst was reduced at 300°C for 2 h with a heating rate of 5°C/min and 100 mL/min hydrogen flow rate. Pd/Al_2O_3 is a commercial catalyst obtained from SCG Chemicals Co., Ltd.

3.3.2 Support and catalyst characterization

Some characterization techniques were used to characterize the prepared catalysts such as X-ray Powder Diffraction (XRD), Thermo gravimetric analysis (TGA), Nitrogen Adsorption Analysis, Temperature Programmed Reduction (TPR), and Temperature Programmed Desorption (TPD).

3.3.2.1 X-ray powder diffraction (XRD) technique

The crystalline phase and structure of the synthesized MCM-41 can be identified using XRD measurement. Analysis was done by applying Bruker diffractometer (Cu Kα radiation, 40 kV, 30 mA) covering the range of 2θ = 1.5-10° at the rate 1°/min, and a scanning rate of 0.02°/step.

3.3.2.2 Thermogravimetric analysis (TGA)

Phase transformation upon the heating treatment is a convenient method to study the organic template decomposition of the sample. The sample were grinded in mortar to homogeneous fine particle. Then, approximately 10 mg of the sample was weighed into a pan to carry out a TGA under 40 mL/min of nitrogen atmosphere. The temperature was scanned from 50 to 900°C with heating rate of 10°C /min.

3.3.2.3 Nitrogen adsorption analysis

Surface area, pore volume and pore size of the catalyst can be determined by Quantachrome Autosorb-1 surface area analyzer. The sample was prepared by weighing approximately 40-50 mg of sample and loaded into a cleaned and dried sample cell. After that, the sample was degassed at the out-gas station at 300°C. The sample cell was then removed from the out-gassing station after nitrogen was filled and was attached to the analysis station. Then, the specific surface area, pore volume, and pore size of the catalyst, were calculated by the software.

3.3.2.4 Temperature programmed reduction (TPR)

Temperature-programmed reduction (TPR) provides information on the active site species of the catalysts. The sample weighed 100 mg was placed into a quartz tube reactor, which was located inside a temperature-regulated furnace. Sample was heated to its activations temperature in air zero (30 mL/min) for 1 h with 1°C/min and was cooled down to below 40°C. The heating rate of 10°C/min, and 30 mL/min of 10% H_2 in Ar was applied for TPR analysis. Water production during the reduction process was removed in a U-shape glass trap at -95°C (slush baths of liquid Nitrogen) before entering the TCD. The signal was measured using thermal conductivity detector (TCD).

3.3.3 Transesterification of soybean oil

Fatty acid methyl esters (FAMEs) of soybean oil were prepared by a typical transesterification reaction catalyzed by potassium hydroxide (KOH). The reaction took place in a 500 mL three-necked round-bottomed flask, equipped with a stirrer and a condenser. The amount of catalyst used was 1 wt.% compared to the starting soybean oil with 9:1 methanol to oil molar ratio. First, KOH was dissolved in methanol and added into the soybean oil. Then, the mixture was stirred at 65°C for 2 h and cool down. Separatory funnel was used in a phase separation, where the lower glycerol phase was removed. The upper phase was washed with 60°C distilled water several times to remove remaining KOH, methanol, and soap. Finally, anhydrous magnesium sulfate ($MgSO_4$) was added into the soybean biodiesel fuel to remove remaining washed water.

3.3.4 Partial hydrogenation of polyunsaturated FAMEs

Partial hydrogenation of polyunsaturated FAMEs was carried out in a 300 mL stainless steel semi-batch reactor at reaction conditions of 100°C, 0.4 MPa, 500 rpm stirring rate, 150 mL/min hydrogen flow rate, which controlled by mass flow controller. First, 1.304 g of supported Pd catalyst and 150 mL of prepared biodiesel were placed into the reactor. Then, the system was purged with hydrogen two times to remove the remaining air. The product samples were collected every 1 h. The total reaction time was 4 h.

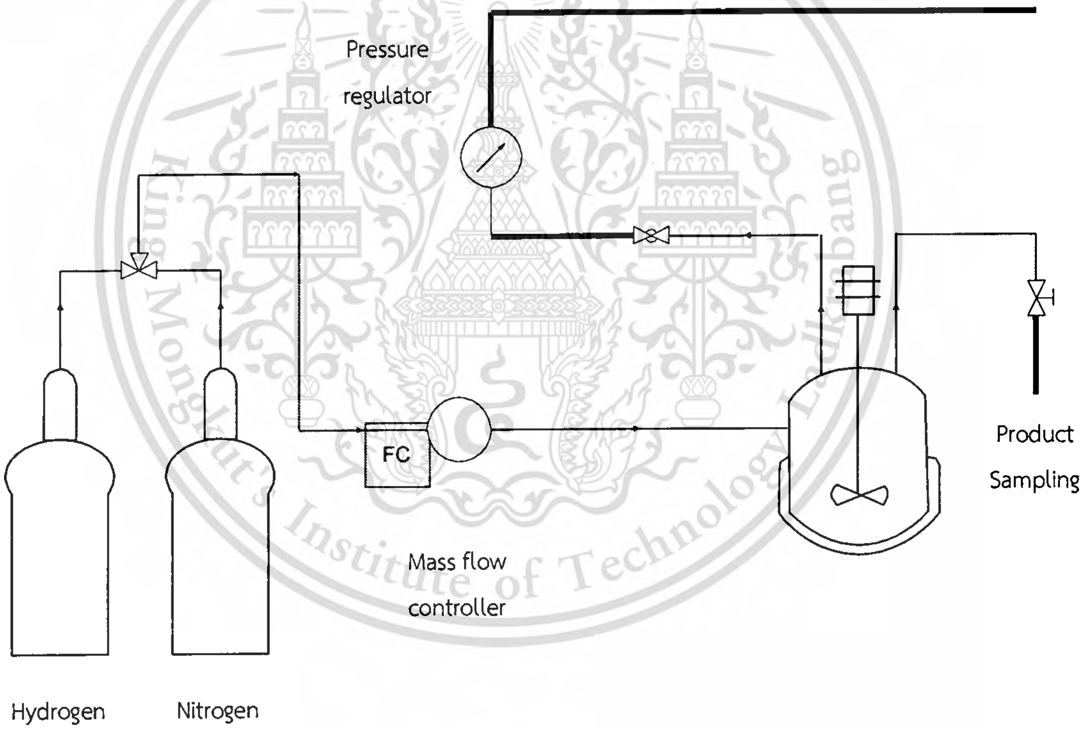


Figure 3.1 Process flow diagram of partial hydrogenation in batch reactor.

3.3.5 Biodiesel analysis

Biodiesel before and after partial hydrogenation reaction were analyzed by some techniques such as, Gas Chromatography (GC), oxidative stability testing, and cold flow properties testing.

3.3.5.1 Chromatography

FAMEs composition was detected by Hewlett Packard gas chromatograph 6890N flame ionization detector (GC-FID) with HP-88 (100 m x 250 µm x 0.2 µm) capillary column. Sample of 0.25 g biodiesel was dissolved in 5 mL n-hexane solvent. GC conditions are the followings: sample injected 1 µL, the helium carrier gas flow rate 2.4 mL/min, an injector temperature was 200°C with a split ratio 75:1, and a detector temperature was 230°C. The oven temperature was held at 155°C for 20 min, then heated up to 230°C at rate of 2°C/min and hold for 2.5 min. The total running time was 60 min. The products were identified by the standard and calculated from chromatogram peak area.

3.3.5.2 Oxidative stability testing

The oxidative stability of biodiesel was tested by Rancimat. The sample was aged at 110°C under a constant air stream 10 L/min. The oxidative stability corresponds to the period of time passing before FAMEs are degraded to such an extent that the formation of volatile acids can be recorded through an increasing of conductivity. This procedure was developed according to EN 14112.

3.3.5.3 Cold flow properties testing

The cold flow properties, including cloud point of biodiesel was investigated by using a Cloud Point Tester that was developed according to ASTM D2500. The sample was poured into a test jar. Then, the entire test subject was placed in a constant temperature cooling bath. At every 1°C, the sample was taken out and inspected for cloud. The cloud point is the temperature at the milky cloud crystals first appear [29].

Chapter 4

Results and Discussions

4.1 MCM-41 AND Pd CATALYSTS CHARACTERIZATION

4.1.1 MCM-41 AND Pd CATALYSTS CHARACTERIZATION

The crystalline structures of as-prepared and calcined MCM-41 were determined by X-ray powder diffraction (XRD) technique. The sample was scanned over the angle range (2θ) from 1.5° to 10° and diffraction pattern was recorded at a step of 0.02°.

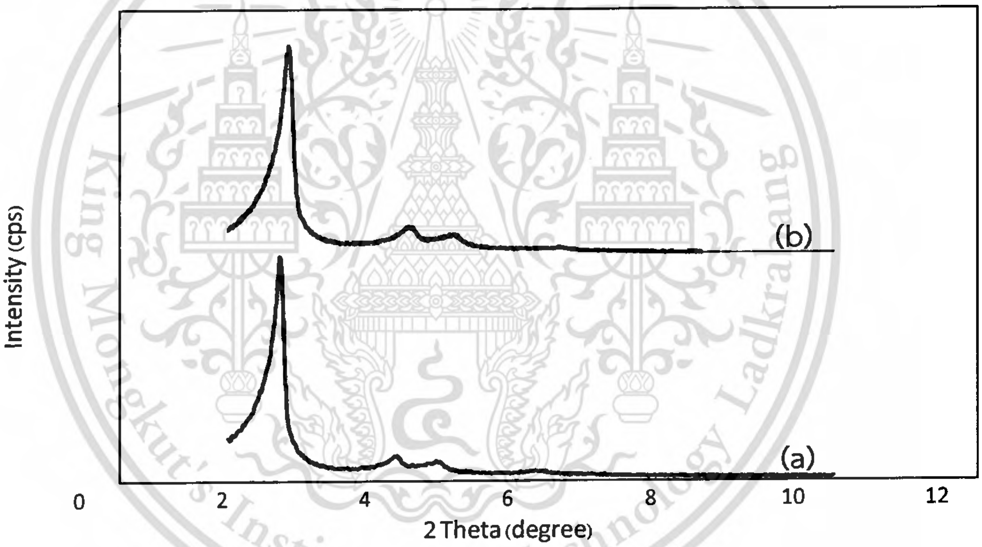


Figure 4.1 XRD patterns of (a) as-prepared and (b) calcined (under air zero at 550°C, heating rate 1°C/min) MCM-41.

The XRD patterns of the as-prepared and calcined MCM-41 are shown in Figure4.1. The ordered structure of MCM-41 gave XRD peak at 2θ of 2.40°, 3.96°, and 4.53°, which indicated hexagonal structure of crystalline MCM-41 material [25]. No difference was observed in the XRD pattern of the as-prepared and calcined MCM-41, indicating that detemplating of CTAB by calcination did not affect porous structure of the prepared MCM-41.

4.1.2 Nitrogen adsorption analysis

The specific surface area, pore volume, and pore size of the supports and catalysts were determined by N_2 gas adsorption using BET method. The surface characteristics of supports and catalysts are shown in Table 4.1.

Table 4.1 Characteristics of catalyst.

Catalyst	Surface Area (m^2/g)	Pore Size (nm)	Pore Volume (mL/g)	Pd Loading [a] (%)	Pd particle Size [b] (nm)
SiO_2	363.0 [c]	-	-	-	-
MCM-41	1160.0	3.25	0.95	-	-
0.5 wt.% Pd/Al_2O_3 (commercial)	163.1 [d]	-	-	0.50	-
0.5 wt.% Pd/SiO_2	-	-	-	0.45	3.87
0.5 wt.% Pd/MCM-41	-	-	-	0.48	1.92

[a] by H_2-TPR

[b] by TEM

[c] data from Kroegchai Matee, Chanakarn Homla-or, Preedawan Duangchan, Catalytic deoxygenation of glycerol to 1-propanol over zeolite and supported Ni catalysts in sequential bed system, Special Project, Faculty of Science, KMITL 2014

[d] data from SCG Chemical

In this research, Pd loaded on three different types of supports were studied. From Table 4.1, each support exhibits different morphology and pore structure. The first one is an Al_2O_3 support, which is a well-known acidic material. Surface area of the commercial Pd/Al$_2$O$_3$ (SCG Chemicals) is 163.1 m^2/g. The second one is amorphous silica, purchased from Chemical Village Co., Ltd with surface area of 360.0 m^2/g. In addition, MCM-41 was also interested to be used as a support. It is a mesoporous material with a hexagonal pore structure. Its attractive properties include large pore volumes, high BET surface area, high thermal stability, and high density of surface silanols. The surface area, pore size, and pore volume of the synthesized MCM-41 was 1,160.0 m^2/g, 3.25 nm, and 0.95 mL/g, respectively. The percentage of Pd loading on 0.5 wt.% Pd/Al$_2$O$_3$ (commercial), 0.5 wt.% Pd/SiO$_2$, and 0.5 wt.% Pd/MCM-41 are 0.50%, 0.45%, and 0.48%, respectively. The results are consistent with the calculated percentage of Pd loading during catalyst preparation. The Pd particle size of 0.5 wt.% Pd/SiO$_2$ and 0.5 wt.% Pd/MCM-41 are 3.87 and 1.92, , respectively.

4.1.3 Temperature program reduction (TPR)

Reducibility and H$_2$ consumption of commercial Pd/Al$_2$O$_3$, Pd/SiO$_2$ and Pd/MCM-41 catalysts were investigated by H$_2$-temperature programmed reduction technique (H$_2$-TPR).

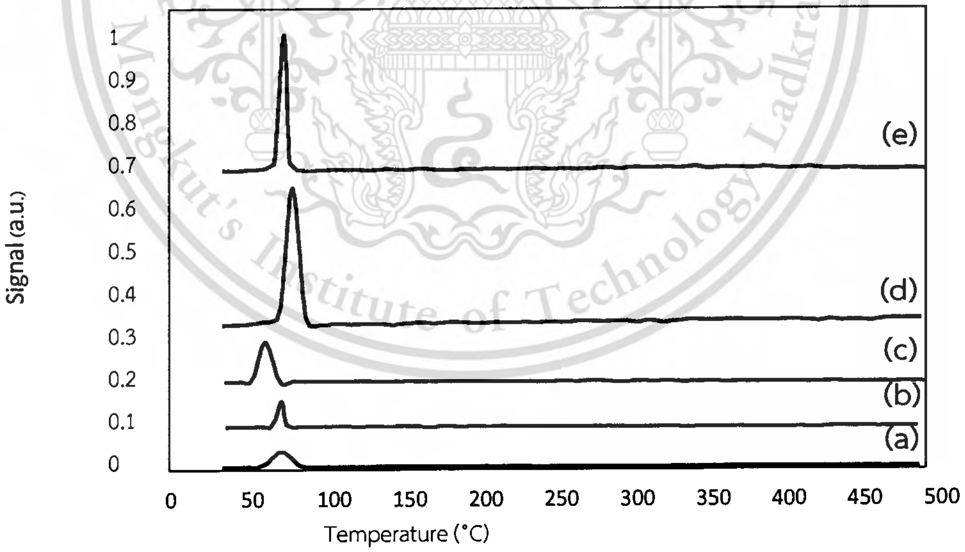


Figure 4.2 TPR profiles of (a) 0.5 wt.% Pd/Al$_2$O$_3$, (b) 0.5 wt.% Pd/SiO$_2$, (c) 0.5 wt.% Pd/MCM-41, (d) 1.0 wt.% Pd/SiO$_2$, and (e) 1.0 wt.% Pd/MCM-41 catalysts

As shown in Figure 4.2, it can be seen that the reduction of Pd^{2+} to metallic Pd (Pd^0) takes place at around 60-80°C for all catalysts. In addition, area under the reduction peak directly provides H_2 consumption for the metal reduction, and proportionally indicates the amount of Pd loading on the catalyst. The percentage of Pd loading on 0.5 wt.% commercial Pd/Al_2O_3, 0.5 wt.% Pd/SiO_2, 0.5 wt.% Pd/MCM-41, 1 wt.% Pd/SiO_2, and 1 wt.% Pd/MCM-41 are shown in Table 4.1.

4.2 CATALYTIC TESTING

4.2.1 Effect of support

In this study, Pd supported on different supports including alumina (Al_2O_3), fumed silica (SiO_2), and mesoporous MCM-41, were investigated for the partial hydrogenation of soybean oil biodiesel.

The partial hydrogenation of polyunsaturated FAMEs over 0.5 wt.% Pd/Al_2O_3, 0.5 wt.% Pd/SiO_2, and 0.5 wt.% Pd/MCM-41 were carried out at the same reaction condition: 100°C, 0.4 MPa H_2 partial pressure, 150 mL/min H_2 flow rate, 500 rpm stirring rate, and 4 h of reaction time. From the result shown in Figure 4.3, the types of support affected the hydrogenation activity of the catalyst. Considering at 1 h of reaction, 0.5 wt.% Pd/MCM-41 exhibited higher activity for C18:3 conversion, as compared with 0.5 wt.% Pd/SiO_2 and 0.5 wt.% Pd/Al_2O_3. The higher initial reaction rate of Pd/MCM-41 was presumably due to better dispersion of Pd particles on the high surface area MCM-41 material. However, after 2 h of reaction, the reaction rate of 0.5 wt.% Pd/MCM-41 was lower. This can be explained by a lower diffusion of unsaturated FAMEs in the mesoporous of Pd/MCM-41, as compared with that in 0.5 wt.% Pd/Al_2O_3. The unsaturated FAMEs can easily diffuse to the Pd active sites on the external surface of core shell commercial Pd/Al_2O_3 catalyst.

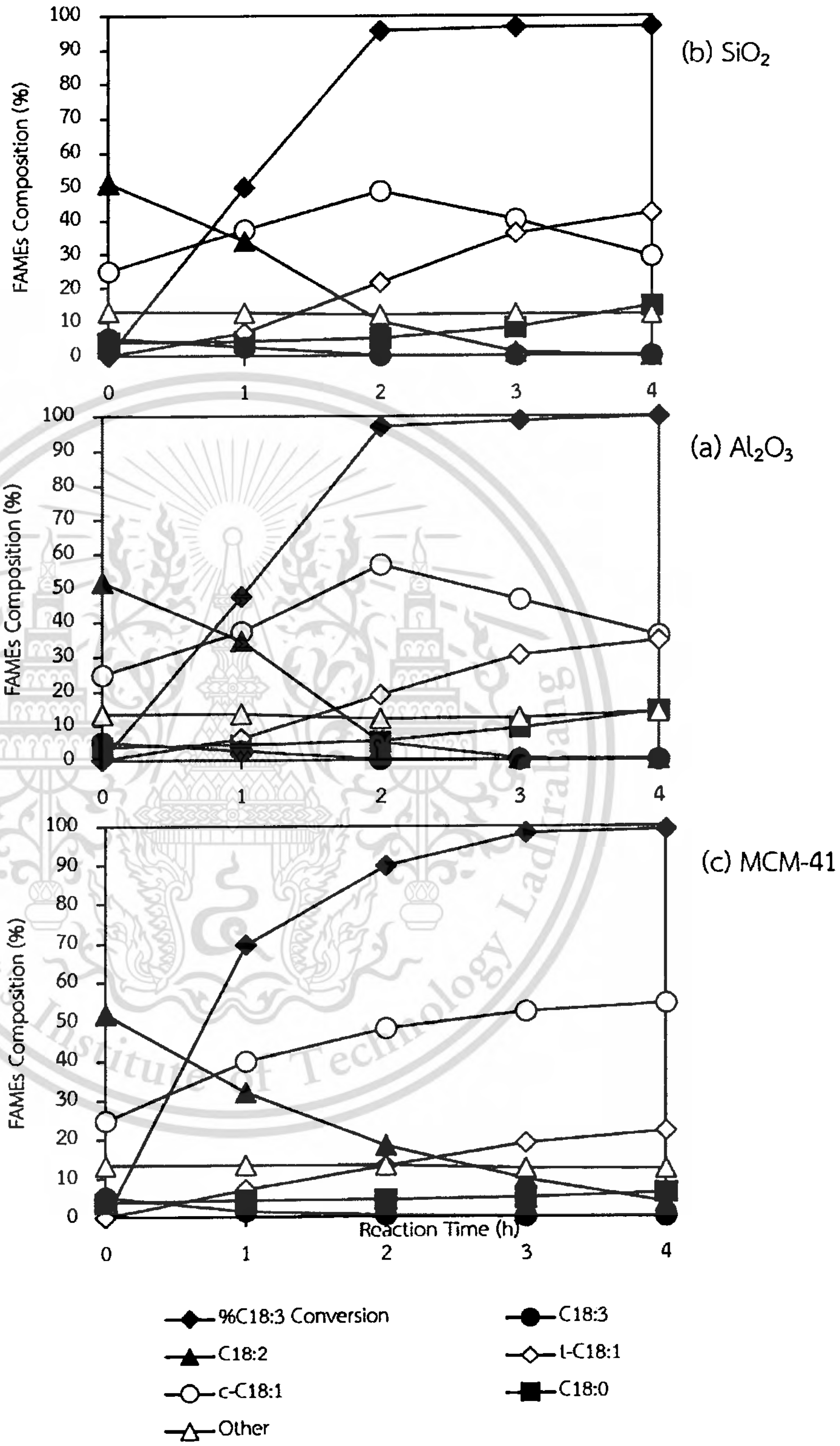


Figure 4.3 FAMEs composition in biodiesel as a function of reaction time over 0.5 wt.% Pd supported on (a) Al_2O_3, (b) SiO_2, and (c) MCM-41 (Reaction conditions: 100°C, 0.4 MPa, 150 mL/min H_2 flow rate, 500 rpm stirring rate, and 1 wt.% catalyst compared with

starting oil).

Another interesting observation is a difference in hydrogenation selectivity of the catalysts. As shown in Table 4.2, it was found that the selectivity towards C18:1 FAMEs at 4 h of reaction was in the following order: 0.5 wt.% Pd/MCM-41 (76.44%) > 0.5 wt.% Pd/SiO_2 (71.70%) > 0.5 wt.% Pd/Al_2O_3 (70.75%). This suggests that 0.5 wt.% Pd/MCM-41 showed partial hydrogenation activity. This can be explained by the small Pd particle size and good dispersion of Pd on the high surface area MCM-41 support as discussed in Section 4.2.3. The small Pd particle size provided restricted Pd surface for η^2-□ adsorption of C18:1. It can be hydrogenated at only one position of double bond resulting in a consecutive hydrogenation from C18:3 and C18:2 to C18:1.

In addition, 0.5 wt.% Pd/SiO_2 catalyst exhibited deeper hydrogenation activity than the others as it provided the largest amount of C18:0 FAMEs (14.76%) as shown in Table 4.3.

As previously discussed, the isomerization of original *cis*-C18:1 to *trans*-C18:1 simultaneously took place during hydrogenation. However, the *cis*-isomers was preferable in term of cold flow properties. It can be seen in Table 4.2 that the selectivity towards *trans*-C18:1 FAMEs was in the following order: 0.5 wt.% Pd/SiO_2 (42.29%) > 0.5 wt.% Pd/Al_2O_3 (34.66%) > 0.5 wt.% Pd/MCM-41(21.94%).

Table 4.2 C18:3 conversion and FAME composition of hydrogenated biodiesel over 0.5 wt.% Pd/Al_2O_3, 0.5 wt.% Pd/SiO_2, and 0.5 wt.% Pd/MCM-41 at 4 h of reaction.

Catalyst	C18:3 conversion (%)	FAME composition (%)			
		cis-C18:1	*trans*-C18:1	*cis-/trans*-ratio	C18:0
0.5 wt.% Pd/Al_2O_3	100.0	36.09	34.66	1.04	14.21
0.5 wt.% Pd/SiO_2	97.0	29.41	42.29	0.69	14.76
0.5 wt.% Pd/MCM-41	99.1	54.50	21.94	2.48	6.19

When compared between 0.5 wt.% Pd/Al_2O_3 and 0.5 wt.% Pd/SiO_2, 0.5 wt.% Pd/Al_2O_3 exhibited lower amount of *trans*-C18:1 presumably due to a high acidity of Al_2O_3, causing a strong adsorption between basic unsaturated bonds of C18:1 FAMEs and acidic sites of the Al_2O_3 support [27]. After the unsaturated bond was hydrogenated by one H atom, part of the alkylidene intermediate could not rotate easily around its original double bond before the added H atom leaves, to form *trans*-isomers [9].

The *cis-/trans*-C18:1 ratio and hydrogenation activity was in a similar trend. The *cis-/trans*-C18:1 ratio was in the following order: 0.5 wt.% Pd/MCM-41 (2.48) > 0.5 wt.% Pd/Al_2O_3 (1.04) > 0.5 wt.% Pd/SiO_2 (0.69). This can be explained by *cis*-C18:1 FAMEs cannot be readily adsorb as compared with 0.5 wt.% Pd/Al_2O_3 and 0.5 wt.% Pd/SiO_2. In addition, it can be seen that the composition of *trans*-C18:1 FAMEs and C18:0 FAMEs was in a similar trend, where 0.5 wt.% Pd/MCM-41 exhibited the smallest amount of *trans*-C18:1 FAMEs (21.94%) and C18:0 FAMEs (6.19%). Considering FAMEs composition, when the amount of *cis*-C18:1 FAMEs is high, the amount of *trans*-C18:1 FAMEs and C18:0 FAMEs will be low. This can be explained by the smaller amount of adsorbed *cis*-C18:1 FAMEs on the catalyst surface that caused low possibility in isomerization and hydrogenation of *cis*-C18:1 to *trans*-C18:1 FAMEs and C18:0 FAMEs, respectively.

4.2.2 Properties of biodiesel

In this study, the oxidative stability and the cloud point of soybean oil biodiesel were investigated after partial hydrogenation, as shown in Table 4.3.

Table 4.3 FAMEs composition and some fuel properties of biodiesel feed and biodiesel products after hydrogenation.

	Biodiesel feed	Hydrogenated biodiesel after 4 h	
		0.5 wt.% Pd/SiO_2	0.5 wt.% Pd/MCM-41
Fuel properties			
Oxidative stability (h)	1.94	50.37	11.71
Cloud point (°C)	4.0	19.2	15.0

Form Table 4.3, it can be seen that partial hydrogenation using Pd catalysts can improve the oxidative stability of soybean biodiesel. However, the cloud point of hydrogenated biodiesel was worse compared with that of feed biodiesel. The oxidative stability and the cloud point of hydrogenated biodiesel using 0.5 wt.% Pd/SiO_2 was higher than that of 0.5 wt.% Pd/MCM-41. This can be explained by a higher amount of C18:0 FAMEs in hydrogenated biodiesel using 0.5 wt.% Pd/SiO_2 compared with 0.5 wt.% Pd/MCM-41 as shown in Table 4.2. It can be suggested that hydrogenated biodiesel over 0.5 wt.% Pd/SiO_2 and 0.5 wt.% Pd/MCM-41 were not suitable to be used below the temperature of 19.2 °C and 15.0 °C, respectively because it will become waxes. The presence of solidified waxes causes the clogging of fuel filters or injectors in engines. This suggests that hydrogenated biodiesel over 0.5 wt.% Pd/MCM-41 shows better performance in terms of cloud point compared with 0.5 wt.% Pd/SiO_2.

Chapter 5

Conclusions and Suggestions

5.1 Conclusions

In this research, soybean biodiesel upgrading by partial hydrogenation of polyunsaturated fatty acid methyl ester was investigated. The catalysts used in this study include 0.5 wt.% Pd supported Al_2O_3 (commercial), SiO_2 and, MCM-41. It was found that these catalysts provide high partial hydrogenation activity, which showed the behavior of consecutive reactions from C18:3 to C18:2, C18:1 and C18:0, hence resulting in an improvement of the oxidative stability. The surface area of support affect the hydrogenation activity and selectivity towards *cis*-C18:1. Pd/MCM-41 presented higher selectivity towards C18:1 as compared with Pd/SiO_2 and Pd/Al_2O_3, due to higher Pd dispersion and small Pd particle size on high surface area MCM-41. The small Pd particle size provided restricted surface for η^2-π adsorption of C18:1, and thus low possibility in hydrogenation and isomerization of original *cis*-C18:1 to C18:0, and *trans*-C18:1, respectively.

5.2 Suggestions for Future Studies

5.2.1) The effect of bi-metallic catalyst on *cis*- and *trans*- selectivity should be investigated further.

Chapter 6
Research Outcomes

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ภาคผนวก

ภาคผนวก ก

Reaction

1) Reaction of 1 wt.% Pd/MCM-41

Table C1 The percentage of FAMEs composition after partial hydrogenation reaction using 1 wt.% Pd/MCM-41 as a catalyst.

Compositions	Feed	Time (h)			
		1	2	3	4
C18:1	4.05	4.31	4.78	5.32	6.57
Cis-C18:1	24.70	34.82	48.40	51.57	47.48
Trans-C18:1	0.00	4.70	13.52	20.77	29.60
C18:2	51.09	38.33	17.81	7.94	2.53
C18:3	5.10	2.78	0.51	0.09	0.00
Others	13.43	12.98	12.72	12.78	12.49

2.) The percentage of conversion loss of sample and product

Table C2 The conversion of missing C18:3 over various catalyst at the reaction temperature of 100 °C.

Catalysts	Reaction time (h)			
	1	2	3	4
0.5 wt.% Pd/Al_2O_3	47.58	97.01	98.79	100.00
0.5 wt.% Pd/SiO_2	49.78	95.73	96.77	96.99
0.5 wt.% Pd/MCM-41	69.63	89.92	98.31	99.12
1 wt.% Pd/SiO_2	52.19	95.83	96.74	100.00
1 wt.% Pd/MCM-41	45.61	89.91	98.27	100.00

Table C3 The conversion of missing C18:2 over various catalyst at the reaction temperature of 100 °C

Catalysts	Reaction time (h)			
	1	2	3	4
0.5 wt.% Pd/Al_2O_3	38.09	99.71	109.06	109.70
0.5 wt.% Pd/SiO_2	38.40	89.85	107.66	109.83
0.5 wt.% Pd/MCM-41	45.26	73.47	90.84	102.75
1 wt.% Pd/SiO_2	47.29	101.64	108.61	109.84
1 wt.% Pd/MCM-41	29.53	74.12	94.28	105.04

Table C4 The conversion of missing C18:1 over various catalyst at the reaction temperature of 100 °C.

Catalysts	Reaction time (h)			
	1	2	3	4
0.5 wt.% Pd/Al_2O_3	4.22	2.45	16.64	43.73
0.5 wt.% Pd/SiO_2	2.10	2.31	13.27	37.47
0.5 wt.% Pd/MCM-41	4.98	5.90	1.65	6.25
1 wt.% Pd/SiO_2	1.79	14.51	47.83	101.34
1 wt.% Pd/MCM-41	1.07	2.61	2.13	5.20

3.) The percentage of *cis*-C18:1 selectivity in various catalyst

Table C5 The percentage of *cis*-C18:1 selectivity

Catalysts	Reaction time (h)			
	1	2	3	4
0.5 wt.% Pd/Al_2O_3	0.14	0.25	0.39	0.49
0.5 wt.% Pd/SiO_2	0.85	0.70	0.53	0.41
0.5 wt.% Pd/MCM-41	0.85	0.78	0.73	0.71
1 wt.% Pd/SiO_2	0.80	0.57	0.34	0.34
1 wt.% Pd/MCM-41	0.88	0.78	0.71	0.61

4.) The percentage of *trans*-C18:1 selectivity in various catalyst

Table C6 The percentage of *trans*-C18:1 selectivity

Catalysts	Reaction time (h)			
	1	2	3	4
0.5 wt.% Pd/Al_2O_3	0.86	0.75	0.61	0.51
0.5 wt.% Pd/SiO_2	0.15	0.31	0.48	0.59
0.5 wt.% Pd/MCM-41	0.15	0.21	0.26	0.28
1 wt.% Pd/SiO_2	0.19	0.43	0.66	0.66
1 wt.% Pd/MCM-41	0.11	0.21	0.28	0.38

ภาคผนวก ข

สรุปค่าใช้จ่ายการดำเนินงานโครงการวิจัย

รหัสโครงการ/รหัสสัญญา 2560-01-05-04

แบบรายงานการใช้จ่ายเงินโครงการวิจัย
สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

รายงานฉบับสมบูรณ์ ประจำปีงบประมาณ 2560

☐ แหล่งงบประมาณแผ่นดิน (แบบปกติ) ☑ แหล่งเงินรายได้

ชื่อโครงการ (ภาษาไทย) ปัจจัยของตัวรองรับที่มีผลต่อปฏิกิริยาไฮโดรจีเนชันแบบบางส่วนของเมทิลเอสเทอร์ชนิดไม่อิ่มตัวเชิงซ้อนเพื่อปรับปรุงคุณภาพน้ำมันไบโอดีเซล

(ภาษาอังกฤษ) Effect of type of support on partial hydrogenation of poly-unsaturated fattyacid methyl esters for biodiesel upgrading

ชื่อ-สกุลหัวหน้าโครงการวิจัยผู้รับทุน/ผู้วิจัย ดร. ณัฐธิดา นุ่มนงศ์

รายงานในช่วงตั้งแต่วันที่ 1 ตุลาคม 2559 ถึง 30 กันยายน 2560

ระยะเวลาดำเนินการ 1 ปี ตั้งแต่วันที่ 1 ตุลาคม 2559 ถึง 30 กันยายน 2560

ข้อมูลการรายงานค่าใช้จ่ายงบประมาณโครงการวิจัย

1. การเบิกจ่ายงบประมาณ

งวดที่ 1 50,000 บาท 100 % วันที่ได้รับอนุมัติให้เบิกจ่ายเงิน (ว/ด/ป) 1 พฤศจิกายน 2559

2. สรุปงบประมาณค่าใช้จ่ายที่ใช้นับตั้งแต่เริ่มทำการวิจัยถึงปัจจุบัน

หมวดค่าใช้จ่าย	**งบประมาณรวมทั้งโครงการ**	**ค่าใช้จ่าย (บาท)**	**คงเหลือ (หรือเกิน)**
งบบุคลากร :ค่าจ้างชั่วคราว	-	-	-
งบดำเนินงาน			
ค่าตอบแทน	-	-	-
ค่าใช้สอย	20,000.00	24,188.00	-4,188.00
ค่าวัสดุ	30,000.00	25,888.41	4,111.59
ค่าสาธารณูปโภค	-	-	-
งบลงทุน: ค่าครุภัณฑ์	-	-	-
รวม	50,000.00	50,076.41	-76.41

(ดร.ณัฐธิดา นุ่มวงศ์)
หัวหน้าโครงการวิจัยผู้รับทุน
30 / เม.ย. /2561

ข้อมูลประวัติคณะผู้วิจัย

ประวัติส่วนตัว

ชื่อ-สกุล	ดร.ณัฐธิดา นุ่มวงศ์
ตำแหน่งปัจจุบัน	อาจารย์ ภาควิชาเคมี คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

ประวัติการศึกษา

ชื่อย่อปริญญา	สาขา	สถาบันที่จบ	ปีที่จบ
วท.บ.	เทคโนโลยีปิโตรเคมี	สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง	2549
ปร.ด.	เทคโนโลยีปิโตรเคมี	วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย	2555

ทุนการศึกษาและทุนวิจัยที่เคยได้รับ

ปี พ.ศ.	ทุนการศึกษาและทุนวิจัย	สถาบันที่ให้
2550	Full Scholarship for Master Student	วิทยาลัยปิโตรเลียมและปิโตรเคมี จุฬาลงกรณ์มหาวิทยาลัย
2551	ทุนปริญญาเอกจุฬาดุษฎีพิพรรธ์	จุฬาลงกรณ์มหาวิทยาลัย
2556	ทุนนักวิจัยรุ่นเยาว์	สถานเอกอัครราชทูตฝรั่งเศสประจำประเทศไทย
2557	ทุนส่งเสริมนักวิจัย งบประมาณเงินรายได้	คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
2558	ทุนส่งเสริมนักวิจัย งบประมาณเงินรายได้	คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
2558	ทุนสนับสนุนทุนวิจัยร่วมกับหน่วยงานภายนอกสถาบัน งบประมาณเงินรายได้	คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
2559	ทุนส่งเสริมนักวิจัย งบประมาณเงินรายได้	คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
2560	ทุนส่งเสริมนักวิจัย งบประมาณเงินรายได้	คณะวิทยาศาสตร์ สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
2560	ทุนพัฒนาศักยภาพในการทำงานวิจัยของอาจารย์รุ่นใหม่ สกว.	สำนักงานกองทุนสนับสนุนการวิจัย (สกว.)

ผลงานวิจัยระดับนานาชาติ

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2. **Numwong N.**, Luengnaruemitchai A., Chollacoop N., and Yoshimura Y., Effect of SiO_2 Pore Size on Partial Hydrogenation of Rapeseed Oil-Derived FAMEs. Applied Catalysis A: General 441–442 (2012) 72– 78

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การเสนอผลงานวิชาการ

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4. Natthida Numwong, Khanokthip Yathongchai, Kittichai Rujipornsakul, Nuttapoom Ruttanajairakul and Tawan Sooknoi, Selective Hydrogenation of trans-2-Hexenal to 2-Hexenol over Cobalt-Based Catalysts, PACCON 2015, Bangkok, Thailand (22-13 January 2015)