CATALYTIC ACTIVITY OF Cu-CeO_2-ZrO_2 FOR BIODIESEL PRODUCTION

Wasupon Wongvitvichot

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
and Case Western Reserve University
2017

Thesis Title: Catalytic Activity of Cu-CeO_2ZrO_2 for Biodiesel Production
By: Wasupon Wongvitvichot
Program: Polymer Science
Thesis Advisors: Prof. Sujitra Wongkasemjit
Prof. Apanee Luengnaruemitchai
Assoc. Prof. Thanyalak Chaisuwan

Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfillment of the requirements for the Degree of Master of Science.

.... College Dean
(Prof. Suwabun Chirachanchai)

Thesis Committee:

....
(Prof. Sujitra Wongkasemjit)

....
(Prof. Apanee Luengnaruemitchai)

....
(Assoc. Prof. Thanyalak Chaisuwan)

....
(Asst. Prof. Bussarin Ksapabutr)

....
(Asst. Prof. Manit Nithitanaku)

ABSTRACT

5872027063: Polymer Science Program
Wasupon Wongvitvichot: Catalytic Activity of Cu-CeO_2-ZrO_2 for Biodiesel Production
Thesis Advisors: Prof. Sujitra Wongkasemjit, Prof. Apanee Luengnaruemitchai, and Assoc. Prof. Thanyalak Chaisuwan 49 pp.

Keywords: Ordered mesoporous ceria-zirconia/ MCM-48/ Nanocasting/ Biodiesel

CeO_2-ZrO_2 was synthesized by co-precipitation (CZ copre) and nanocasting (MSP CZ) methods for supporting 9%wt Cu catalyst loaded by deposition-precipitation (DP) method (CuCZ copre and Cu-MSP CZ, respectively). Both CuCZ copre and Cu-MSP CZ were used in esterification reaction for biodiesel production. Structure and specific surface area of the synthesized supports and catalysts were characterized by XRD and BET tecnhiques. It was found that the specific surface area of CZ copre was less than MSP CZ support. The XRD result of CuCZ copre exhibited the diffraction peak of CuO, indicating the agglomeration of Cu species on support while that of Cu-MSP CZ showed no diffraction peaks of any Cu species, indicating that Cu was well dispersed on the MSP CZ support. Both CuCZ copre and Cu-MSP CZ were treated with sulfuric acid to test their catalytic activity using oleic acid and methanol as starting materials by microwave heating. The optimal conditions obtained were following: 2.0 M sulfuric acid, 5 wt% catalyst, and 12:1 methanol:oleic acid molar ratio at 60 °C for 1h.

บทคัดย่อ

วสุพล วงศ์วิทย์วิโชติ : ความว่องไวในการเกิดปฏิกิริยของคอปเปอร์ซีเรียและเซอร์โคเนียสำหรับกระบวนการผลิตไบโอดีเซล (Catalytic activity of Cu-CeO$_2$ZrO$_2$ for biodiesel production) อ.ที่ปรึกษา: ศาสตราจารย์ ดร.สุจิตรา วงศ์เกษมจิตต์, ศาสตราจารย์ ดร. อาภาณี เหลืองนฤมิตชัย และรองศาสตราจารย์ ดร. ธัญญลักษณ์ ฉายสุวรรณ์ 49 หน้า

สารออกไซด์ผสมของซีเรียเซอโคเนียถูกสังเคราะห์ด้วยวิธีการตกตะกอนร่วมและวิธีการใช้แม่พิมพ์ขนาดนาโนเมตรเพื่อใช้เป็นตัวรองรับตัวเร่งปฏิกิริยาคอปเปอร์ปริมาณ 9 เปอร์เซ็นต่อน้ำหนักด้วยวิธีการฝังและตกตะกอน เพื่อนำไปเป็นตัวเร่งปฏิกิริยาเอสเทอริฟิเคชันสำหรับการผลิตไบโอดีเซล โครงสร้างและพื้นที่จำเพาะของทั้งตัวรองรับและคอปเปอร์บนตัวรองรับถูกพิสูจน์เอกลักษณ์ด้วยเทคนิคการวิเคราะห์องค์ประกอบสารด้วยเทคนิคการเลี้ยวเบนของรังสีเอ็กซ์ และเทคนิคการหาพื้นที่ผิวจำเพาะและขนาดของรูพรุน ตัวรองรับซีเรียเซอโคเนียที่สังเคราะห์ด้วยวิธีการตกตะกอนร่วมมีพื้นที่จำเพาะผิวน้อยกว่าตัวรองรับซีเรียเซอโคเนียที่สังเคราะห์ด้วยวิธีการใช้แม่พิมพ์ขนาดนาโนเมตร จากการทดสอบด้วยเทคนิคการวิเคราะห์องค์ประกอบสารด้วยเทคนิคการเลี้ยวเบนของรังสีเอ็กซ์ ตัวเร่งปฏิกิริยาคอปเปอร์ที่อยู่บนตัวรองรับที่เกิดจากการสังเคราะห์ด้วยวิธีการตกตะกอนร่วม แสดงเอกลักษณ์ของผลึกคอปเปอร์ ซึ่งเกิดจากการรวมกันของผลึกคอปเปอร์ ในขณะที่ตัวเร่งปฏิกิริยาคอปเปอร์ที่อยู่บนตัวรองรับที่สังเคราะห์ด้วยวิธีการใช้แม่พิมพ์ขนาดนาโนเมตรไม่พบเอกลักษณ์ดังกล่าวของกลุ่มก้อนของผลึกคอปเปอร์ แสดงให้เห็นถึงการกระจายตัวของคอปเปอร์ที่ดี เมื่อเติมตัวเร่งปฏิกิริยาร่วมด้วยกรดซัลฟิวริกเพื่อเพิ่มประสิทธิภาพของตัวเร่งปฏิกิริยาในการสังเคราะห์ไบโอดีเซลในระบบการให้ความร้อนด้วยรังสีไมโครเวฟ โดยมีกรดโอเลอิกและเมทานอลเป็นสารตั้งต้น จากการทดลองพบว่า สภาวะที่ดีที่สุดในการเกิดปฏิกิริยาเอสเทอริฟิเคชั่นเพื่อผลิตไบโอดีเซลคือ การใช้ความเข้มข้นของกรดซัลฟิวริก 2 โมลาร์ น้ำหนักตัวเร่งปฏิกิริยาที่ 5 เปอร์เซ็นโดยน้ำหนัก อัตราส่วนโดยโมลของเมทานอลและโอเลอิกที่ 12 ต่อ 1 ที่อุณภหภูมิ 60 องศาเซลเซียส เป็นเวลา 1 ชั่วโมง

ACKNOWLEDGEMENTS

I would like to express my sincere thanks to my advisor and co advisors, Prof. Sujitra Wongkasemjit, Prof. Apanee Leungnarumitchai, and Assoc. Prof. Thanyalak Chaisuwan for their kind suggestion and invaluable guidance in this research at all time. I am most grateful for their teaching and advice, not only the research methodologies, but also many other methodologies in life.

I would like to express the deepest appreciation to my committee, Asst. Prof. Bussarin Ksapabutr and Asst. Prof.Manit Nithitanakul for suggestions, and comments are definitely imperative for accomplishing my thesis.

I would like to express special thanks to Ms. Sureerat Jampa, Ms. Hussaya Maneesuwan, Ms. Tidarat Komalwanichand, and Mr. Sakollapath Pithakratanayothin for their suggestions, encouragement, cheerfulness, kindness, and friendly assistance. I would not have achieved this far, and this thesis would not have been completed without all the support given to me. I had a lot of memorable and enjoyable time with all of them who made the best time to me.

I would like to take this opportunity to thank all members and staffs of The Petroleum and Petrochemical College, Chulalongkorn University.

I would like to thank my friends and so many people whose names may not all be appeared for their friendly and cheerfulness and encouragement.

I most gratefully acknowledge my parents for their support, encourage and countless love.

Finally, I am grateful for the scholarship and funding of the thesis work supported by the Grant for International Reseach Integration: Chula research Scholar, Ratchadapisek Sompotch Endowment Fund, Chulalongkorn University, Thailand.

TABLE OF CONTENTS

CHAPTER **PAGE**

LIST OF TABLES

LIST OF FIGURES

FIGURE **PAGE**

FIGURE **PAGE**

CHAPTER I
INTRODUCTION

Biodiesel, renewable and eco-friend energy, can very well substitute fossil fuel since its chemical structure consists of fatty acid methyl esters which is derived from vegetable oil or animal fats (Ma *et al.,* 1999; Lukić Ivana *et al.,* 2010; Avhad *et al.,* 2015). The main component of vegetable oils and animal fats is triglyceride which is produced via esterification of free fatty acids (FFA) and glycerol. Free fatty acids can be either saturated or unsaturated, and these structures do affect properties and stabilities of biodiesel. Some natural triglyceride contains higher level of unsaturated fatty acid than diesel fuel, influencing low viscosity and liquid state at room temperature. On the other hand, more saturated fatty acids in structure affect solid state at room temperature, making more difficult for an engine to directly use triglyceride. This problem can be overcome by using biodiesel. The conventional biodiesel is produced via alcoholysis that composes of transesterification and esterification reactions. Triglyceride and alcohol were used as raw materials for biodiesel production in transesterification. Biodiesel can also be produced via esterification using FFA and alcohol as reactants. Alcohols used in the alcoholysis process are methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol is the most popular one for alcoholysis because of its low cost, physical and chemical advantages, namely, more polar and smallest hydrocarbon group. In addition, methanol can immediately react with triglyceride and free fatty acid (Ma *et al.,* 1999; Avhad *et al.,* 2015). Both transesterification and esterification result in by-products as glycerol and water, respectively, but need a catalyst to accelerate the reactions (Ma *et al.,* 1999).

Generally, catalysts used in the reaction are either acid or base. The catalyst for transesterification depends on the amount of FFA in oil. Both acid and basic catalysts can be utilized for oil having low content of FFA, however the acid catalyst is also used for oil containing more amount of FFA because the basic catalysts cause the undesired reaction called saponification reaction which generates soap and reduces the final biodiesel yield while causes the formation of ester-glycerol emulsion, thus, the separation and purification of products become complicated. The basic catalyst used in transesterification reaction is well known for biodiesel production with a shorter reaction time than the acid catalyst. The homogeneous basic catalyst, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), has been widely used for biodiesel production due to its high activity, low cost, and commercial availability. Although the basic catalysts are well known to accelerate the transesterification reaction rate, the acid catalysts, such as sulfuric acid (H_2SO_4), are tolerant towards the FFA content in feed stocks. There are some drawbacks of the homogeneous catalysts: 1) the post-reaction treatment is required for removal of residual catalyst from the reaction mixture and disposal, 2) the homogeneous catalyst cannot be reutilized. With these two drawbacks, heterogeneous catalyst becomes a good economic and ecologic catalyst since the separation of the heterogeneous catalyst from the product mixture is simple and easy. Moreover, the catalysts could be reutilized, depending on the nature of the catalyst, e.g. active site, structural, morphology, porosity and thermal stability. Porous material which was used as heterogeneous catalyst for biodiesel production needs to have suitable morphology in order to provide a good diffusion for oil to the active site. It is believed that the uniform dispersion of metal catalyst onto the porous support (porous material) would enable availability of large number of active site and increase surface for the reaction (Avhad *et al.,* 2015).

Among porous materials, mesoporous (pore size 2-50 nm) is suitable and popular to be used as catalyst support, and among the order mesoporous M41S family MCM-41 (one dimensional, hexagonal channel), MCM-48 (three dimensional, cubic channel), and MCM-50 (one dimensional, planar), MCM-48 is the most interesting one because its cubic structure and interconnecting channel provide resistant blocking and good mass transfer (Motasemi *et al.,* 2012). Thus, MCM-48 is a choice to be used as a catalyst support or a template for nanostructure via nanocasting process to synthesize non-silica mesoporous materials, such as, mesoporous carbon, metal oxides and sulfide. The nanocasting process can induce the fabrication of products taking place in the nanospace provided by pores of the porous template, which is removed after the synthesis of the non-silica mesoporous materials (Avhad *et al.,* 2015).

Cerium oxide or ceria (CeO_2) is a good candidate as catalyst support for biodiesel production (Ma *et al.,* 1999) because of its well-known ability to exchange lattice oxygen, oxygen storage capacity, and stability (Avhad *et al.,* 2016). Zirconiun dioxide (ZrO_2) or zirconia, having good thermal stability, oxygen storage, redox property, and amphoteric characteristic (Shay, 1993; Verma *et al.,* 2016), is widely used as acid catalyst for biodiesel production, such as, sulfate zirconia that is a well-known heterogeneous acid catalyst for various organic reactions. Both mesoporous ceria and zirconia are normally synthesized by sol-gel method. However, this method presents agglomeration problem, which can be solved by using the nanocasting process because the template can control structure and morphology of the material.

Copper (Cu), one of the transition metal, has the valence in D orbital showing good electrical and thermal conductivity. Copper catalyst shows acid property and high selectivity. The acid properties are important property for biodiesel production. Both ceria and zirconia used as support for copper catalyst exhibit highly strong interaction and good dispersion (Li *et al.,* 2013; Saluja *et al.,* 2016). Among the methods for loading metal on support, deposition-precipitation (DP) seems to provide better dispersion (Okoye *et al.,* 2016).

Microwave heating is an interesting technology for transesterification, esterification or hydrolysis reaction since the materials are rapidly, homogeneously heated, leading to an increase in the reaction rate. This method is more efficient than the conventional heating because it reduces time and energy (Mazubert *et al.,* 2013).
In the research, Cu is loaded on mesoporous ceria-zirconia support by DP method for biodiesel production using oleic acid and methanol as starting materials. Ceria-zirconia support was synthesized by nanocasting using MCM-48 as a hard template. The optimal conditions for esterification were studied.

CHAPTER II
LITERATURE REVIEW

2.1 Biodiesel

Biodiesel, fatty acid methyl ester, is an alternative energy for diesel fuel, thus has been more attractive. Biodiesel is an environmentally friendly since it is produced from renewable resources, such as vegetable oils or animal fats. Transesterification is the most popular reaction to produce biodiesel because it can reduce viscosity of oil (Ma *et al.,* 1999).

In the past, direct use of triglyceride blending with petroleum oils is not satisfied due to its high viscosity and poor ignition quality. Thus, alcoholysis, transesterification or esterification reaction (Chuah *et al.*), is widely used to solve those problems. Biodiesel production by transesterification needs to use fatty acid triglyceride, methanol, and catalyst. The kinetics of transesterification reaction consists of three reversible steps, viz. conversion of triglyceride (TG) to diglyceride (DG), DG to monoglyceride (MG), and MG to glycerol. Each step uses one molecule of methanol to obtain one molecule fatty acid methyl ester (FAME). Therefore, one TG requires three methanol molecules to obtain product. The products consist of three FAMEs and one glycerol which is the by-product (Figures 2.1 and 2.2).

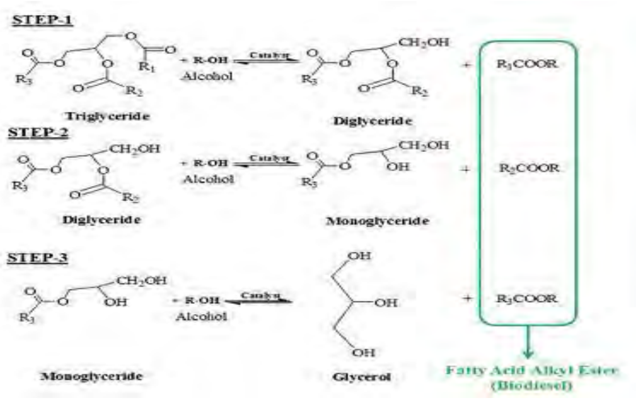

Figure 2.1 Stepwise transesterifiaction reaction of vegetable oils (Avhad *et al.,* 2016).

Figure 2.2 Esterification reaction of free fatty acid (Avhad *et al.,* 2016).

The catalyst for transesterification could be either acid or base, depending on type of FFA (Ma *et al.,* 1999). Liao *et al.* (2013) used *Jatropha curcas* oil with methanol and CaO impregnated with KOH. *Jatropha curcas* oil was pretreated by sulfuric acid to prevent saponification process, and the results showed high purity of alkyl ester above 96.5% (Chuah *et al.*).

Esterification, a reaction in alcoholysis for biodiesel production, is suitable for a resource having high FFA, using acid catalyst to prevent saponification reaction. Acid catalyst accelerates the reaction to obtain FAME as biodiesel and water as by-product (Ma *et al.,* 1999). Zhang *et al.* (2012) reported on biodiesel production from cooking waste containing high FFA. They used esterification reaction to produce FAME (Liu *et al.,* 2013).

The precursors for biodiesel production include oil, alcohol, and catalysts. Ethanol and methanol are the most popular to be used to react with catalyst and triglyceride or FFA (Ma *et al.,* 1999). It was also reported that methanol was easily evaporated when the reaction complete (Verma *et al.,* 2016). Main precursor for biodiesel production is the feed stock oil, such as soybean oil (28%), palm oil (22%), animal fats (20%), coconut oil (11%), etc. Most feed stock oil is edible, meaning that the use of the edible oils for biodiesel production is competing with human consumption for food. Thus, alternative feedstocks, specifically non-edible plants and waste oil, such as cooking waste oil, *jatropha cuscas* oil, were extensively studied (Avhad *et al.,* 2015).

Verma *et al.* (2016) reported on the use of non-edible oil like cooking waste oil, *jatropha cuscas* oil, or edible oils like rice brain oil, chicken fat, having very high acid value/FFA content. In this case, two steps of acid-base transesterification process were needed for biodiesel production (Verma *et al.,* 2016). Ma *et al.* (1999) reported that fat and oil as TG were hydrophobic because they made from one mole of glycerol and three mole of FFA having a long carbon chain and unsaturated bonds. The main component of fatty acid was oleic acid, usually being used in the experiment (Ma *et al.,* 1999). Enweremadu *et al.* (2009) reported the method for biodiesel production using alkaline, acidic, and enzymatic catalysts which depend on the undesirable compounds (Enweremadu *et al.,* 2009).

The most common alkali catalysts for transesterification are NaOH, KOH, and sodium methoxide. One major problem from the alkali-catalyzed transesterification is the formation of soap from saponification reaction, reducing catalytic efficiency since the soap increases viscosity and results in difficulty to separate glycerol. Go *et al.* (2016) stated that the base catalyst was not capable of converting FFA to FAME. However, higher amount of alcohol used in ISTE (in-situ (Trans-esterification) results in suppressing saponification reaction (Avhad *et al.,* 2015).

Acid catalysts are insensitive to FFA and better than alkaline catalysts for vegetable oil with FFA greater than 1%. Acid-catalyzed transesterification is started by mixing oil directly with the acidified alcohol, resulting in the simultaneous occurrence of separation and transesterification in one step. The advantages of using solid acid catalyst are: insensitive to FFA content, simultaneous occurrence of esterification and transesterification, easy separation of the catalyst, no need to wash FAME, high yield, small amount of the catalyst required, reusable and environment friendly catalyst (Enweremadu *et al.,* 2009). Liu *et al.* (2013) used heterogeneous aminophosphonic acid catalyst under the reaction condition of 9 wt% and 11:1 ethanol:stearic acid at 353 K, and obtained more than 90% conversion of esterification in 7 h (Liu *et al.,* 2013). Tantirungrotechai *et al.* (2011) obtained over 90% of FAME after 3 h reaction time at 200 °C, using CaO loaded on mesoporous material MCM-41.

2.2 Porous Materials

2.2.1 M41S Family

Schumacher *et al.* (2000) reported that M41S materials possess well-defined pore structures. The most popular ones are MCM-41, having a hexagonal array, and MCM-48, having a cubic pore structure with cubic Ia3d space group and interconnected pore (Figure 2.3). The pore network of MCM-48 provides more favorable mass transfer kinetics than the unidirectional pore system of MCM-41 (Mazubert *et al.,* 2013).

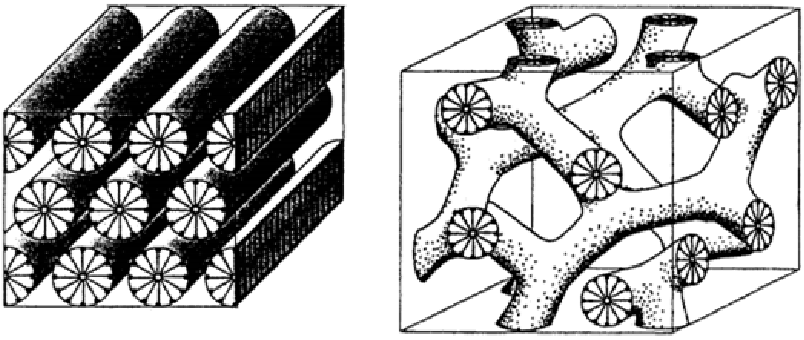

Figure 2.3 Structures of MCM-41 (left) and MCM-48 (right).

Longloilert *et al.* (2011) successfully synthesized high quality of MCM-48 cubic structure using silatrane and cetyltrimethaylammonium bromide (CTAB) as a structure directing agent by sol-gel process. Silatrane was easily synthesized from silica and triethanolamine, thus, inexpensive and provided moisture stability lasting up to several weeks (Charoenpinijkarn *et al.,* 2001). The synthesized MCM-48 has cubic Ia3d space group with high surface area of around 1,300 m^2/g. Moreover, it shows narrow pore-size distribution of 2.86 nm and the truncated octahedral shape with well-ordered pore system (Longloilert *et al.,* 2011).

2.2.2 Ceria and Zirconia

Yu *et al.* (2011) loaded calcium ion on ceria for using as a homogenous catalyst in transesterification reaction. Ceria can improve heterogeneous catalytic stability remarkably due to defects induced by the substitution of Ca ions to force ions on the surface (Verma *et al.,* 2016).

Thitsartarn *et al.* (2015) reported that CaO/CeO_2 provided high basicity while Ce corporate Si support was higher basicity. The highest dispersion of active sites on the catalyst surface resulted in the highest total basicity; and the large ordered-pore of the catalyst was favorable for diffusion of bulky reactant and products. The catalyst can be used up to at least 15 times with insignificant decrease in catalytic activity (Okoye *et al.,* 2016).

Ceria as a support meets the requirements of high-temperature catalytic reaction. A new catalyst composition involves in ceria doped with transition metal oxide to improve catalyst activity, e.g. zirconia, a transition metal, can form solid with ceria to promote the kinetics of cerium ion reduction and enhance oxygen storage of ceria. The main features of ceria-zirconia are: higher thermal resistance if compared with conventional CeO_2-containing catalyst, higher reduction efficiency of redox couple Ce^{4+}-Ce^{3+}, and good oxygen storage/release capacity. These features result in a higher degree of conversion, especially at a lower temperature (Trovarelli *et al.,* 2001). The acid-based properties and thermal stabilities are important option for biodiesel production and use supported for acid catalyst (Saluja *et al.,* 2016).

Zhang *et al.* (2013) prepared sulfuric acid modified zirconia known to be effective heterogeneous catalyst for esterification reaction. However, SO_4^{2+} was rapidly leached, resulting in non-reusability. Chlorosulfuric acid was used in place of sulfuric acid, giving high catalytic activity, 100% of FAME, and long durability in alcoholysis reaction (Zhang *et al.,* 2013). Zirconia has such a property that can interact with $-CO_2H$ of TG or FFA, making it easier for alcohol to attack and eliminate water molecule to yield the corresponding ester (Enweremadu *et al.,* 2009).

2.2.3 Nanocasting

Usually, metal oxide catalysts are prepared via sol-gel process. This process also provides some drawbacks if the process takes place too fast, causing agglomeration (Saluja *et al.,* 2016) or if calcination at too high temperature causes structure collapse (Enweremadu *et al.,* 2009). Recently, new method to synthesize zirconia nanoparticles is called nanocasting which needs a hard template, such as ordered mesoporous silicas as SBA-15, or a soft template, such as CTAB. Nanocasting is a powerful method for synthesis of nonsiliceous materials with controlling composition and structure ordering. The nanocasting pathway creating nanostructured materials is shown in Figure 2.4.

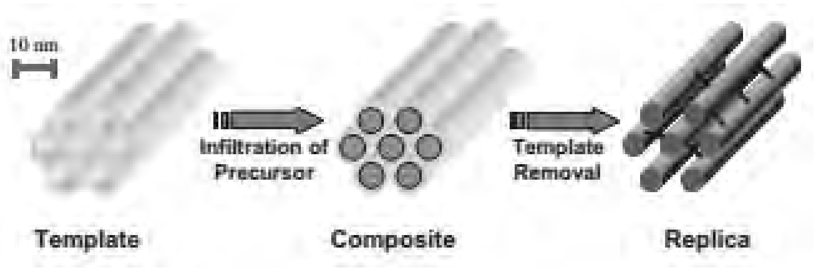

Figure 2.4 Schematic illustration of the nanocasting pathway.

Microwave-digested 3D mesoporous silica can be used as a hard template to fabricate various ordered crystalline gyroidal metal oxides, such as CeO_2. Nevertheless, silica as a hard template can only be leached under strongly alkaline condition or hydrofluoric acid (HF) (Li *et al.,* 2013).

Deeprasertkul *et al.* (2014) synthesized mesoporous ceria with a high surface area and ordered structure via nanocasting method using MCM-48 as a hard-template. The temperature-programmed reduction showed only surface reduction temperature at 400°–600°C, referring to the strong reduction at a lower temperature (Wei *et al.,* 2012).

Kawashima *et al.* (2008) reported their catalytic activities tested for transesterification at 60 °C for 10 h using 6:1 methanol:oil. The $CaZrO_3$ and CaO-CeO_2 catalysts had high durability and activity, and were able to provide methyl ester yields of biodiesel (Kawashima *et al.,* 2008). Venkatesh *et al.* (2014) used CaO, ZrO_2, CeO_2-ZrO_2, CeO_2, and CeO_2-ZrO_2-MgO_2 for transesterification and SO_4^{2-}/CeO_2, SO_4^{2-}/CeO_2-ZrO_2 for esterification. The pure ceria and zirconia have both acid and basic sites. However, the pure ceria consists of less amount of the acid site than the basic site whereas it is opposite for the pure zirconia. Due to a little bit smaller ion size of zirconia, it is expected to generate stronger acid sites in the mixed oxide. In addition to, ceria-zirconia doped magnesia showed more basic site than ceria doped magnesia because of more basic sites on the surface of ceria-zirconia. Ceria-zirconia or ceria improved stability and activity of magnesia, resulting in higher reusability and efficiency (Venkatesh *et al.,* 2014).

2.2.4 Cu Loaded Metal Oxide Support

Yakovlev *et al.* (2009) reported that oxide form of a transition metal with variable valence was needed for activation of oxy-group in the oxygen-containing compounds in bio-crude-oil. However, a transition metal in its reduced state was required to activate dihydrogen. The oxides of such metal as Mo, W, Co, Mn, Zr, and Ce, possess the mobile oxygen under the indicated conditions. Among these oxides, ceria-zirconia presented the most appropriate materials for the catalyst supports since the valence of these metals could change under the biodiesel hydrodeoxygenation (HDO) conditions. The screening of catalyst supports showed that CeO_2 and ZrO_2 were the most effective in the target process (Yakovlev *et al.,* 2009).

Gurunathan *et al.* (2015) prepared heterogeneous metal oxide catalyst consisting of positive metal ions, which acted as electron acceptors and oxygen negative ions that acted as proton acceptors. In term of its efficiency for transesterification, the catalyst provided adsorptive site for methanol whereas the (O-H) bonds were readily broken into methoxide anions and hydrogen cations. The methoxide anion reacted with TG molecules to yield FAME. Gurunathan *et al.* (2015) also used copper doped zinc oxide. The best conditions were to use 12 wt% catalyst, 1:8 oil:methanol at 60 °C for 50 min. the catalyst could be reused up to 5 times (Gurunathan *et al.,* 2015).

Gurbani *et al.* (2009) compared two different preparation methods for synthesizing 7 wt%. $CuO\text{-}CeO_2$ catalysts: a conventional wet impregnation and a deposition-precipitation method using Na_2CO_3 as a precipitating agent. The conventional wet impregnation method provided a great activity and selectivity, as well as high surface area and good interaction whereas the deposition-precipitation method was for preparing a catalyst with very high dispersion (Gurbani *et al.,* 2009).

2.3 Microwave

Range of electromagnetic irradiation and frequency of microwave irradiation is 1.01 to 1 m and 0.3 to 300 GHz, respectively, but generally microwave is oven operated at 2.45 GHz frequency.

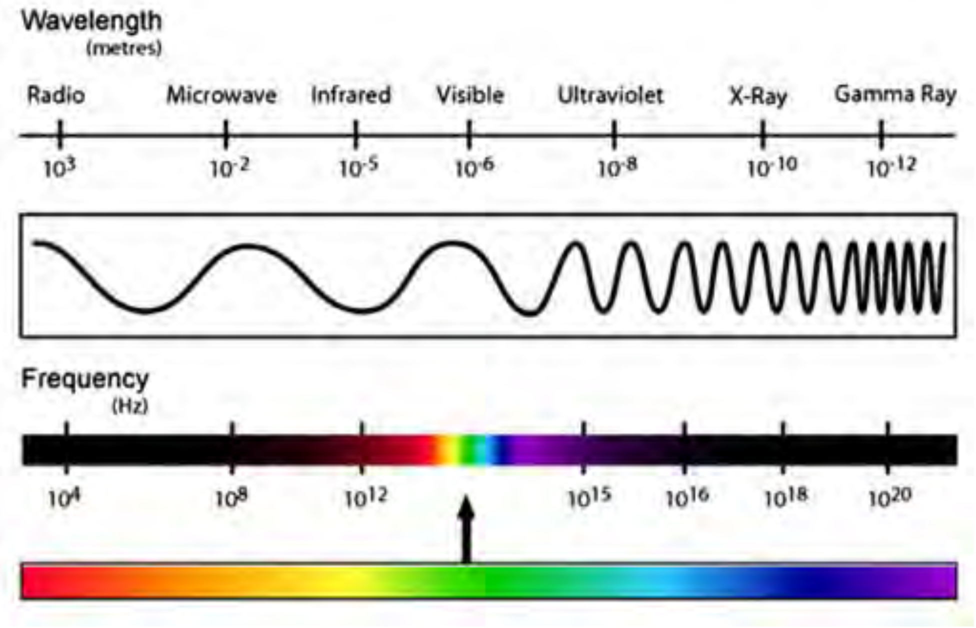

Figure 2.5 The electromagnetic spectrum (Motasemi *et al.* 2012).

This method is well-established to accelerate and enhance chemical reactions because not only it delivers energy directly to the reactant, but also heat transfer is more effective than conventional heating, causing a shorter time to complete the reaction. Another advantages are able to reduce the reaction time, obtain high yields, enhance the reaction speed, and make the separation process easier in comparison with conventional heating (Motasemi *et al.,* 2012). Two main mechanisms of microwave heating are dipolar polarization and ionic conduction.

Zhang *et al.* (2014) reported on the parameters affecting microwave irradiation power, namely, temperature, reaction time, the molar ratio of methanol to oil, and catalyst concentration. The maximum yield of 96% from the yellow horn oil was obtained under optimal microwave-assisted method conditions of 500 W microwave irradiation power at 60 °C for 6 min, using 1 wt% catalyst and 6:1 (V/V) molar ratio of methanol to oil (Zhang *et al.,* 2014).

CHAPTER III
EXPERIMENT

3.1 Materials

3.1.1 Chemicals

- Silica (SiO_2) 99.8% supplied by Nippon Aerosil, Japan.
- Triethanolamine (TEA) purchased from QRëc chemical, Thailand.
- Cerium (III) nitrate hexahydrate (($Ce(NO_3)_3.6H_2O$) 99% purchased from Sigma Aldrich, Germany.
- Zirconium (IV) oxide chloride octahydrate ($ZrOCl_2.8H_2O$) 99% purchased from Merck, Germany.
- Oleic acid 90% purchased from Sigma Aldrich, USA.
- Copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) Merck, Germany.
- Sodium hydroxide ($NaOH$) 99% purchased from Lab scan, Thailand.
- Cetyltrimethylammonium bromide (CTAB) by Fluka, Germany.
- Sodium carbonate (Na_2CO_3) 99.8% purchased from Ajax, Thailand.
- Methyl heptadecanoate purchased from Sigma Aldrich, USA.
- N-heptane 99% purchased from Lab scan, Thailand.
- Sulfuric acid 95-98% purchased from Lab scan, Thailand.
- Acetronitrile 99.9% purity purchased from Lab scan, Thailand.
- Ethylene glycol (EG) 99% purity purchased from J.T. Baker, USA.
- Methanol 99.9% purity purchased from Lab scan, Thailand.
- Ethanol 99.9% purity purchased from Lab scan, Thailand.

3.2 Experimental

3.2.1 Synthesis of Silatrane

The mixture of fumed silica (0.1 mole), EG (100 ml), and TEA (0.125 mole) is refluxed at 200 °C under nitrogen atmosphere for 12 h in oil bath. The excess EG and water are removed under vacuum at 110 °C. Then, the product is washed by acetronitrile for removing TEA and EG residues. The silatrane product is vacuum-dried overnight before characterization using TGA and FT-IR. The synthesis follows Wongkasemjit's synthetic method.

3.2.2 Synthesis of MCM-48

Longloilert's synthetic method is followed by dissolving CTAB in 2 M NaOH solution at 50 °C. The mixture is continuously stirred while adding silatrane and the mixture is kept stirring at 50 °C for 1 h. Subsequently, the mixture is transferred to a Teflon-lined stainless steel auto clave and treated with operating temperature of 140 °C for 16 h. Then, the obtained solid product is collected by filtration before drying. The surfactant is removed by calcination at 550 °C for 6 h.

3.2.3 Synthesis of Mesoporous CeO_2-ZrO_2 (MSP CZ)

Mesoporous CeO_2-ZrO_2 is synthesized via nanocasting method using MCM-48 as a template. $Ce(NO_3)_3.6H_2O$ and $ZrOCl_2.8H_2O$ are dissolved in 5 ml of ethanol under stirring at room temperature until obtaining clear solution. MCM-48 is then added into the clear solution with continuous stirring for 4 h at room temperature. The mixture is taken into an oven set at 100 °C to evaporate ethanol. The obtained solid is calcined at 550 °C for 6 h. The product is then removed the template using 2 M NaOH, followed by washing with deionized water until neutral and drying at 80 °C overnight.

3.2.4 Synthesis of CeO_2-ZrO_2 by Co-Precipitate Method (CZ copre)

Pojanavaraphan's synthetic method is followed by dissolving $Ce(NO_3)_3.6H_2O$ and $ZrOCl_2.8H_2O$ in 0.75 to 0.25 molar ratio in 75 and 25 ml of deionized water, respectively. Both solutions are mixed together, adjusted pH to 8 by Na_2CO_3 as a precipitating agent. The mixture is then heated at 80 ° C, followed by aging for 1 h. The product is filtered, washed with boiling distilled water until no ions, and dried at 80 °C overnight before calcination in air at 400 °C for 6 h to obtain catalyst (Pojanavaraphan *et al.*, 2013).

3.2.5 Synthesis of Cu Loaded MSP CZ and Cu Loaded CZ copre

Cu loaded MSP CZ is synthesized via deposition-precipitation (DP) technique. $Cu(NO_3)_2.3H_2O$ is dissolved in deionized water, followed by adding the synthesized MSP CZ. The mixture is continuously stirred for 1 h at room temperature before adjusting to pH 7 using Na_2CO_3 as precipitating agent. The mixture is then heated at 80 °C, followed by 1 h aging. The resulting solid is filtered, washed with boiling distilled water, and dried at 80 °C overnight before calcination in air at 500 °C for 6 h to obtain catalysts.

3.2.6 Treated Catalyst by Sulfuric Acid (SCu-MSP CZ and SCuCZ copre)

Both Cu-MSP CZ and CuCZ copre are treated by various concentrations of sulfuric acid (1.0, 1.5, 1.75, 2.0, 2.25, and 2.5 M). H_2SO_4 is added to 0.2 g of the catalyst and then the mixture is kneaded for 30 min with heating at 100 °C overnight.

3.2.7 Synthesis of Biodiesel

Oleic acid, methanol, and sulfuric acid treated on Cu-MSP CZ catalyst are mixed with stirring for 5 min and the mixture is transferred to a microwave reactor vessel. The reaction temperature and time are varied to find an optimal condition. The obtained mixture is centrifuged to separate catalyst from the biodiesel product mixture. The catalyst is washed by hexane and methanol while biodiesel is extracted and washed by hexane and distillation water, respectively before heating at 80 °C for 1.5 h, followed by characterization using gas chromatography.

3.3 Characterization

The phase of the mesoporous products is characterized on a Rigaku DMAX 2200HV X-ray diffractometer (XRD) with a scanning speed of 1 °C/min and CuKα source (λ= 0.154 Å) in a range of 2θ = 20°–80°. The specific surface area is measured by the Brunauer-Emmett-Teller (BET) method and the pore size distribution is calculated by the Barrett-Joyner-Halenda (BJH) on a Quantasorb Jr. (Autosorb-1). Prior to each analysis, the product is degassed at 250 °C for 12 h. Thermal properties are analyzed by Thermogravimetry (TGA) on Pyris Diamons Perkin Elmer using a heating rate of 10 °C/min under nitrogen atmosphere. Fatty acid methyl esters are determined by Gas chromatography (GC) on Hewlett-Packard 5800 GC equipped with 100 m × 0.25 mm HP–88 fused-silica capillary column. Helium is used as carrier gas with a flow rate of 70 mL/min. The injector temperature is set at 200 °C with a split ratio of 75:1; whereas the detector and the oven temperatures are set at 230 ° and 130 °C, respectively. After isothermal temperature period of 2 min, the temperature is increased to 220 °C with a rate of 2 °C/min and held for 15 min. The entire analysis time is 62 min. The concentration of metal in all samples is analyzed using Atomic absorption spectroscopy (AAS) on Varian Model SpectraAA30 equipped with a GTA 110 graphite furnace and deuterium lamp. The structure and the composition of FAME are determined by a Nicolet Nexus 670 Fourier transform infrared spectrometer (FT-IR) at room temperature.

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Characterization of Silatrane Precursor

Figure 4.1a shows FTIR spectrum of silatrane. It is consistent with the result of the previous work (Charoenpinijkarn *et al.,* 2001), composing of C-H stretching (2800–2976 cm^{-1}), C-H bending (1380–1460 cm^{-1}), C-N (1270cm^{-1}), Si-O-CH_2 (1015-1085 cm^{-1}), C-O (1013-1070 cm^{-1}), Si-O-CH (970,883 cm^{-1}) and Si-N stretching (560-590 cm^{-1}). Thermogram of silatrane in Figure 4.1b shows the weight loss at 350 °C with 22.0% of ceramic yield, corresponding to the amount of silicon dioxide (SiO_2).

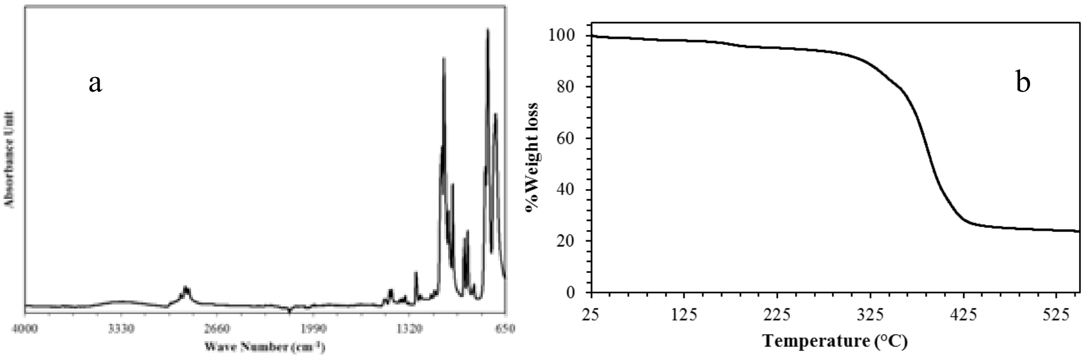

Figure 4.1 a) FTIR spectrum and b) TGA of silatrane precursor.

4.2 Characterization of MCM-48

4.2.1 X-Ray Diffraction (XRD)

XRD pattern of MCM-48 in Figure 4.2 corresponds to the results observed previously, composing of 4 peaks at {211}, {220}, {420}, and {332}. The pattern shows three dimensional cubic structure, as described by Longloilert and coworkers (Longloilert *et al.,* 2011).

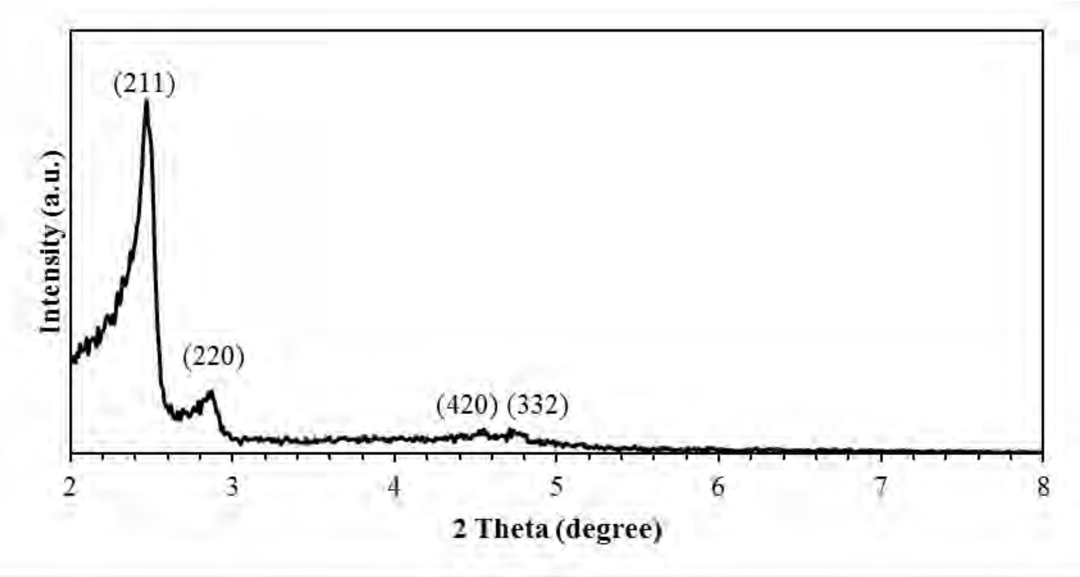

Figure 4.2 Small-angle XRD pattern of MCM-48.

4.2.2 N_2 Adsorption/Desorption Isotherms

N_2 adsorption/desorption isotherms of MCM-48 (Figure 4.3a) shows Type IV isotherm, as defined by IUPAC classification, confirming mesoporous structure of MCM-48. In addition, the pore size distribution around 3.62 nm (Figure 4.3b), and surface area about 1,870 m^2/g confirm characteristics of the mesoporous structure.

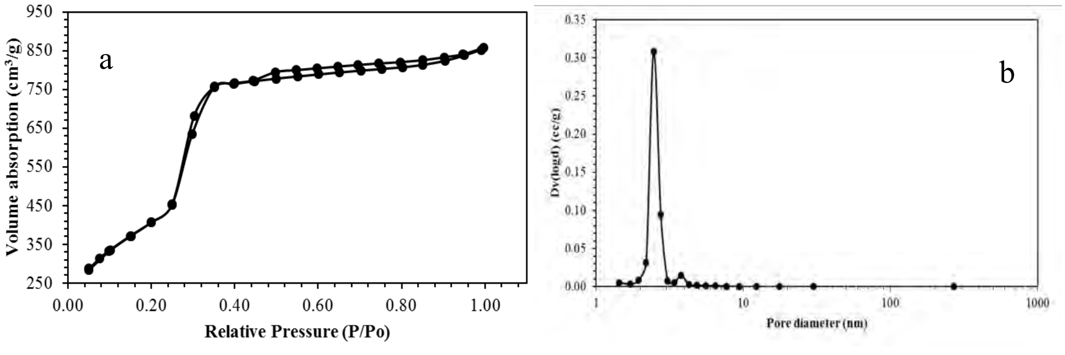

Figure 4.3 a) Nitrogen adsorption-desorption isotherm and b) Pore size distribution of MCM-48.

4.3 Characterization of Ceria-Zirconia Support

4.3.1 Mesoporous Ceria-Zirconia Support Synthesized by Nanocasting Method (MSP CZ)

XRD pattern of mesoporous CeO_2-ZrO_2 support (MSP CZ) after removal of MCM-48 template (Figure 4.4) consists of 8 peaks at 2Θ = 28.49, 32.90, 47.52, 56.39, 59.14, 69.00, 76.66, and 78.93°, which correspond to fluorite structure of CeO_2-ZrO (Zhang *et al.,* 2006; Pojanavaraphan *et al*., 2013).

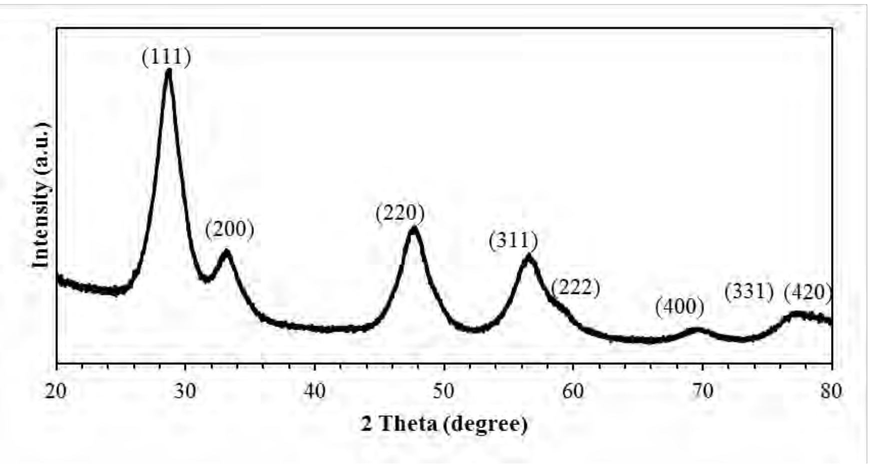

Figure 4.4 XRD pattern of mesoporous CeO_2-ZrO_2 support.

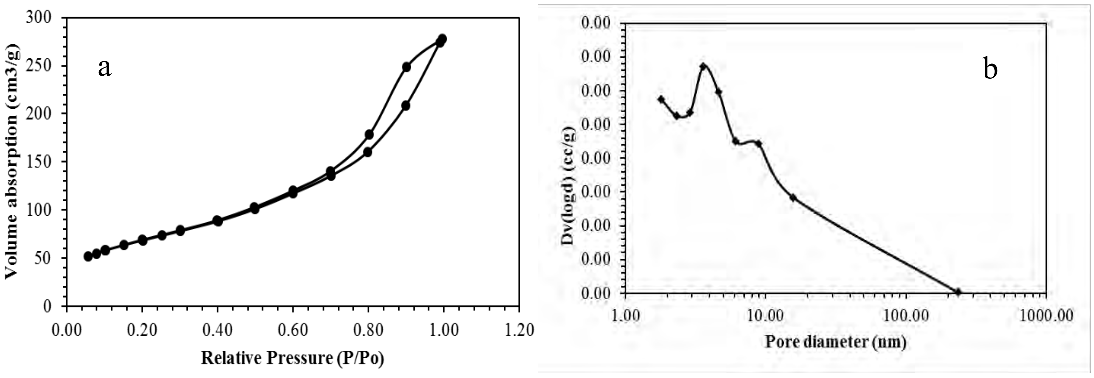

Figure 4.5 a) N_2 adsorption-desorption isotherm and b) Pore size distribution of mesoporous CeO_2-ZrO_2 support.

4.3.2 Ceria-Zirconia Support Synthesized by Co-Precipitating Method (CZ copre)

The XRD pattern of CZ copre in Figure 4.6 shows main 8 peaks as MSP CZ, indicating fluorite structure similar to MSP CZ (Pojanavaraphan *et al.*, 2013).

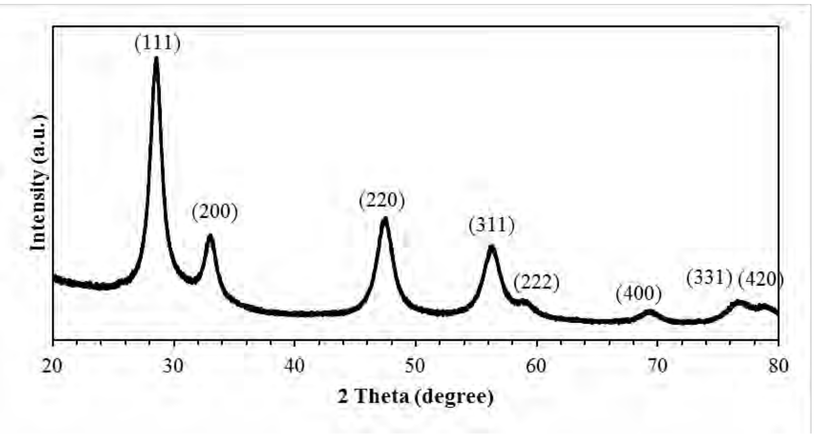

Figure 4.6 XRD pattern of CeO_2-ZrO_2 support.

CZ copre presents a type IV isotherm with hysteresis loop and surface area of 95.3 m^2/g, as shown in Figure 4.7a. This result indicates mesoporous material. However, Figure 4.7b shows the pore size distribution around 3.62 nm. The surface shows with much lower surface area than MSP CZ because MSP CZ is synthesized by nanocasting process using MCM-48 template, resulting in more ordered structure that affects to high surface area (Ji *et al.*, 2008).

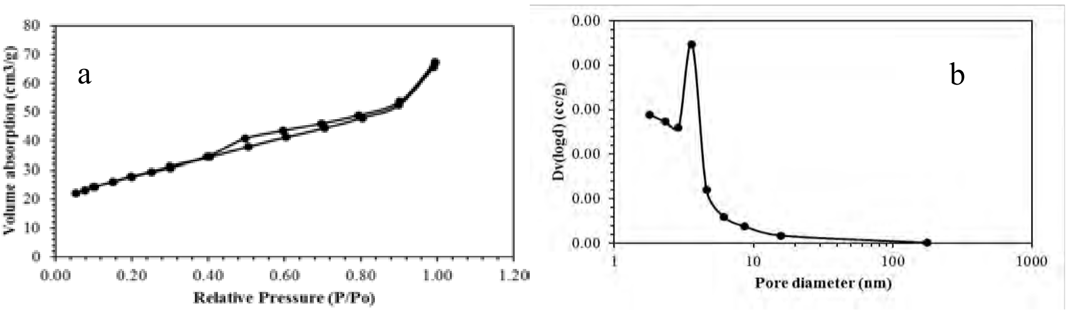

Figure 4.7 a) N_2 adsorption-desorption isotherm and b) Pore size distribution of CeO_2-ZrO_2 support.

4.4 Characterization of Cu-CZ

4.4.1 CuO/ Mesoporous Ceria-Zirconia Support (Cu-MSP CZ

The XRD pattern of Cu-MSP CZ in Figure 4.8 consists of 8 peaks, consistent with the XRD pattern of the pure MSP CZ, at 2ϴ = 28.49, 32.90, 47.52, 56.39, 59.14, 69.00, 76.66, and 78.93° (Zhang *et al.,* 2006; Pojanavaraphan *et al.*, 2013).

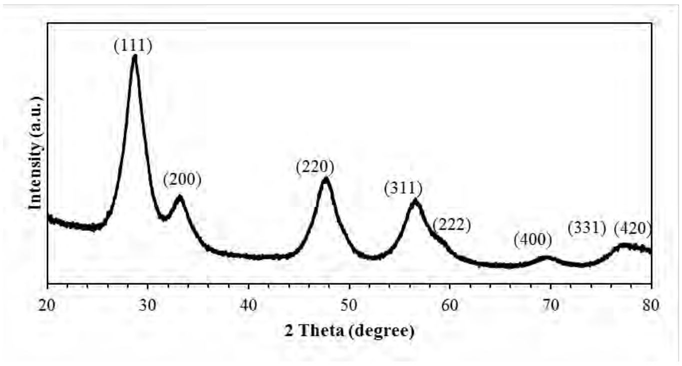

Figure 4.8 XRD pattern of Cu-MSP CZ.

N_2 adsorption-desorption isotherm of Cu-MSP CZ in Figure 4.9a shows that Cu-MSP CZ is also a mesoporous material with surface area and pore size distribution in Figure 4.9b of 176.2 m^2/g and 3.62 nm, respectively. However, the surface area of Cu-MSP CZ is less than the pure MSP CZ because Cu species disperse on the surface of MSP CZ and block the pores, causing a decrease of the surface area and an increase of the pore size distribution.

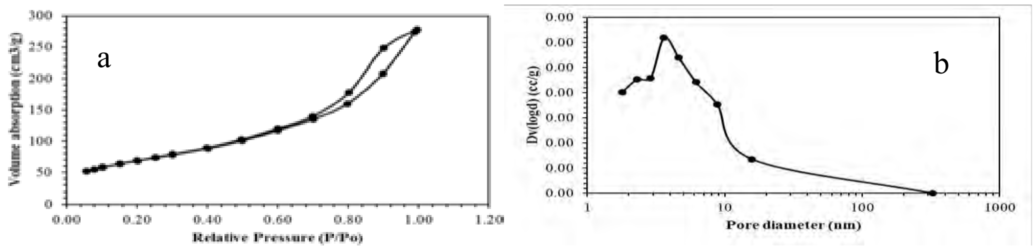

Figure 4.9 a) N_2 adsorption-desorption isotherm and b) Pore size distribution of mesoporous CuO/CeO_2-ZrO_2.

4.4.2 CuO/ Ceria-Zirconia Support (CuCZ copre)

XRD pattern of CuCZ copre in Figure 4.10 rather consists of 10 peaks at 2Θ = 28.49, 32.90, 47.52, 56.39, 59.14, 69.00, 76.66, and 78.93°, in which the main peaks exhibit the fluorite structure of the CZ support and the other two peaks at 35.53 and 38.70° present the agglomeration of Cu species. Those planes are Tenorite (CuO) and Cuprite (Cu_2O) structures, resulting in a lower surface area than Cu-MSP CZ (Zou *et al*., 2006; Jia *et al*., 2010).

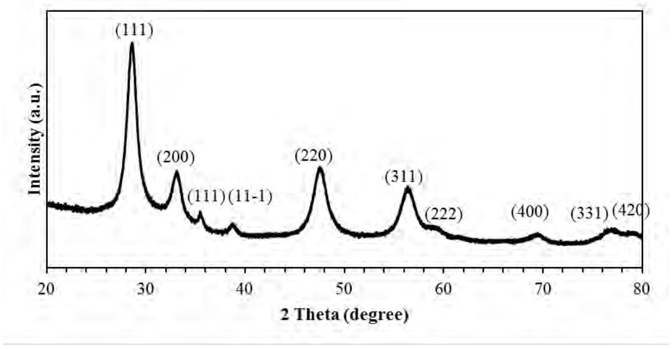

Figure 4.10 XRD pattern of CuCZ copre.

N_2 adsorption-desorption isotherm of CuCZ copre in Figure 4.11a again shows mesoporous material with surface area and pore size distribution in Figure 11b of 77.3 m^2/g and 3.62 nm, respectively. It is worth noting that the surface area of CuCZ copre is less than CZ copre due to agglomeration and blockage of Cu species on the surface of CZ copre that reduce surface area of CZ copre (Jia *et al*., 2010).

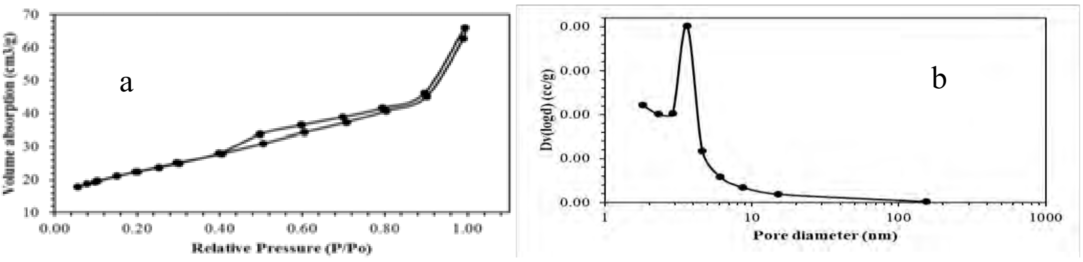

Figure 4.11 a) N_2 adsorption-desorption isotherm and b) Pore size distribution of CuCZ copre.

4.5 Biodiesel Production

The catalytic activity of the synthesized catalysts is investigated on esterification reaction. The reactants for the esterification reaction are oleic acid and methanol, the concentration of sulfuric acid, molar ratio of methanol to oleic acid, reaction temperature, reaction time, %loading of the catalyst, and reusability of the catalyst are studied.

4.5.1 Effect of Sulfuric Acid Concentration Treated on Cu-CZ

From Figure 4.12, it can be observed that the increase of H_2SO_4 concentration from 1.0 to 2.0 M causes the increase of %FAME from 61.3 to 85.6% for SCu-MSP CZ and from 71.2 to 81.2% for SCuCZ copre. In this case, 2.0 M H_2SO_4 is optimum condition since H_2SO_4 concentrations beyond 2.5 M only result in %FAME constant. The reason is that the increasing of H_2SO_4 concentration treated on the synthesized catalyst causes fast progress of esterification reaction and high amount of water, as byproduct, which can deactivate the active site of the catalyst (Shu *et al.*, 2010; Grecea *et al.*, 2012; Patel *et al.*, 2013).

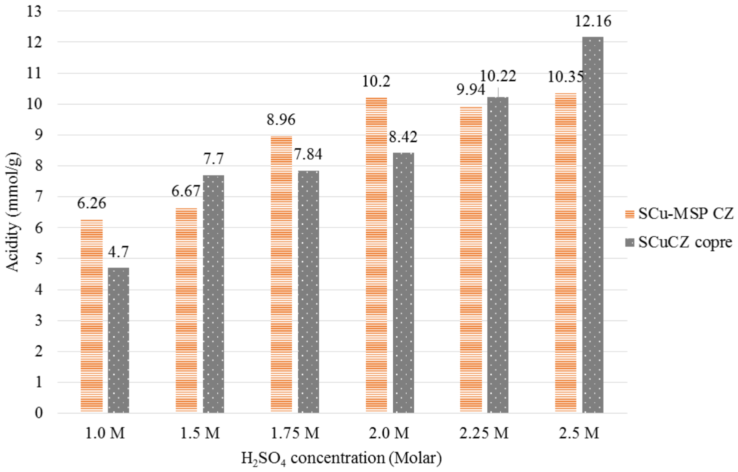

Figure 4.12 Effect of sulfuric acid concentration using 3%wt of SCu-MSP CZ and SCuCZ copre on %FAME at 60 °C for 1h and 12:1 methanol:oleic acid.

4.5.2 Effect of Molar Ratio of Methanol to Oleic Acid

The molar ratio of methanol to oleic acid is one of the most important parameter, and in this study (Figure 4.13), for SCu-MSP CZ, the molar ratio of methanol to oleic acid is varied from 9:1 to 12:1. It is found that %FAME is increased from 76.2 to 86.4% and from 82.3 to 87.4% for SCuCZ copre when the molar ratio of methanol to oleic acid is varied from 9:1 to 15:1. These results indicate that excess methanol affects the increase of %FAME. However, the ratios more than 12:1 for SCu-MSP CZ and 15:1 for SCuCZ copre cause %FAME to decrease because too much methanol is adsorbed on the catalyst surface and limit the contact of the active site. (Motasemi *et al*., 2012; Zhang *et al*., 2012; Liu *et al*., 2013).

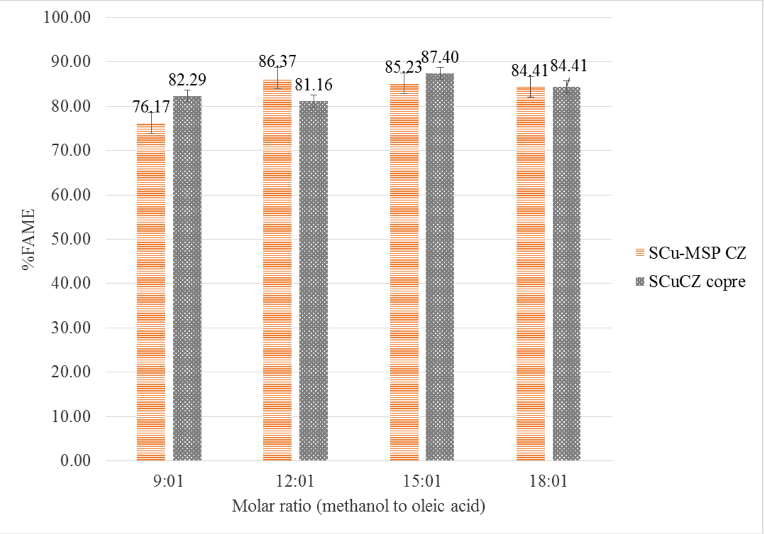

Figure 4.13 Effect of methanol to oleic acid molar ratio using 3%wt of 2.0 M SCu-MSP CZ and SCuCZ copre on %FAME at 60 °C for 1h.

4.5.3 Effect of Reaction Temperature

Generally, the reaction temperature is set at higher than 60 °C to reduce the viscosity of the reactants (Zhang *et al*., 2014). In this study, see Figure 4.14, the reaction is thus varied from 60°, 70°, 80°, to 90 °C. The %FAME of SCu-MSP CZ shows around 86.4% at 60 °C and slightly increases to 88.8% when the reaction temperature is increased to 90 °C. This means that the temperature parameter has not much effect on SCu-MSP CZ which has ordered structure, high surface area, and more active site. For SCuCZ copre, when the temperature increases from 60° to 70 °C, %FAME is increased to 87.4%, and slightly decreased to 87% when heating the reaction to 90 °C. It is stated that %FAME decreased because the temperature is much over boiling point of methanol, causing bubbles to obstruct the forward reaction (Berrios *et al.,* 2007; Zu *et al*., 2009).

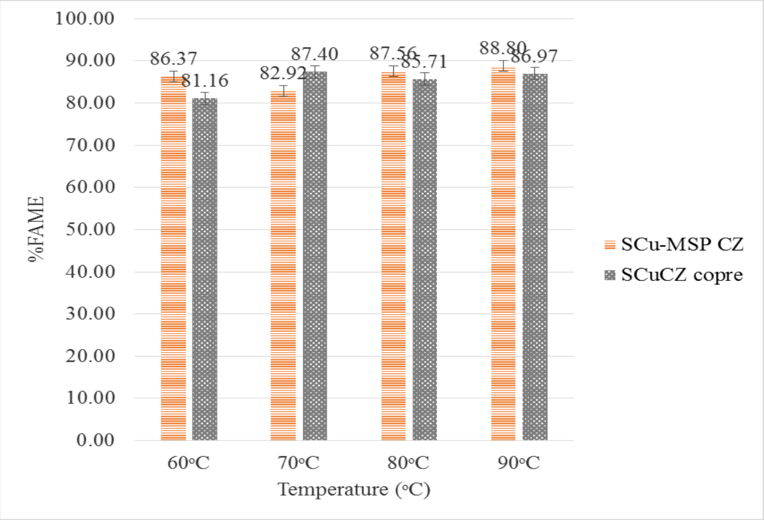

Figure 4.14 Effect of reaction temperature using 3%wt of 2.0 M SCu-MSP CZ and SCuCZ copre on %FAME for 1h and 12:1 methanol:oleic acid.

4.5.4 Effect of Reaction Time

Figure 4.15 shows that %FAME increases as increasing the reaction time until 1.5 h and becomes constant when prolonging the reaction time. For SCu-MSP CZ, %FAME is increased from 74.6 to 89.1% when reaction time increases from 30 min to 1.5 h. %FAME clearly increases in the period of 30 min to 1 h and slightly increases after that. When the reaction time increases from 1.5 to 2 h, %FAME becomes steady. In contrast, for SCuCZ copre, the yield gradually increases from 30 min to 2 h. The highest %FAME of SCuCZ copre is slightly lower than that of %FAME of SCu-MSP CZ. Therefore, the optimum condition of the reaction time selected is 1.5 h (Chongkhong *et al*., 2007; Patel *et al*., 2013; Doyle *et al*., 2014; Venkatesh *et al*., 2014).

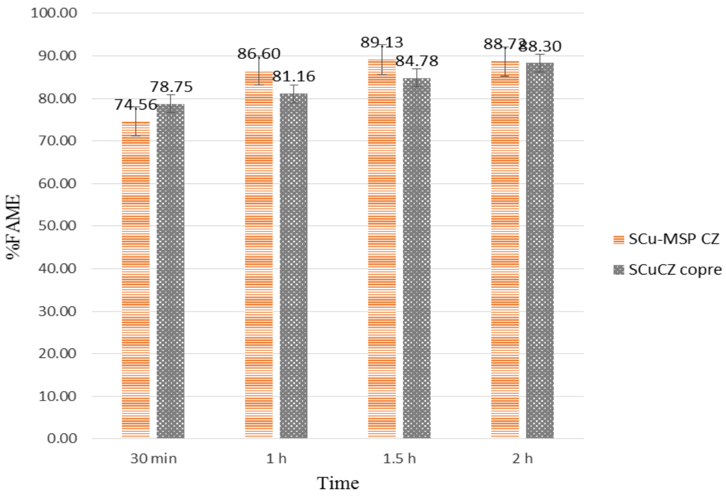

Figure 4.15 Effect of reaction time using 3%wt of 2.0 M SCu-MSP CZ and SCuCZ copre on %FAME at 60 °C and 12:1 methanol:oleic acid for 1.5h.

4.5.5 Effect of Amount of Catalyst

The amount of SCu-MSP CZ and SCuCZ copre catalyst for esterification reaction was studied by using 12:1 molar ratio of methanol:oleic acid for 1.5 h at 60 °C. These catalysts showed dramatical increase in %FAME when the amount of the catalyst increases from 3 to 5% wt, as shown in Figure 4.16. The increase of the catalyst was sufficient to increase conversion. The %FAME produced by using 5% wt SCu-MSP CZ and SCuCZ copre were 98 and 94%, respectively. When the amount of the catalyst was more than 5% wt, the %FAME decreased to 90% because excess catalyst causes the reversible reaction rapidly (Ghesti *et al.,* 2009; Mazubert *et al.,* 2013). Thus, the optimum of the catalyst amount is 5%wt (Ghesti *et al.,* 2009; Chakraborty *et al.,* 2013; Mazubert *et al.,* 2013; Ong *et al.,* 2014).

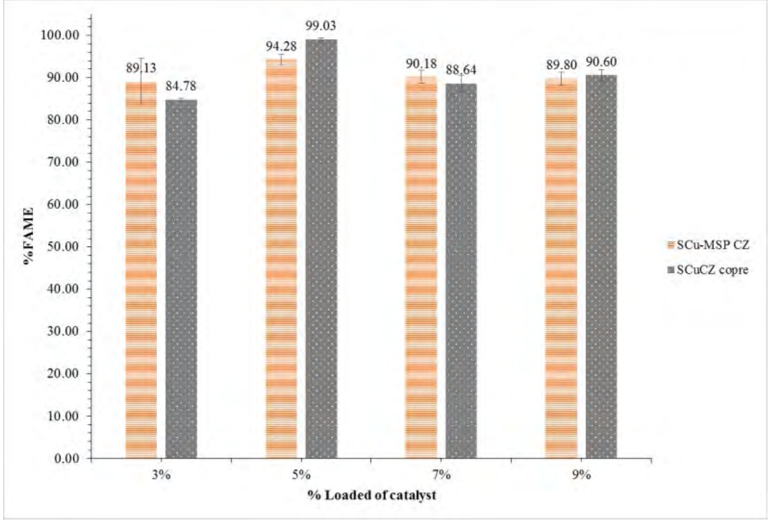

Figure 4.16 Effect of amount of catalyst using 2.0 M SCu-MSP CZ and SCuCZ copre on %FAME at 60 °C and 12:1 methanol:oleic acid for 1.5h.

4.5.6 Effect of Comparison Types of Catalysts

The catalytic activities of SCuCZ copre and SCu-MSP CZ are different because of their physical properties. The pore size of these catalysts is 3.16 nm. The largest dimension of biodiesel, methyl oleate, is 2.5 nm (Granados *et al.*, 2007). The pore size of the catalysts is close to the dimension of biodiesel. Thus, the product and the reactant may have a difficulty to diffuse through the pores. However, the active sites of SCu-MSP CZ locate both on the surface and inside the pore while most active sites of SCuCZ copre were on the surface. Thus, it can be stated that more reaction prefer to occur with SCuCZ, resulting in a higher catalytic activity (Chakraborty *et al.*, 2013).

Figure 4.17 shows %FAME of homogeneous H_2SO_4 catalyst, giving 90% which is higher than those of MSP CZ and CZ copre because homogeneous H_2SO_4 catalyst easily reacts with reactant, oleic acid and methanol. The MSP CZ and CZ copre catalysts were thus treated with H_2SO_4 to increase their activity, active site, for the reaction. The %FAME results showed that both S-MSP CZ and SCZ copre were close to that of homogeneous H_2SO_4 catalyst. Although SCZ copre and S-MSP CZ had less chance to contact with the reactants, the carboxylic group of the reactant moiety could interact with Ce(IV) and Zr(IV) sites of the catalyst, leading to activation of carbonyl group. Moreover, Cu itself loaded on the supports by DP method also increased acidity of the catalyst, resulting in a higher activity of SCu-MSP-CZ and SCuCZ copre catalysts than those of S-MSP CZ and SCZ copre. The SCuCZ copre catalyst under mild condition presents the highest %FAME of 99% (Fernández María *et al.,* 2007; Ghesti *et al.,* 2009; Banerjee *et al.,* 2015).

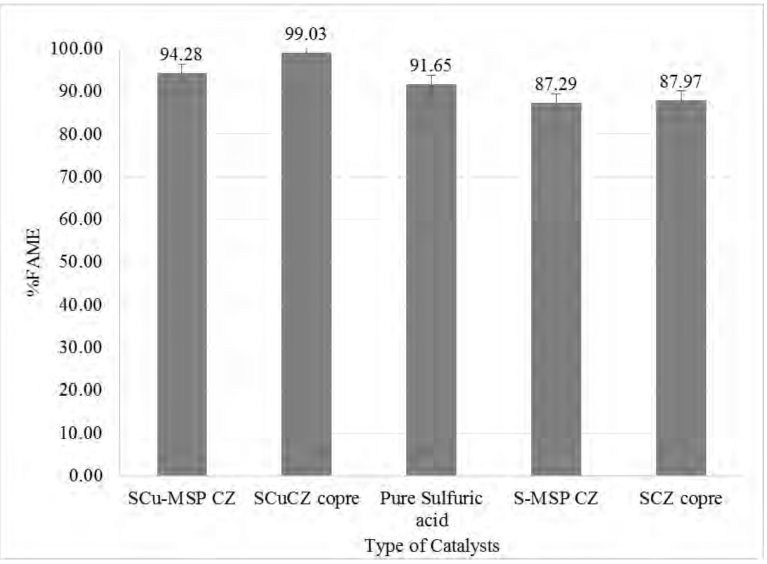

Figure 4.17 Effect of catalyst types using 5%wt of 2.0 M SCu-MSP CZ and SCuCZ copre on %FAME at 60 °C for 1.5h and 12:1 methanol:oleic acid.

4.5.7 Effect of Reusability

The reusability of the catalysts was evaluated after reaction. The used catalysts were separated from the product mixture, washed with hexane and methanol to remove the polar and non-polar reactants or products trapped on the surface or inside the catalysts, and dried in oven at 60 °C. The reusability of the catalysts was investigated for 3 cycles, as shown in Figure 4.18. As can be seen, the activity of the catalysts significantly decreased due to the decrease of the active site on the catalyst. The product yield decreased from 96 to 67, and 30%. The acidity of the catalysts was examined using 2.25 M NaOH both before and after each testing, shown in Figure 4.19. The acidity of the catalysts decreased as %FAME of each testing because H_2SO_4 was leached out. Obstructing the active sites by reactants is another reason to cause the decrease of % FAME (Grecea *et al.*, 2012; Zhang *et al.*, 2014; Banerjee *et al.*, 2015).

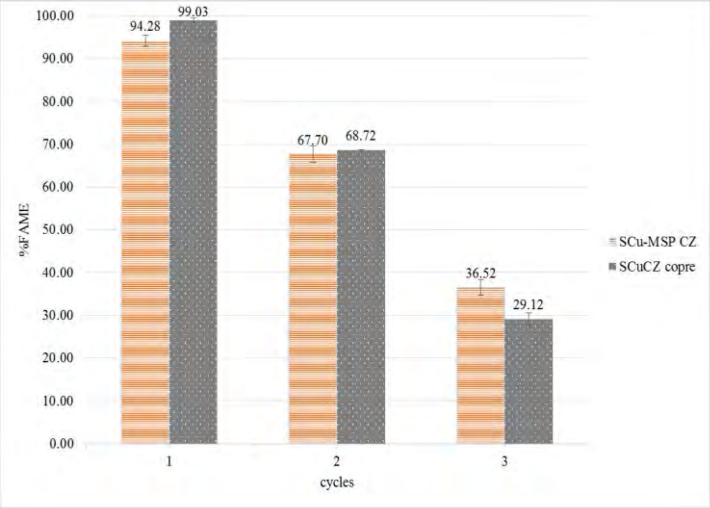

Figure 4.18 Effect of resuability using 5%wt of 2.0 M SCu-MSP CZ and SCuCZ copre on %FAME at 60 °C and 12:1 methanol:oleic acid for 1.5h.

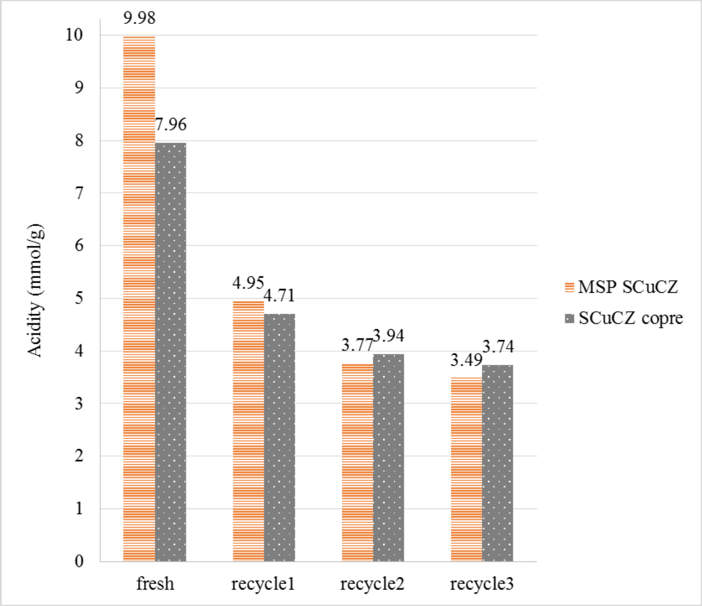

Figure 4.19 Acidity of the catalysts for reusability.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Cu-MSP-CZ and CuCZ copre catalysts were synthesized via nanocasting process using MCM-48 as template and co-precipitating method, respectively, for esterification reaction. The XRD result of CuCZ copre exhibits diffraction peaks of Cu species while that of Cu-MSP-CZ showed no Cu species peaks. The MSP-CZ support provided the higher specific surface area than CZ copre. Both Cu-MSP-CZ and CuCZ copre catalysts were treated with sulfuric acid by wet impregnation method for increasing acidity of the catalysts.

The catalytic acitivity was examined via esterification reaction using oleic acid and methanol as reactants. The optimal conditions providing high %FAME were to use 5 wt% catalyst treated with 2.0 M sulfuric acid, 12:1 molar ratio of methanol to oleic acid at 60 ^{o}C for 1.5 h, giving 99 and 94.3% FAME for SCuCZ copre and SCu-MSP-CZ, respectively. Reusability of the catalyst resulted in leaching out of H_2SO_4, implying that these catalysts are not suitable to reuse. However, SCu-MSP-CZ and SCuCZ copre provided more efficient than S-MSP-CZ, SCZ copre, and pure H_2SO_4.

5.2 Recommendation

The stability and changing the catalyst of the modified catalyst should also be studied to enhance the efficiency of the catalytic activity for esterification reaction.

APPENDICES

Appendix A Gas Chromatography (GC)

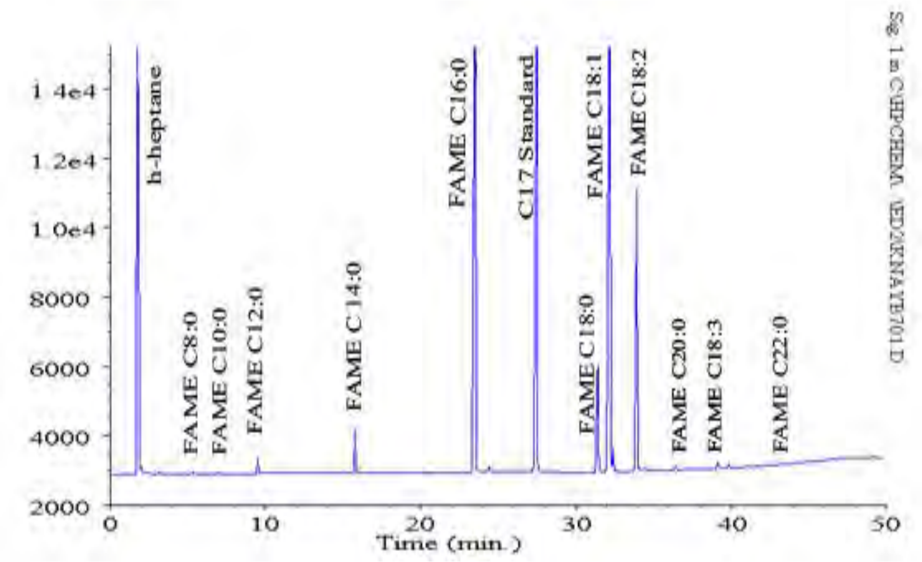

Figure A1 Chromatogram of fatty acid methyl ester (FAMEs) in biodiesel.

The methyl ester yield and conversion are determined using Equations (B.1).

$$C = \frac{\left(\sum A\right) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \qquad \text{(B.1)}$$

C	Methyl ester content or fatty acid methyl esters (FAMEs)
$\sum A$	The overall area of methyl esters from C_{14} to C_{24}
A_{EI}	The peak area aligned with methylheptadecanoate solution
C_{EI}	Concentration in mg/ml of methyl heptadecanoate solution
V_{EI}	Volume of methyl heptadecanoate solution
m	Weight in mg of the sample

Table A1 %FAME of SCu-MSP CZ treated by sulfuric acid at various concentrations

Sample (condition)	Sample weight (g)	Peak area of ester	Peak area of standard	Standard conc.	Standard volume (ml)	Peak area of FAME	%FAME	Avg. %FAME	SD
1.0 M SCu-MSP-CZ (60^{o}C, 1 h, 12:1, 3%wt)	0.0123	170370	38626	0.2506g/25ml	0.25	131744	69.49	61.29	11.60
1.5 M SCu-MSP-CZ (60^{o}C, 1 h, 12:1, 3%wt)	0.0125	114945	23473	0.2506g/25ml	0.25	91472	78.13	76.80	2.17
	0.0515	314857	65292	1.0001g/100ml	1	249565	74.29		
1.75 M SCu-MSP-CZ (60^{o}C, 1 h, 12:1, 3%wt)	0.0125	105628	21506	1.0001g/100ml	0.5	84122	78.42	77.95	0.63
	0.0254	493545	102263			391282	75.39		
	0.0252	457292	92631			364661	78.19		
	0.0251	415340	85228			330112	77.23		
2.0 M SCu-MSP-CZ (60^{o}C, 1 h, 12:1, 3%wt)	0.0126	99944	19800	0.2506g/25ml	0.25	80144	80.50	85.58	2.77
	0.0125	239150	45486			193664	85.36		
	0.0127	307818	55364			252454	89.98		
	0.0128	157290	29257			128033	85.68		
2.25 M SCu-MSP-CZ (60^{o}C, 1 h, 12:1, 3%wt)	0.0129	315323	60008	1.0001g/100ml	0.5	255315	82.65	82.41	1.22
	0.0252	486391	93472			392919	83.49		
	0.0252	413019	81256			331763	81.09		
2.5 M SCu-MSP-CZ (60^{o}C, 1 h, 12:1, 3%wt)	0.0126	162548	29701	1.0001g/100ml	1	132847	88.26	82.06	4.34
	0.0502	374047	75826			298221	78.42		
	0.0514	278490	55037			223453	79.07		
	0.0507	410533	79825			330708	81.80		

Table A2 %FAME of SCuCZ copre treated by sulfuric acid at various concentrations

Sample (condition)	Sample weight (g)	Peak area of ester	Peak area of standard	Standard conc.	Standard volume (ml)	Peak area of FAME	%FAME	Avg. %FAME	SD
1.0 M SCuCZ copre (60^{o}C, 1 h, 12:1, 3%wt)	0.0126	123019	28931	0.2506g/25ml	0.25	94088	64.66	64.89	0.33
	0.0125	79813	18781			61032	65.12		
1.5 M SCuCZ copre (60^{o}C, 1 h, 12:1, 3%wt)	0.0251	279643	60488	1.0001g/100ml	0.5	219155	72.25	71.50	1.05
	0.0259	295477	63381			232096	70.76		
	0.025	358201	80319			277882	69.26		
1.75 M SCu-MSP-CZ (60^{o}C, 1 h, 12:1, 3%wt)	0.0126	105538	22541	0.2506g/25ml	0.25	82997	73.20	72.70	0.71
	0.0126	188438	40685			147753	72.20		
2.0 M SCuCZ copre (60^{o}C, 1 h, 12:1, 3%wt)	0.0126	105169	20775	0.2506g/25ml	0.25	84394	80.79	81.16	0.75
	0.0129	293414	56185			237229	82.02		
	0.0258	349875	67838	1.0001g/100ml	0.5	282037	80.65		
2.25 SCuCZ copre (60^{o}C, 1 h, 12:1, 3%wt)	0.0128	160180	31300	0.2506g/25ml	0.25	128880	80.58	78.86	2.44
	0.0128	87863	17782		0.25	70081	77.13		
2.5 M SCuCZ copre (60^{o}C, 1 h, 12:1, 3%wt)	0.0125	158893	31299	0.2506g/25ml	0.25	127594	81.73	82.12	0.67

Table A3 %FAME of SCu-MSP CZ using various molar ratios of methanol to oleic acid

Sample (condition)	Sample weight (g)	Peak area of ester	Peak area of standard	Standard conc.	Standard volume (ml)	Peak area of FAME	%FAME	Avg. %FAME	SD
9:1 mol ratio (60^{o}C, 1 h, 3%wt, 2.0 M SCu-MSP-CZ)	0.0127	194094	40419	0.2506g/25ml	0.25	153675	75.0231	76.17	2.91
	0.0125	329024	66276			262748	79.47933		
	0.0255	334189	70045	1.0001g/100ml	0.5	264144	74.02		
12:1 mol ratio (60^{o}C, 1 h, 3%wt, 2.0 M SCu-MSP-CZ)	0.0125	0.0125	45486	0.2506g/25ml	0.25	193664	85.3576	86.37	2.46
	0.0127	0.0127	55364			252454	89.97713		
	0.0128	0.0128	21591			91224	82.71941		
	0.0128	0.0128	29257			128033	85.6768		
15:1 mol ratio (60^{o}C, 1 h, 3%wt, 2.0 M SCu-MSP-CZ)	0.0129	328386	61136	0.2506g/25ml	0.25	267250	84.92	85.23	0.44
	0.0129	422234	73725			348509	91.83		
18:1 mol ratio (60^{o}C, 1 h, 3%wt, 2.0 M SCu-MSP-CZ)	0.013	238884	44945	0.2506g/25ml	0.25	193939	83.18	84.41	1.74
	0.0126	293642	55341			238301	85.64		

Table A4 %FAME of SCuCZ copre using various molar ratios of methanol to oleic acid

Sample (condition)	Sample weight (g)	Peak area of ester	Peak area of standard	Standard conc.	Standard volume (ml)	Peak area of FAME	%FAME	Avg. %FAME	SD
9:1 mol ratio (60^{o}C, 1 h, 3%wt, 2.0 M SCuCZ copre)	0.0126	135329	26269	0.2506g/25ml	0.25	109060	82.57	82.29	1.13
	0.0129	134035	25917			108118	81.04		
	0.0252	457437	92596	1.0001g/100ml	0.5	364841	78.26		
12:1 mol ratio (60^{o}C, 1 h, 3%wt, 2.0 M SCuCZ copre)	0.0126	105169	20775	0.2506g/25ml	0.25	84394	80.79	81.16	0.75
	0.0129	293414	56185			237229	82.02		
	0.0252	325696	65251	1.0001g/100ml	0.5	260445	79.27		
15:1 mol ratio (60^{o}C, 1 h, 3%wt, 2.0 M SCuCZ copre)	0.013	285097	50249	0.2506g/25ml	0.25	234848	90.09	87.40	3.81
	0.0126	285168	54226			230942	84.70		
18:1 mol ratio (60^{o}C, 1 h, 3%wt, 2.0 M SCuCZ copre)	0.013	238884	44945	0.2506g/25ml	0.25	193939	83.18	84.41	1.74
	0.0126	293642	55341			238301	85.64		

Table A5 %FAME of SCu-MSP CZ at various reaction temperatures

Sample (condition)	Sample weight (g)	Peak area of ester	Peak area of standard	Standard conc.	Standard volume (ml)	Peak area of FAME	%FAME	Avg. %FAME	SD
60^{o}C (1 h, 12:1, 3%wt, 2.0 M SCu-MSP-CZ)	0.0125	239150	45486	0.2506g/25ml	0.25	193664	85.36	86.37	2.46
	0.0127	307818	55364			252454	89.98		
	0.0128	157290	29257			128033	85.68		
	0.0517	429922	80168	1.0001g/100ml	1	349754	84.47		
70^{o}C (1 h, 12:1, 3%wt, 2.0 M SCu-MSP-CZ)	0.026	432540	81616	1.0001g/100ml	1	350924	82.77	82.92	1.55
	0.0129	88059	16981	0.2506g/25ml	0.25	71078	81.31		
	0.0128	138263	26031			112232	84.41		
	0.0128	149776	28573			121203	83.05		
80^{o}C (1 h, 12:1, 3%wt, 2.0 M SCu-MSP-CZ)	0.013	122865	21284	0.2506g/25ml	0.25	101581	92.00	87.17	2.53
	0.0128	204801	38838			165963	83.66		
	0.0129	181082	32859			148223	87.63		
	0.0129	181082	32859			148223	86.96		
90^{o}C (1 h, 12:1, 3%wt, 2.0 M SCu-MSP-CZ)	0.013	189162	33690	0.2506g/25ml	0.25	155472	88.96	87.17	2.53
	0.0127	168324	31004		0.25	137320	85.38		

Table A6 %FAME of SCuCZ copre at various reaction temperatures

Sample (condition)	Sample weight (g)	Peak area of ester	Peak area of standard	Standard conc.	Standard volume (ml)	Peak area of FAME	%FAME	Avg. %FAME	SD
60^{o}C (1 h, 12:1, 3%wt, 2.0 M SCuCZ copre)	0.0126	105169	20775	0.2506g/25ml	0.25	84394	80.79	81.16	0.75
	0.0129	293414	56185			237229	82.02		
	0.0258	349875	67838	1.0001g/100ml	0.5	282037	80.65		
70^{o}C (1 h, 12:1, 3%wt, 2.0 M SCuCZ copre)	0.0128	173358	31939	0.2506g/25ml	0.25	141419	86.69	87.40	1.38
	0.0129	173224	31905		0.25	141319	86.05		
	0.0129	181082	32859		0.25	148223	87.63		
	0.0124	480125	88667		0.25	391458	89.22		
80^{o}C (1 h, 12:1, 3%wt, 2.0 M SCuCZ copre)	0.0124	200396	37379	0.2506g/25ml	0.25	163017	88.14	85.71	3.43
	0.013	103163	19389		0.25	83774	83.29		
90^{o}C (1 h, 12:1, 3%wt, 2.0 M SCuCZ copre)	0.013	220682	40755	0.2506g/25ml	0.25	179927	87.81	86.97	1.18
	0.0126	135786	25470		0.25	110316	86.14		

Table A7 %FAME of SCu-MSP CZ at various reaction times

Sample (condition)	Sample weight (g)	Peak area of ester	Peak area of standard	Standard conc.	Standard volume (ml)	Peak area of FAME	%FAME	Avg. %FAME	SD
30 min (60^{o}C, 12:1, 3%wt, 2.0 M SCu-MSP-CZ)	0.013	82395	15099	0.2506g/25ml	0.25	67296	85.92	74.56	2.67
	0.0128	95435	19428			76007	76.59		
	0.0129	135895	27796			108099	75.55		
	0.0129	143176	30577			112599	71.54		
1 h (60^{o}C, 12:1, 3%wt, 2.0 M SCu-MSP-CZ)	0.0125	239150	45486	0.2506g/25ml	0.25	193664	85.36	86.60	2.96
	0.0127	307818	55364			252454	89.98		
	0.0517	429922	80168	1.0001g/100ml	1	349754	84.47		
1.5 h (60^{o}C, 12:1, 3%wt, 2.0 M SCu-MSP-CZ)	0.0126	119343	20602	0.2506g/25ml	0.25	98741	95.32	89.13	5.36
	0.0126	207543	38915			168628	86.18		
	0.0126	93251	17534			75717	85.89		
2 h (60^{o}C, 12:1, 3%wt, 2.0 M SCu-MSP-CZ)	0.0129	100450	17906	0.2506g/25ml	0.25	82544	89.55	88.72	1.92
	0.0125	101977	18597			83380	89.89		
	0.0125	234149	44327			189822	85.85		
	0.0126	502971	91368			411603	89.60		

Table A8 %FAME of SCuCZ copre at various reaction times

Sample (condition)	Sample weight (g)	Peak area of ester	Peak area of standard	Standard conc.	Standard volume (ml)	Peak area of FAME	%FAME	Avg. %FAME	SD
30 min (60^{o}C, 12:1, 3%wt, 2.0 M SCuCZ copre)	0.0127	121123	23861	0.2506g/25ml	0.25	97262	80.43	78.75	2.37
	0.013	114188	22845			91343	77.08		
1 h (60^{o}C, 12:1, 3%wt, 2.0 M SCuCZ copre)	u	105169	20775	0.2506g/25ml	0.25	84394	80.79	81.16	0.75
	0.0129	293414	56185			237229	82.02		
	0.0258	349875	67838	1.0001g/100ml	1	282037	80.65		
1.5 h (60^{o}C, 12:1, 3%wt, 2.0 M SCuCZ copre)	0.0128	118893	22254	0.2506g/25ml	0.25	96639	85.02	84.78	0.33
	0.013	106931	19854			87077	84.55		
2 h (60^{o}C, 12:1, 3%wt, 2.0 M SCuCZ copre)	0.0129	109703	109703	0.2506g/25ml	0.25	89765	87.46	88.30	1.17
	0.013	96668	96668			79266	87.81		
	0.013	100972	100972			83102	89.64		

Table A9 %FAME of SCu-MSP CZ at various amount of catalyst

Sample (condition)	Sample weight (g)	Peak area of ester	Peak area of standard	Standard conc.	Standard volume (ml)	Peak area of FAME	%FAME	Avg. %FAME	SD
3%wt (60^{o}C, 1.5h, 12:1, 2.0M SCu-MSP-CZ)	0.0126	119343	20602	0.2506g/25ml	0.25	98741	95.32	89.13	5.36
	0.0126	207543	38915			168628	86.18		
	0.0126	93251	17534			75717	85.89		
5%wt (60^{o}C, 1.5h, 12:1, 2.0M SCu-MSP-CZ)	0.0127	94596	16452	0.2506g/25ml	0.25	78144	93.69	94.28	1.31
	0.0127	206673	36048			170625	93.36		
	0.013	119487	20012			99475	95.78		
	0.0126	122778	20547			102231	98.92		
7%wt (60^{o}C, 1.5h, 12:1, 2.0M SCu-MSP-CZ)	0.0124	110427	21086	0.2506g/25ml	0.25	89341	85.59	90.18	1.53
	0.013	122250	21512			100738	90.24		
	0.0127	140794	25632			115162	88.62		
	0.013	244193	42411			201782	91.68		
9%wt (60^{o}C, 1.5h, 12:1, 2.0M SCu-MSP-CZ)	0.0126	277218	49688	0.2506g/25ml	0.25	227530	91.04	89.80	1.53
	0.0128	121724	21721			100003	90.10		
	0.0126	115080	21291			93789	87.58		
	0.0127	147446	26386			121060	90.50		

Table A10 %FAME of SCuCZ copre at various amount of catalyst

Sample (condition)	Sample weight (g)	Peak area of ester	Peak area of standard	Standard conc.	Standard volume (ml)	Peak area of FAME	%FAME	Avg. %FAME	SD
3%wt (60^{o}C, 1.5h, 12:1, 2.0M SCuCZ copre)	0.0128	118893	22254	0.2506g/25ml	0.25	96639	85.02	84.78	0.33
	0.013	106931	19854			87077	84.55		
5%wt (60^{o}C, 1.5h, 12:1, 2.0M SCuCZ copre)	0.0124	356977	60689	0.2506g/25ml	0.25	296288	98.63	99.03	0.41
	0.013	117251	19031			98220	99.45		
	0.0128	317891	52459			265432	99.02		
7%wt (60^{o}C, 1.5h, 12:1, 2.0M SCuCZ copre)	0.0126	88725	16236	0.2506g/25ml	0.25	72489	88.76	88.64	2.00
	0.0125	70959	13010			57949	89.26		
	0.0125	78633	14877			63756	85.88		
	0.0128	125178	22227			102951	90.65		
9%wt (60^{o}C, 1.5h, 12:1, 2.0M SCuCZ copre)	0.0127	94054	16570	0.2506g/25ml	0.25	77484	92.23	90.60	1.30
	0.0125	99781	18320			81461	89.11		
	0.0126	111893	20092			91801	90.84		
	0.0126	141273	25507			115766	90.23		

Table A11 Reusability of SCu-MSP-CZ for FAME

Sample (condition)	Sample weight (g)	Peak area of ester	Peak area of standard	Standard conc.	Standard volume (ml)	Peak area of FAME	%FAME	Avg. %FAME	SD
1 cycle (60^{o}C, 1.5h, 12:1, 5%wt 2.0M SCu-MSP-CZ)	0.0127	94596	16452	0.2506g/25ml	0.25	78144	93.69	94.28	1.31
	0.0127	206673	36048			170625	93.36		
	0.013	119487	20012			99475	95.78		
	0.0126	122778	20547			102231	98.92		
2 cycles (60^{o}C, 1.5h, 12:1, 5%wt 2.0M SCu-MSP-CZ)	0.0128	235375	53629	0.2506g/25ml	0.25	181746	66.32	67.70	1.94
	0.0125	234621	52763			181858	69.07		
3 cycles (60^{o}C, 1.5h, 12:1, 5%wt 2.0M SCu-MSP-CZ)	0.0127	104085	35670	0.2506g/25ml	0.25	68415	37.83	36.52	1.86
	0.0128	49719	17763			31956	35.21		

Table A12 Reusability of SCuCZ copre for FAME

Sample (condition)	Sample weight (g)	Peak area of ester	Peak area of standard	Standard conc.	Standard volume (ml)	Peak area of FAME	%FAME	Avg. %FAME	SD
1 cycle (60^{o}C, 1.5h, 12:1, 5%wt 2.0M SCuCZ copre)	0.0124	356977	60689	0.2506g/25ml	0.25	296288	98.63	99.03	0.41
	0.013	117251	19031			98220	99.45		
	0.0128	317891	52459			265432	99.02		
2 cycles (60^{o}C, 1.5h, 12:1, 5%wt 2.0M SCuCZ copre)	0.0129	105448	23230	0.2506g/25ml	0.25	82218	68.73	68.72	0.02
	0.0129	243898	53744			190154	68.71		
3 cycles (60^{o}C, 1.5h, 12:1, 5%wt 2.0M SCuCZ copre)	0.0127	70734	29151	0.2506g/25ml	0.25	41583	28.14	29.12	1.39
	0.013	50029	19526			30503	30.10		

Table A13 Comparison types of catalyst for FAME

Sample (condition)	Sample weight (g)	Peak area of ester	Peak area of standard	Standard conc.	Standard volume (ml)	Peak area of FAME	%FAME	Avg. %FAME	SD
2.0M SCu-MSP-CZ (5%wt, 60^{o}C, 1.5h, 12:1)	0.0127	94596	16452	0.2506g/25ml	0.25	78144	93.69	94.28	1.31
	0.0127	206673	36048			170625	93.36		
	0.013	119487	20012			99475	95.78		
	0.0126	122778	20547			102231	98.92		
2.0M SCuCZ copre (5%wt, 60^{o}C, 1.5h, 12:1)	0.0124	356977	60689	0.2506g/25ml	0.25	296288	98.63	99.03	0.41
	0.013	117251	19031			98220	99.45		
	0.0128	317891	52459			265432	99.02		
Pure H_2SO_4 (5%wt, 60^{o}C, 1.5h, 12:1)	0.013	70884	11807	0.2506g/25ml	0.25	59077	96.41	91.65	3.19
	0.0127	129995	23386			106609	89.92		
	0.0129	144338	25670			118668	89.77		
	0.0127	141426	25309			116117	90.50		
2.0M S-MSP-CZ (5%wt, 60^{o}C, 1.5h, 12:1)	0.0128	226381	40149	0.2506g/25ml	0.25	186232	90.78	87.29	2.89
	0.0125	142869	26394			116475	88.44		
	0.0129	118045	22096			95949	84.32		
	0.0126	220197	41493			178704	85.62		
2.0M SCZ copre (5%wt, 60^{o}C, 1.5h, 12:1)	0.013	145347	26401	0.2506g/25ml	0.25	118946	86.81	87.97	2.39
	0.0129	101132	18779			82353	85.16		
	0.0128	184736	33052			151684	89.81		
	0.0127	195110	35045			160065	90.09		

Appendix B Acid-Base Titration Method

The acidity of catalysts was calculated as following, Equation (A.2)

$$c(H^+) = \frac{c(OH) \times \Delta V}{m} \qquad (A.2)$$

Where $c(H^+)$ = the acid quantity of sulfonated samples
$c(OH^-)$ = the concentration of the NaOH solution
ΔV = the volume of the NaOH solution consumed in titration
M = the quality of the catalyst samples in ultrasonic oscillation reaction

CURRICULUM VITAE

Name: Mr. Wasupon Wongvitvichot

Date of Birth: December 16, 1992

Nationality: Thai

University Education:

2011–2015 Bachelor Degree of Polymer Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom, Thailand

Work Experience:

April - May 2013	Position:	Internship Student
	Company name:	Nanotech. NSTDA, Thailand

Proceedings:

1. Wongvitvichot, W., Chaisuwan, T., Luengnaruemitchai, A., and Wongkasemjit, S. (2017, May 15-17) Catalytic activity of Cu-CeO_2-ZrO_2 for biodiesel production. The TechConnect World Innovation Conference, Washington D.C., America.
2. Wongvitvichot, W., Chaisuwan, T., Luengnaruemitchai, A., and Wongkasemjit, S. (2017, May 23) Catalytic activity of Cu-CeO_2-ZrO_2 for biodiesel production. Proceedings of the 9th Research Symposium on Petrochemical and Materials Technology; and 23th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.