PREPARATION, CHARACTERIZATION AND MECHANISTIC STUDY ON TRANSESTERIFICATION OF REFINED USED COOKING OIL FOR BIODIESEL PRODUCTION USING ZINC AND CALCIUM OXIDES-BASED CATALYSTS

NUR FATIN BINTI SULAIMAN

UNIVERSITI TEKNOLOGI MALAYSIA

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NUR FATIN BINTI SULAIMAN

A thesis submitted in fulfilment of the
requirements for the award of the degree of
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Dedicated to my beloved parents,
Sulaiman Ahmad and Foziah Jusoh @ Mohd Yusoff ,
to my siblings, family and family in law,
for the continuos support and prayers.
To my dearest husband, Mohamad Helmi Bin Abd Mubin,
to my loving daughter, Nur Aleesa,
my source of strength,
thanks for always being there for me.
To my friends,
thank you so much,
for their patience, support, love and encouragement.
May Allah bless all of you...

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In the name of Allah S.W.T, the Most Gracious and the Most Merciful,

All praise to Allah, For His Mercy has given me patience and strength to complete this work.

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Thank you so much.

ABSTRACT

Environmental concerns in fossil fuel depletion intensified the search for alternative fuel from renewable resources. Biodiesel is commonly produced by transesterification of vegetable oil in the presence of homogeneous catalyst. These catalysts, however, dissolve into the vegetable oil and large amount of water is required to clean the biodiesel that can cause saponification. Previously, extensive studies have been conducted on alkaline earth metal oxides such as calcium and magnesium oxides with manganese, iron, zirconium and cerium as the dopants. This research thus focused on the use of heterogeneous base catalysts that are easily separated and environmentally friendly for the biodiesel production. Zinc and calcium oxides-based supported on alumina were used as catalysts for the transesterification reaction of refined used cooking oil due to their highly basic characteristic. In order to improve the catalytic activity, the bimetallic and trimetallic oxides catalysts with copper, nickel, chromium and titanium as their co-catalysts were investigated. All the alumina supported catalysts were prepared by wetness impregnation method. The screening of biodiesel production using synthesized catalysts was monitored by gas chromatography-flame ionization detector (GC-FID). The two most potential catalysts were selected for the optimization and characterization study. Cu/Zn/γ-Al_2O_3 catalyst calcined at 800°C with 10:90 wt.% dopant ratio to based and 3 times of alumina coating, exhibited the highest biodiesel production (89.50%) at mild reaction conditions (65°C, 10 wt.% catalyst loading, 1:20 oil:methanol mole ratio and 2 hours of reaction time). Cr/Ca/γ-Al_2O_3 catalyst calcined at 700°C with 10:90 wt.% dopant ratio to based and 3 times number of alumina coating gave 86.64% of biodiesel production at 65°C, 6 wt.% catalyst loading, 1:18 oil:methanol mole ratio and 3 hours of reaction time. The physicochemical properties of the potential catalysts were accomplished using nitrogen analysis (NA) and CO_2-temperature programmed desorption (CO_2-TPD) that indicated high surface area (>140 m^2/g) and high basicity (>3 mmol/g). X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) analysis showed the polycrystalline structure with small particles sizes (<50 nm). Energy dispersive X-ray (EDX) spectroscopy, X-ray fluorescence (XRF), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) analyses confirmed the existence of Al, O, Zn, Cu, Ca and Cr species in each potential catalyst. The optimization of catalyst preparation conditions and biodiesel production parameters were verified by response surface methodology (RSM) method and they were in good agreement with the experimental values. The mechanistic study on both potential catalysts follows the Langmuir-Hinshelwood (LH) model which involves the initial adsorption of reactants molecules on active sites of the catalyst surface. The specification analysis of produced biodiesel utilizing Cu/Zn/γ-Al_2O_3 and Cr/Ca/γ-Al_2O_3 catalysts showed that the refined used cooking oil has potential to be used in large-scale biodiesel production using reaction conditions found in the present study.

ABSTRAK

Kebimbangan alam sekitar dalam kekurangan bahan api fosil telah meningkatkan pencarian bahan bakar alternatif dari sumber yang boleh diperbaharui. Biodiesel biasanya dihasilkan melalui transesterifikasi minyak sayuran dengan kehadiran mangkin homogen. Mangkin ini, walau bagaimanapun, terlarut di dalam minyak sayuran dan sejumlah besar air diperlukan untuk membersihkan biodiesel yang boleh menyebabkan saponifikasi. Sebelum ini, kajian menyeluruh telah dijalankan ke atas oksida logam alkali bumi seperti kalsium dan magnesium oksida dengan mangan, ferum, zirkonium dan serium sebagai dopan. Dengan itu, kajian ini memberi tumpuan kepada penggunaan mangkin bes heterogen yang mudah dipisahkan dan mesra alam untuk penghasilan biodiesel. Mangkin berasaskan zink oksida dan kalsium oksida berpenyokong alumina telah digunakan sebagai mangkin untuk tindak balas transesterifikasi minyak masak terpakai yang ditapis disebabkan oleh ciri kebesannya yang tinggi. Untuk meningkatkan aktiviti pemangkinan, mangkin oksida dwilogam dan trilogam dengan kuprum, nikel, kromium and titanium sebagai ko-mangkinnya telah disiasat. Kesemua mangkin berpenyokong alumina telah disediakan dengan kaedah pengisitepuan basah. Penyaringan penghasilan biodiesel menggunakan mangkin yang disintesis telah dipantau menggunakan kromatografi gas-pengesan pengionan nyala (GC-FID). Dua mangkin yang paling berpotensi telah dipilih bagi kajian pengoptimuman dan pencirian. Mangkin Cu/Zn/γ-Al_2O_3 yang dikalsinkan pada 800°C dengan nisbah dopan terhadap bahan asas 10:90 wt.% dan 3 kali salutan alumina telah menunjukkan penghasilan biodiesel tertinggi (89.50%) pada keadaan tindak balas sederhana (65°C, muatan mangkin 10 wt.%, nisbah mol minyak:metanol 1:20 and 2 jam masa tindak balas). Mangkin Cr/Ca/γ-Al_2O_3 yang dikalsinkan pada 700°C dengan nisbah dopan terhadap bahan asas 10:90 wt.% dan 3 kali salutan alumina memberikan penghasilan biodiesel 86.64% pada 65°C, muatan mangkin 6 wt.%, nisbah mol minyak:metanol 1:18 dan 3 jam masa tindak balas. Sifat fisikokimia mangkin berpotensi tersebut telah dikaji menggunakan analisis nitrogen (NA) dan penyahjerapan pengaturcaraan CO_2 (CO_2-TPD) yang menunjukkan luas permukaan yang tinggi (>140 m^2/g) dan kebesan yang tinggi (>3 mmol/g). Pembelauan sinar-X (XRD) dan analisis mikroskopi electron pengimbas pemancaran medan (FESEM) menunjukkan struktur polihablur dengan saiz zarah yang kecil (<50 nm). Analisis spektroskopi serakan tenaga sinar-X (EDX), pendarfluor sinar-X (XRF), mikroskopi elektron penghantaran (TEM) and spektroskopi fotoelektron sinar-X (XPS) mengesahkan kewujudan spesies Al, O, Zn, Cu, Ca dan Cr di dalam setiap mangkin yang berpotensi. Pengoptimuman keadaan persediaan mangkin dan parameter penghasilan biodiesel telah disahkan melalui kaedah permukaan gerak balas (RSM) dan ia menunjukkan persetujuan yang baik dengan nilai eksperimen. Kajian mekanistik ke atas kedua-dua mangkin yang berpotensi adalah mengikuti model Langmuir-Hinshelwood (LH) yang melibatkan penjerapan awal molekul reaktan pada tapak aktif permukaan mangkin. Analisis spesifikasi bagi biodiesel yang dihasilkan menggunakan mangkin Cu/Zn/γ-Al_2O_3 and Cr/Ca/γ-Al_2O_3 menunjukkan bahawa minyak masak terpakai yang ditapis berpotensi untuk digunakan dalam penghasilan skala besar biodiesel menggunakan keadaan tindak balas yang ditemukan dalam kajian ini.

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LIST OF ABBREVIATIONS AND SYMBOLS

ANOVA	-	Analysis of Variance
ATR-FTIR	-	Attenuated Total Reflection-Fourier Transform Infrared
BBD	-	Box-Behnken Design
BET	-	Brunauer-Emmet-Teller
CO_2-TPD	-	Temperature Programmed Desorption
Cu Kα	-	X-ray diffraction from Copper K energy levels rate of conversion (percentage)
FAME	-	Fatty Acid Methyl Ester
FESEM	-	Field Emission Scanning Electron Microscope
EDX		Energy Dispersive X-Ray
FTIR	-	Fourier Transform Infrared Spectroscopy
GC-FID	-	Gas Chromatography-Flame Ionization Detector
JCPDS	-	Joint Committee on Powder Diffraction Standard
NA		Nitrogen Adsorption
RSM	-	Response Surface Methodology
TGA-DTA	-	Thermogravimetry Analysis-Differential Thermal Analysis
TEM	-	Transmission Electron Microscopy
XPS	-	X-Ray Photoelectron Spectroscopy
XRD	-	X-Ray Diffraction
XRF	-	X-Ray Fluorescence
α	-	Alpha
γ	-	Gamma
θ	-	Half angle of diffraction beam
λ	-	Wavelength
%	-	Percentage

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The world was facing an acute energy crisis due to the fact that high energy demand from the fossil fuels such as coal, petroleum and natural gas at present and compete with the feedstocks requirement for chemical industries. The demand of these non-renewable sources of energy which are getting consumed by us at an extraordinary rate is increasing rapidly. Since 1850's, petroleum has been the most main fuel and energy source which is about 90% of vehicular fuels need are met by oil. Petroleum also is becoming as raw material for many chemical products including pharmaceuticals, solvents, fertilizers, pesticides, plastics and others. In any case, there has been increasing concern about an energy crisis caused by potential petroleum depletion since petroleum is non-renewable.

The need for increased energy security and concern about high oil costs drove researchers to seek for renewable and sustainable energy sources to overcome the reliance on petroleum. Besides, the effect of gas emissions from fossil fuels and the environmental is another factor to seek for green and ecologically benign fuels. Emissions of carbon dioxide, CO_2 to the atmosphere from the combustion of fossil fuels have ended up a worldwide concern due to the related climate change, which has unfavorable impacts on human society. In order to overcome this crisis in depending on a fossil fuels, increasing the renewable energy capacity that can reduces greenhouse gases emissions is very important. As stated by Anuar and Abdullah, (2016), the renewable energy should ensure a cleaner environment that can

reduce the impact of any future energy crisis on fossil fuel-constrained economies. Attention continues to be focused on biomass-derived fuels or known as biofuels for energy production. One of the liquid biofuels considered for this application is biodiesel.

1.2 Biodiesel

Biodiesel has become the world's attention as one of a very promising alternative energy as a substitute for fossil diesels because it has similar properties to fossil diesels. Biodiesel is the most commonly used liquid biofuels in the transport sector, representing about 82% of biofuels production in European Union (Mardhiah *et al.*, 2017). The advantages of the biodiesel compared with the conventional fossil diesels are their renewability, biodegradability, non-toxicity and low exhaust emissions due to the free of sulphur and aromatics in biodiesel (Hassan and Rahman, 2017). In this 21st century, biodiesel has experienced a major surge worldwide due to these advantages. Figure 1.1 shows the global biodiesel production from 2000 to 2016 in 1000 metric tons of oil equivalent. Meanwhile, Figure 1.2 illustrates Malaysia biodiesel production and consumption by year. From this statistic in 2016, biodiesel production amounted to approximately 82 billion metric tons of oil equivalent worldwide.

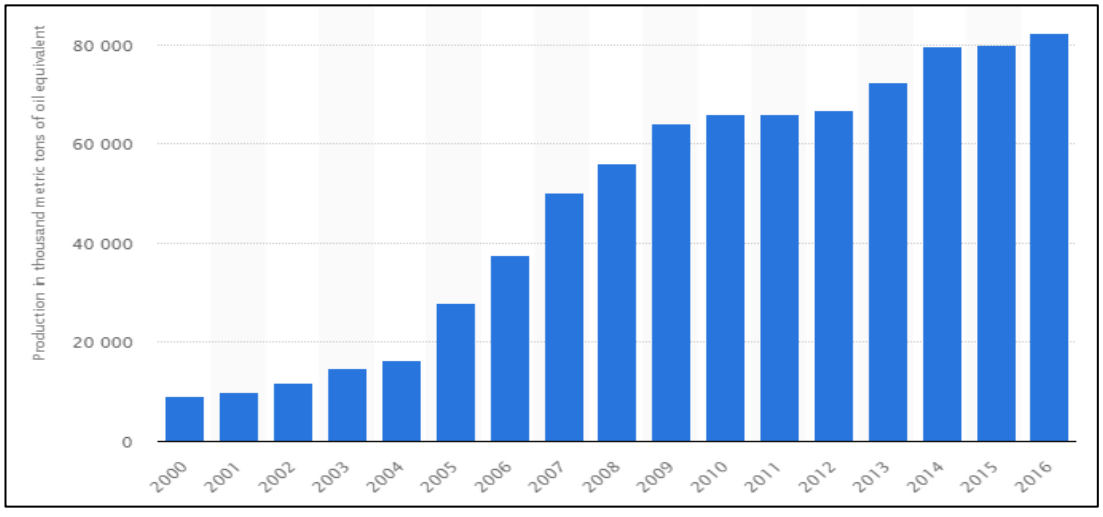

Figure 1.1 Global biodiesel production from 2000 to 2016 in 1000 metric tons of oil equivalent from The Statistics Portal (Hajjari *et al.*, 2017)

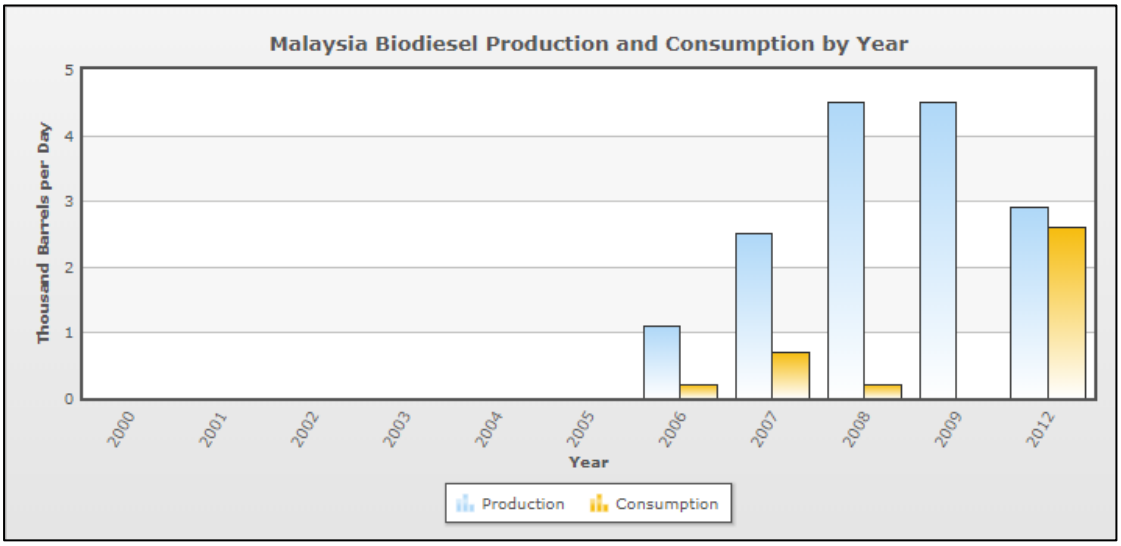

Figure 1.2 Malaysia biodiesel production and consumption by year from United States Energy Information Administration (Mahmudul *et al.*, 2017)

The name of biodiesel (bio-means life (Greek) and diesel from Rudolf diesel/ petro-diesel) has been given from transesterification of vegetable oil that use as a diesel fuel and renewable nature. Technically, the term "biodiesel" refers to mixtures of fatty acid alkyl esters (FAAE) produced by transesterification of vegetable oils or animal fats with alcohols or via esterification of free fatty acids (FFA) with alcohols. Transesterification is a process where triglyceride reacts with an alcohol such as methanol to give methyl ester of fatty acids (FAME) and glycerol. The overall transesterification reaction is presented by the stoichiometric equation shown in Figure 1.3.

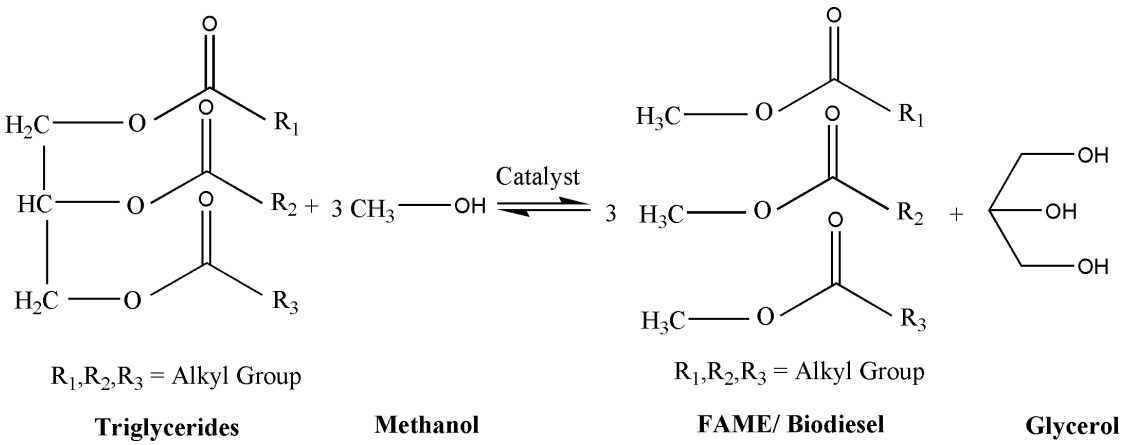

Figure 1.3 Generalized schematic representation of transesterification reaction

Biodiesel can be produced from variety of feedstocks including soybean, cottonseed, palm, peanut, rapeseed, sunflower and rice bran from vegetable oils with tallow, chicken fat and fish oils from animal fats as well as waste cooking oil and grease. Biodiesel is commonly used in conventional compression-ignition engines without any modifications, either in pure form or blended with petro-diesel. According to Knothe and Razon, (2017), the similarity in fuel properties between biodiesel and petro-diesel was the reason of the direct application of biodiesel in diesel engines. Table 1.1 listed the fuel properties of biodiesel compared to petro-diesel. Based on Table 1.1, biodiesel possess viscosity much closer to the petro-diesel and it has higher flash point, higher lubricity and smaller carbon footprint (Agarwal *et al.*, 2017). Therefore, this research had focused on producing biodiesel with similar fuel properties as petro-diesel via transesterification of refined used cooking oil.

Table 1.1: The American Society for Testing Materials (ASTM) standards for petro-diesel and biodiesel fuel properties

Fuel properties specification	**Petro-diesel**	**Biodiesel**
Standard	ASTM D975	ASTM D6751
Composition	HC (C10-C21)	FAME (C12-C22)
Kinematic viscosity @ 40ºC (mm^2/s)	1.9-4.1	1.9-6.0
Specific gravity (g/mL)	0.85	0.88
Flash point (ºC)	60 to 180	100 to 190
Cloud point (ºC)	-15 to 5	-3 to 12
Pour point (ºC)	-35 to -15	-15 to 16
Water content, vol.%	0.05	0.05
Carbon content, wt.%	87	77
Hydrogen content, wt.%	13	12
Oxygen content, wt.%	0	11
Sulphur content, wt.%	0.05	0.05
Cetane number	40 to 55	48 to 60
HC: Hydrocarbon; FAME: Fatty acid methyl ester		

1.3 Catalysis in Biodiesel Production

Catalysis plays an important role in numerous industrial processes which incorporates food production, energy production, chemical production and environmental protection. Basically, the catalyst is needed in any of the reaction in order to increase the rate performance of the process. In this transesterification reaction, both acid and base catalysts can be used to enhance the biodiesel production. Lately, much research has been reported relating to the development of heterogeneous catalysts for transesterification of various vegetable oils with methanol (Baskar and Aiswarya, 2016; Verma and Sharma, 2016).

Many researchers have pointed out the drawback related with the use of homogeneous catalysts in biodiesel production (Pukale *et al.,* 2015; Abdullah *et al.,* 2017). Conventional biodiesel production had used base-catalyzed homogeneous reaction such as sodium hydroxide and potassium hydroxide and the process are illustrated in Figure 1.4. This requires various operating procedures in order to recover the catalyst for further use. The large amount of water and energy was needed for washing and drying the biodiesel product, thus it will form soap as unwanted by-product.

Therefore, there is currently a shift toward the development of industrial processes for biodiesel production using solid catalysts. The major benefit of using heterogeneous catalysts is that no polluting by-products are formed and the catalysts do not mix with biodiesel. Furthermore, the heterogeneous catalyst would reduce the extra operating costs from the catalyst neutralization, product washing and continual replacement of catalyst, thus producing higher purity of biodiesel. There is no requirement for catalyst neutralization since the solid catalyst could easily be removed from the reaction mixture by simple filtration. Figure 1.5 represents a typical heterogeneously base-catalyzed biodiesel process. Meanwhile, Table 1.2 depicts the comparison of homogeneous and heterogeneous catalyzed transesterification reaction.

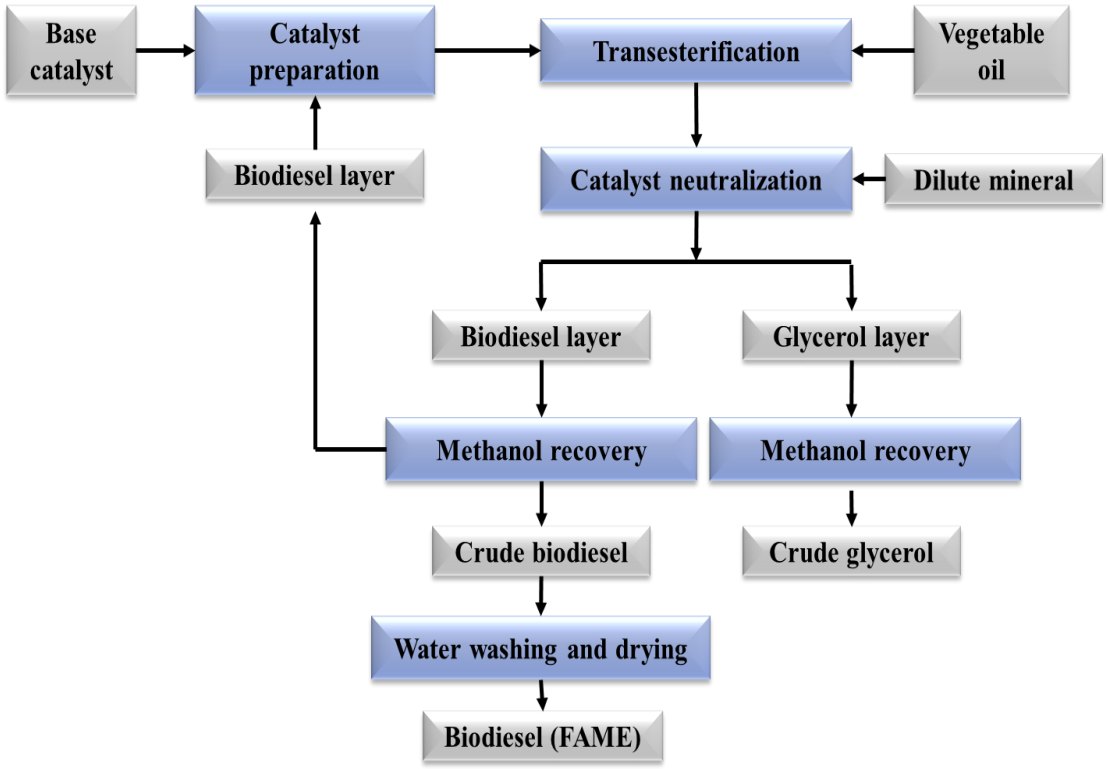

Figure 1.4 A typical homogeneous base-catalyzed biodiesel process

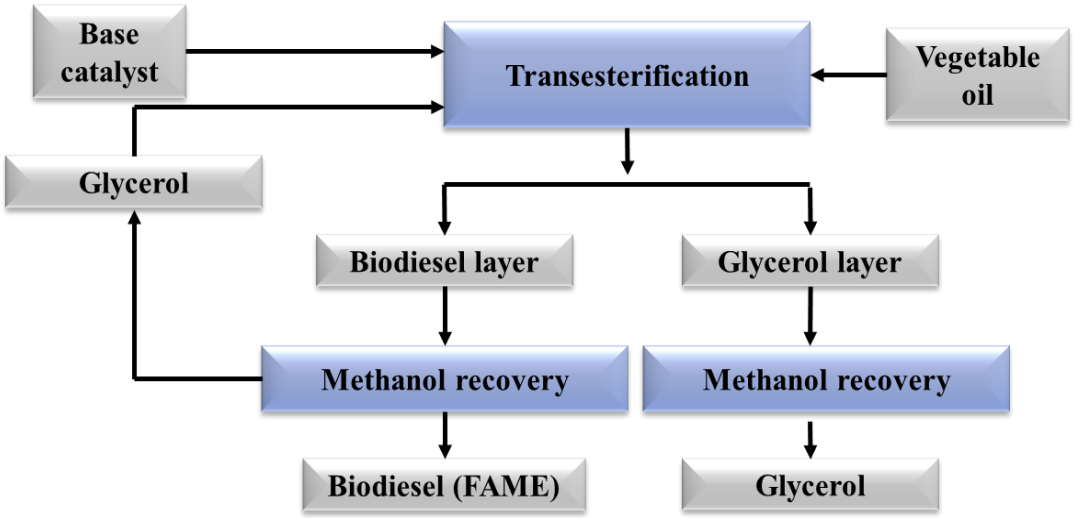

Figure 1.5 A typical heterogeneous base-catalyzed biodiesel process

Table 1.2: Comparison of homogeneous and heterogeneously catalyzed transesterification

Factors	**Homogeneously catalysis**	**Heterogeneously catalysis**
Reaction rate	Fast and high conversion	Fast and high conversion
After treatment	Catalyst cannot be recovered, must be neutralized	Can be recovered
Processing methodology	Limited use of continuous methodology	Continuous fixed operation is possible
Presence of water/ free fatty acids	Sensitive	Not sensitive
Catalyst reuse	Not possible	Possible
Cost	Comparatively costly	Potentially cheaper

Physicochemical properties of solid base catalyst are dependent on their preparation methods, pretreatment process and the way of handling the catalyst itself. There are numbers of preparation methods for producing solid base catalyst such as co-precipitation method (Lee *et al.,* 2015), hydration dehydration method (Mijan *et al.,* 2015), sol gel (Mohadesi *et al.,* 2014) and chemical vapor deposition (CVD) methods (You *et al.*, 2017). Physicochemical properties such as morphology, surface area, particle size and basicity normally could influence the catalytic activity. The importance of solid base catalysts has come to be known for their environmental friendly qualities. Much significant progress has been made over the past two decades in catalytic materials and solid base-catalyzed reactions (Hattori, 2001).

Typically, metal oxides are identified as the most significant and extensively used as catalyst. As described by Hattori, (2015), metal oxides had both proton and electron transfer abilities, thus can be used in redox catalysis as well as acid-base reactions. A strong basic strength can be formed after a high temperature treatment applied in order to obtain a carbonate free metal oxide surface. Surface defect which can be detected using surface area analysis display the significant sites for

heterogeneous catalysis that can change the reactivity of any reaction (Aransiola *et al.*, 2014). Hence, the higher the surface area indicates higher reactivity.

Alkaline earth metal oxides such as calcium oxide, CaO possess a rock-salt structure with alternating metal cations and oxygen anions. An alkaline earth metal oxide exposing more of electron rich planes, thus give a greater number of defect sites (Marinković *et al.*, 2016). From alkaline earth metal oxide group, CaO has been widely used as a catalyst in the transesterification reaction due to its high basicity, low solubility in organic solvents and low price. On the other hand, zinc oxide, ZnO is a cheap, re-usable, stable and environmentally catalyst that used in many catalytic reactions. Nanoparticles of ZnO comprises a good optical, electrical and chemical properties. Furthermore, ZnO is one of the most extensively studied materials due to its outstanding optoelectronic properties with potential applications in many different fields of technology (Downs *et al.*, 2017). ZnO is generally used as catalyst support and it has been established that impregnation with alkaline metals gives a good basic solid catalyst for the transesterification of vegetable oils (Alba-Rubio *et al.*, 2010).

Despite of high catalytic activity by using single metal oxides catalyst in biodiesel production, the addition of dopants offers a route to achieve better performance due to the increased surface basic properties. There is a demand to develop desirable solid base catalysts from mixed metal oxide with a high activity. The important use of transition metals as co-catalysts are the ability to be in a variety of oxidation state, interchange between the oxidation states and formation of complexes with the reagents. The availability and lower costs are additional factors for the consideration.

Supporting metal oxides on high surface area materials is another alternative of increasing their stability as catalysts and reducing the cost in preparing the catalysts. The high surface area of supported material allows good dispersion of the catalytically active metal and easily recovered after the reaction (Matsubu *et al.*, 2017). Furthermore, supports are a good way of minimizing in mass transfer limitations for heterogeneous catalysts in liquid phase reaction by providing greater

accessibility through the existence of pores. Gamma aluminium oxide (γ-Al_2O_3) has been widely used as a support of active species in industrial processes due to its high thermal stability and surface area of 300 m^2/g, mesopore size of 5 to 15 nm, pore volume of 0.60 cm^3/g and ability to be shaped into pallets (Evangelista *et al.*, 2016).

Therefore, in this study, the modification with more active substance in order to prepare a base heterogeneous catalyst was introduced in biodiesel production due to the simplifications in the existing process. To the best of our knowledge, the utilization of wetness impregnation method to synthesize zinc and calcium oxides based catalyst with addition of transition metals (Cr, Ti, Ni, Cu) as co-catalysts in alumina supported for the transesterification of biodiesel has not been revealed yet.

1.4 Response Surface Methodology (RSM)

RSM is a collection of mathematical and statistical techniques based on the fit of a polynomial equation to the experimental data. It describes the behavior of a data set with the objective of making statistical previsions. RSM can be applied when a response of interest is influenced by several independent variables. The main objective of RSM application is to optimize the levels of independent variables in order to achieve the best system performance.

Toward this objective, linear or square polynomial function is employed to describe the experimental design and thus, explored the modeling for the optimization. The stages in the application of RSM as an optimization technique are as follows: (1) the selection of the independent variables from the screening studied; (2) the choice of the experimental design and carrying out according to the experimental matrix; (3) the mathematic-statistical analysis through the fit of a polynomial function; (4) the evaluation of the model's fitness; (5) the verification of the predicted value from experimental design and (6) the determination of the optimum values for each variable.

RSM has been successfully applied in the study on optimization of biodiesel production from rapeseed oil, soybean oil, cotton seed oil and other vegetable oils (Silva *et al.,* 2011; Dwivedi and Sharma, 2015; Kostić *et al.,* 2016; Onukwuli *et al.,* 2017; Baskar *et al.,* 2018). However, there is no literature reported on the optimization of the transesterification reaction from refined used cooking oil over potential catalyst in this research. Therefore, RSM modelling coupled with Box-Behnken design was used to determine the optimum catalyst conditions and biodiesel production parameters that could lead to the maximum biodiesel yield.

1.5 Mechanistic Study

In heterogeneous catalysis, adsorption of reactants and desorption of products take place on the surface of a solid catalyst. Two hypotheses have been proposed for solid acid catalyzed transesterification reaction mechanisms which are Eley–Rideal (ER) and Langmuir-Hinshelwood (LH), represent the foundation of modern heterogeneous transesterification mechanisms. According to the ER mechanism, it is performed by a direct pickup of species from the surface by a liquid phase molecule. Meanwhile, in the LH mechanism, there are three main steps that occurred on the catalyst surface which are adsorption of reactants, surface reaction and desorption of products. Therefore, this present study might provide an understanding on the mechanism of heterogeneous base-catalyzed transesterification reaction.

1.6 Problem Statement

Concerns about greenhouse gas emissions, global warming and limitation of crude oil resources have encouraged researchers to develop an alternative fuel. The depleting fossil oil reserves give big influence in the interest in finding alternative source of energy. In order to overcome those problems and to further enhance the awareness of the environment, the biomass has become the global attention as one of a great promising substitute and sustainable energy. Biodiesel derived from

renewable resources such as vegetable oil or animal fats is expected to be one of the biomass-base alternative fuel to substitute the diesel oil.

Conventional biodiesel production is commercially synthesized in the presence of homogeneous base catalysts mainly alkali-metal hydroxides and methoxides (NaOH, KOH and $NaOCH_3$) as reported by Konwar *et al.,* (2014). However, it should be noted that this conventional process has several drawbacks. This requires various operating and capital costs downstream arising from the inability to recover the catalyst. Particularly, these catalysts are sensitive to the presence of water and free fatty acid (FFA). Homogeneous base catalyst dissolved into the vegetable oil or animal fat. Thus, large amount of water is required for washing purpose. On the other hand, the presence of water leads to the soap formation. As a result, the saponification could lower the biodiesel quality and makes the biodiesel production becomes difficult, time consuming, expensive and complicated.

Moreover, the acid-catalyzed transesterification process typically uses hydrochloric acid and phosphoric acid as catalysts. However, the reaction process needed longer time, higher oil to methanol ratio, higher reaction temperature and pressure (Veljković *et al.,* 2015; Melero *et al.,* 2015). As the acid catalysts are more corrosive, it is not preferable due to the large operation costs in industrial process. Furthermore, several solid base catalysts have been investigated for transesterification including alkaline earth oxides, alkaline earth metal oxides, rare earth oxides, basic zeolite, hydrotalcites and organic base catalysts (Hattori, 2015). Despite showing higher activity than acid catalysts, solid base catalyst was unfavorable for feedstock containing high free fatty acids. These catalysts deactivate faster in the presence of air and moisture, thus free fatty acids would react with the catalyst forming soap. Therefore, in this study, base heterogeneous catalytic reaction was introduced in biodiesel production under mild reaction conditions. The process of heterogeneous base-catalyzed transesterification is expected to be effective as it can reduce the extra operating costs and gives minimal impact into the environment.

This research work focused on the mixed metal oxides catalyst with the incorporation of transition metal as co-catalysts supported on alumina for the transesterification in biodiesel production. The supported catalyst can be used in direct applications for the automotive and petroleum industries due to its stability and reusability (Wefers, 1990; Zabeti *et al.,* 2009). The advantage of this mixed metal oxides can be traced to a favorable combination of its textural properties such as surface area, pore size distribution, pore volume and its base characteristics which are related to surface chemical composition and phase composition (Teo *et al.*, 2014; Joshi *et al.*, 2015). The use of mixed metal oxides would reduce the leaching properties and the reaction time in the biodiesel production as proved by Wong *et al.,* (2015).

Previous studies by Wang *et al.,* (2007) and Patil *et al.,* (2010) reported a two-step catalytic transesterification of biodiesel process. However, the two-step method faces the problem in catalyst removal and time consuming, thus would increase the cost of biodiesel production. In order to overcome this situation, single step transesterification reaction using heterogeneous mixed metal oxides catalyst was introduced. In addition, another factor that affect the cost of biodiesel production is based on the raw materials that used as a feedstock. Most of the biodiesel is widely produced from the costly edible oils like soybean oil, sunflower oil, rapeseed oil and rice bran oil (Baskar and Aiswarya, 2016; Arora *et al.*, 2014; Anuar and Abdullah, 2016). However, the application of such feedstocks in biodiesel production could maximize competition between demand of vegetable oils with human consumption. This research had introduced refined used cooking oil as an alternative feedstock which has not been investigated.

1.7 Aim and Objectives of Study

The main aim of this research is to develop the most effective catalyst in the transesterification of refined used cooking oil to biodiesel under mild conditions. Thus, the objectives of this research are:

i) To synthesize zinc and calcium oxides-based catalysts supported on alumina with different series of dopants.

ii) To test and measure the catalytic activity of the prepared catalysts in the transesterification of refined used cooking oil by using gas chromatography-flame ionization detector (GC-FID).

iii) To characterize the potential prepared catalysts using various analytical technique in order to understand the physicochemical properties of the catalysts.

iv) To optimize the catalyst preparation parameters and biodiesel production conditions using response surface methodology (RSM)-Box-Behnken design (BBD).

v) To postulate the mechanism over potential catalysts.

vi) To verify the fuel properties of synthesized biodiesel according to ASTM D6751 and EN14214 standards.

1.8 Scope of Study

This research was emphasized on base-catalyzed transesterification of biodiesel from refined used cooking oil by using alumina supported zinc (Zn) and calcium (Ca) with addition of nickel (Ni), copper (Cu), titanium (Ti) and chromium (Cr) as co-catalysts. Three types of catalysts including monometallic, bimetallic and trimetallic oxides catalysts were synthesized via wetness impregnation method. Then, the catalytic activity of the prepared catalysts was tested and monitored by using gas chromatography (GC-FID). From the screening stages, the both potential catalysts from each based were optimized on different calcination temperatures, dopant ratios to based and number of alumina coatings and further validated by response surface methodology (RSM) via Box-Behnken design (BBD).

Next, the both potential catalysts were characterized in order to explore its physicochemical properties. The surface characteristics of the prepared catalysts were analyzed using nitrogen adsorption (NA). X-Ray diffraction (XRD) was used

to determine the degree of crystallinity, particle shape and sizes for the prepared catalysts. X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray (EDX), X-ray Fluorescence (XRF) and transmission electron microcopy (TEM) were used to study the chemical state and the elemental composition of the catalysts. The surface morphology was examined using field emission scanning electron microscopy (FESEM), while CO_2-TPD was used to measure the basicity and basic site distributions of the catalysts. Thermogravimetric analysis–differential thermal analysis (TGA-DTA) was conducted to study the weight loss of the catalyst with change of temperature.

From the characterization analysis, the both potential catalysts were further investigated in the optimization of biodiesel parameters including percentage catalyst loadings, oil to methanol ratios and reaction times and verified by RSM. The both potential catalysts were also studied on reusability and reliability testing as well as regeneration activity under optimum conditions. The mechanistic study of transesterification reaction on the catalyst surface was conducted via attenuated total reflection-Fourier transform infrared (ATR-FTIR) and the product was analyzed using GC-FID. Lastly, the verification of fuel properties on product was examined according to ASTM D6751 and EN14214 standards.

1.9 Significance of Study

The harmful effect of global warming, depletion of fossil fuel resources and the rising numbers of environmental related problems had become the main factors that contribute to the global transformation in the development of biodiesel. The used of biodiesel as a source of fuel offers several advantages including renewable and sustainable resources, non-toxic and environmental friendly where it reduces the emission of CO_2 and hazardous compound such as aromatic, sulfur, particulate matter and NO_x. Hence, the use of biodiesel will significantly reduce the effect of global warming and utilizes a green chemistry concept. Generally, biodiesel displays good oil qualities with higher cetane number and higher combustion efficiency. In addition, no sulfur content in biodiesel provides greater lubricity than conventional

diesel fuel, thus improves the durability of the engine. The advantage of biodiesel production from this study is easily to operate because it only required to process at low temperature in order to give optimum performance.

In addition, the application of a heterogeneous or solid catalyst has gained interest in the biodiesel production. The catalysts are not dissolved in the reaction mixture which made it easier to be separated from the product. On top of that, the base heterogeneous catalyst has several advantages including reusability, easier operational procedures, effortless catalyst separation and reduction of environmental pollutions. All the materials in the fabrication of the catalyst are cheap, stable and easily available. The catalysts are safe to handle because it can be used at low reaction temperature.

Accordingly, the novelties of this research study are as follows:

1. The development of highly basic metal oxide catalysts from alkaline earth metal (Ca) and transition metal (Zn) as based catalysts with the use of alumina beads as a support in order to increase the stability of the catalyst. The addition of second and third metal as co-catalysts were carried out in order to increase the performance on transesterification for biodiesel production.
2. The invention of a simple method that only required low temperature for the biodiesel production from refined used cooking oil.
3. The optimization on the catalyst preparation conditions and biodiesel production parameters over two potential catalysts by using response surface methodology (RSM) via Box-Behnken design (BBD).
4. The mechanistic study on the catalyst surface of triglyceride model substitution using attenuated total reflection-Fourier transform infrared (ATR-FTIR).

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