ALUMINA SUPPORTED CALCIUM/LANTHANIDE OXIDES CATALYSTS FOR BIODIESEL PRODUCTION FROM REFINED COOKING OIL

NURIDAYAH BINTI YUSMAIDI

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Faculty of Science
Universiti Teknologi Malaysia

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DEDICATION

Special dedication to all my beloved family

and to all my friends.

Thank you for your endless love, support, sacrifices, prayers and advices.

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In the Name of Allah, the Beneficent, the Merciful,

Alhamdulillah, praise is to Allah for giving me enough time to complete this work

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ABSTRACT

In recent years, fossil fuels have played a key role in the researcher's quest for energy sustainable system. The exploration of fossil fuels replacement has become a focus of intense interest, making it possible to resolve numerous current social problems such as the increasing prices of crude petroleum and environmental stress condition like global warming and air pollution due to the burning of fossil fuels. The application of this biodiesel is growing. However, the optimization of each reaction parameters to attain a high yield has not yet been explored in detail. This study has focused on the use of the heterogeneous base catalyst for biodiesel production. Biodiesel was prepared from the refined cooking oil by transesterification using methanol in the presence of calcium oxides-based supported on alumina by wetness impregnation method. Calcium oxides-based supported on alumina were used as catalysts for the transesterification reaction of refined cooking oil due to their highly basic characteristic. A comparison of the lanthanum oxides, cerium oxides and praseodymium oxides as a dopant was synthesized. The catalytic performance of the prepared catalysts was examined by gas chromatography-flame ionization detector (GC-FID). The three most potential catalyst was selected for the optimization of the transesterification and characterization study. $Ce/Ca/Al_2O_3$ catalyst calcined at 900ºC with 3 times of alumina coating and 10:90 wt.% dopant ratio to based, showed the highest biodiesel yield of 94.25% at mild reaction conditions (65°C, 1:18 oil:methanol mole ratio, 10 wt.% catalyst loading within 3 hours). The physicochemical properties of the potential catalysts were studied using nitrogen analysis (NA) and CO_2-temperature programmed desorption (CO_2-TPD) has 130.79 m^2/g surface areas and 1.6132 mmol/g basicity. X-ray diffraction (XRD) and field electron emission microscopy (FESEM) analysis showed $Ce/Ca/Al_2O_3$ catalyst had a polycrystalline structure with small particle sizes. X-ray fluorescence (XRF), Energy dispersive X-ray (EDX) and transmission electron microscopy (TEM) confirmed the existence of Ce, La, Pr, Ca, Al and O species in each potential catalyst. At the end of this study, it was proven that $Ce/Ca(10:90)/Al_2O_3$ catalyst can catalyze the transesterification reaction of refined cooking oil gave highest biodiesel yield (94.25%).

ABSTRAK

Dewasa ini, bahan api fosil memainkan peranan penting dalam pencarian penyelidik untuk sistem mampam tenaga. Oleh itu, penerokaan penggantian bahan api fosil telah menarik perhatian, memungkinkan untuk menyelesaikan pelbagai masalah sosial semasa ini. Sebagai contohnya kenaikan harga petroleum mentah dan keadaan tekanan alam sekitar seperti pemanasan global dan pencemaran udara disebabkan oleh pembakaran bahan api fosil. Penggunaan biodiesel ini semakin meningkat, namun begitu pengoptimuman setiap parameter reaksi untuk mecapai hasil yang tinggi belum diterokai secara terperinci setakat ini. Kajian ini memberi tumpuan kepada penggunaan mangkin bes heterogen untuk penghasilan biodiesel. Secara amnya, pemangkin pepejal mudah dipisahkan, ia boleh diperolehi semula dan tidak meghakis serta ia mempunyai ciri kebesan yang tinggi. Biodiesel telah dihasilkan daripada minyak masak terpakai yang ditapis melalui transesterifikasi bersama-sama methanol dengan kehadiran bes kalsium oksida berpenyokong alumina telah disediakan dengan kaedah pengisitepuan basah. Satu perbandingan dengan lanthanum, cerium dan praseodymium oksida sebagai dopan telah dilakukan. Aktiviti pemangkin yang disediakan telah dipantau menggunakan kromatografi gas-pengesan pengionan nyala (GC-FID). Pemangkin yang paling berpotensi telah dipilih untuk kajian pengoptimuman transesterifikasi dan pencirian. Mangkin $Ce/Ca/Al_2O_3$ yang dikalsinkan pada 900ºC dengan 3 kali salutan alumina dan 10:90 wt.% nisbah dopan terhadap bahan asas, menunjukkan hasil biodiesel yang tertinggi sebanyak 94.25% pada keadaan tindak balas sederhana (65ºC, 10 wt.% muatan mangkin dalam masa 3 jam). Sifat fisikokimia daripada mangkin berpotensi dikaji dengan menggunakan analisis nitrogen (NA) dan penyahjerapan pengaturcaraan CO_2 (CO_2-TPD) mmpunyai luas permukaan yang tinggi iaitu 130.79 m^2/g dan menunjukkan kealkian yang tinggi iaitu 1.6132 mmol/g. Pembelauan sinar-X (XRD) dan analisis mikroskopi electron pengimbas pemancaran medan (FESEM) menunjukkan struktur polikristal dengan saiz zarah yang kecil. Pendarfluor sinar-X (XRF), analisis spektroskopi serakan tenaga sinar-X (EDX) and mikoskopi elecktron penghantaran (TEM) mengesahkan kewujudan spesies Ce, La, Pr, Ca, Al dan O di dalam setiap mangkin yang berpotensi. Pada akhir kajian ini, terbukti bahawa $Ce/Ca(10:90)/Al_2O_3$ mangkin boleh meningkatkan transesterifikasi minyak masak terpakai yang ditapis untuk menghasilkan hasil biodiesel yang tinggi (94.25%).

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LIST OF ABBREVIATIONS AND SYMBOLS

ASEAN	-	Association of Southeast Asian Nations
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
GC-FID	-	Gas Chromatography-Flame Ionization Detector
JCPDS	-	Joint Committee on Powder Diffraction Standard
NA	-	Nitrogen Adsorption
TGA	-	Thermogravimetry Analysis
XRD	-	X-Ray Diffraction
XRF	-	X-Ray Fluorescence
λ	-	Wavelength
%	-	Percentage
wt%	-	Weight percentage
θ	-	Half angle of diffraction beam

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, South Asian countries still rely on non-renewable sources of energy which are available in limited supplies and will be extinct in the future. According to the national energy mix, energy production is classified into two categories, non-renewable energy and renewable energy. Renewable energy like solar, water, wind and biomass are always available to be tapped, environmentally friendly and are naturally replenished over long time frames. Since the last century, the total energy consumption is strongly dependent on non-renewable energy resources and thus, pushing it to the lowest point. Non-renewable energy like coal and natural gas has been recently used by the entire human civilization. Figure 1.1 shows a statistical review of energy consumption in ASEAN countries. Increasing the penetration of renewable energy resources can be considered as an effort aimed to reduce our dependence on non-renewable energy resources (Mamat *et al.*, 2019). Table 1.1 reviews the energy generation situation in South-East Asia. Regional fuel use varies according to the availability of resources. The largest shares of natural gas energy were in Brunei (99%), Singapore (95%) and Malaysia (43.7%).

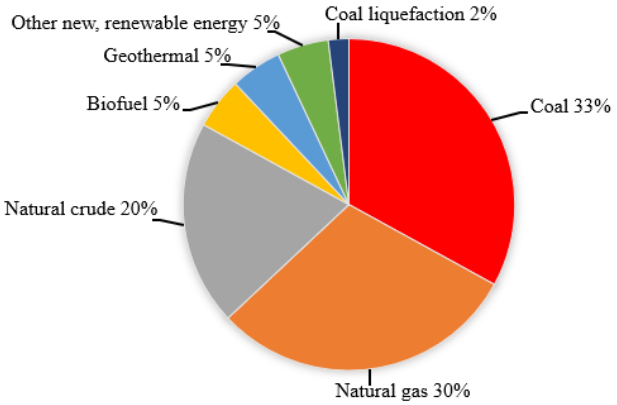

Figure 1.1 Consumption of energy in ASEAN countries (Mamat *et al.*, 2019)

Table 1.1: Reviews of energy generation situation in South East Asia (Mamat *et al*., 2019)

Countries	**Coal (%)**	**Natural gas (%)**	**Oil (%)**	**Hydro (%)**	**Other renewable (%)**
Brunei	–	99	1	–	–
Indonesia	51	24	13	8	–
Laos	–	–	–	58	–
Malaysia	43.7	43.7	1.3	8.7	0.7
Myanmar	–	20.7	–	74.7	–
Philippines	42.8	24.2	7.4	11.8	–
Singapore	–	95	–	–	–
Thailand	14	41	43	1	–
Vietnam	28.94	21.89	40.04	–	5.63

In recent years, some researchers claimed that excessive consumption of fossil fuels in process and transportation would lead to lots of negative impacts in social and environmental issues (Abdullah and Sulaiman, 2013). In order to overcome this issue, a greener approach could be applied to synthesize the fossil fuels replacement like biodiesel. Biodiesel or also called as fatty acid methyl esters (FAME) is one type of renewable and environmentally benign fuels obtained from any biologically resources containing triacylglycerols such as animal fats, waste cooking oil and vegetable oils.

Different kinds of oil feedstocks were used in the manufacturing of biodiesel, including the first-generation fuels that can be categorized as edible oil including canola oil, palm oil, soybean oil, sunflower oil, coconut oil, olive oil and frying oil (Anastopoulos *et al.*, 2009; Hanis *et al.*, 2017; Lee *et al.*, 2015). The second-generation fuels component of the non-edible including neem oil, Jatropha curcas seed oil, Karanja oil, sea mango oil, castor oil and waste cooking oil (Lim and Teong, 2010). Finally, microalgae-based oil is one of the third-generation fuels. Table 1.2 shows the potential biodiesel feedstock in Asia (Atabani *et al*., 2012).

Table 1.2: Current potential biodiesel feedstocks in Asia (Atabani *et al*., 2012)

Country	**Feedstock**
China	Jatropha/rapeseed/waste cooking oil
India	Jatropha/peanut/*Pongamia pinnata* (karanja)/rapeseed/soybean/sunflower
Indonesia	Coconut/jatropha/palm oil
Japan	Waste cooking oil
Malaysia	Palm oil
Philippines	Coconut/jatropha
Singapore	Palm oil
Thailand	Coconut/jatropha/palm

Several methods can be practiced for biodiesel production, such as thermal cracking (pyrolysis), micro-emulsions, direct use of vegetable oil and transesterification (Knothe and Gerpen, 2005). These methods were intended to decrease the viscosity and oxygen contain in the oil feedstocks (Mamat *et al*., 2019). The utmost economical method for transforming the organic oils or fats (triglyceride molecule) with alcohols into FAME in the present of the appropriate catalyst is the transesterification reaction. Figure 1.2 represents catalytic transesterifications reaction of triglyceride to form esters (biodiesel) and glycerol molecules. There are many types of alcohols can be used such as amyl alcohol, butanol, propanol, ethanol and methanol. Nevertheless, methanol is more commonly used in the production of biodiesel owing to its simple chain alcohol structure, fast and homogeneous reaction as well as economically helpful (Musa, 2016).

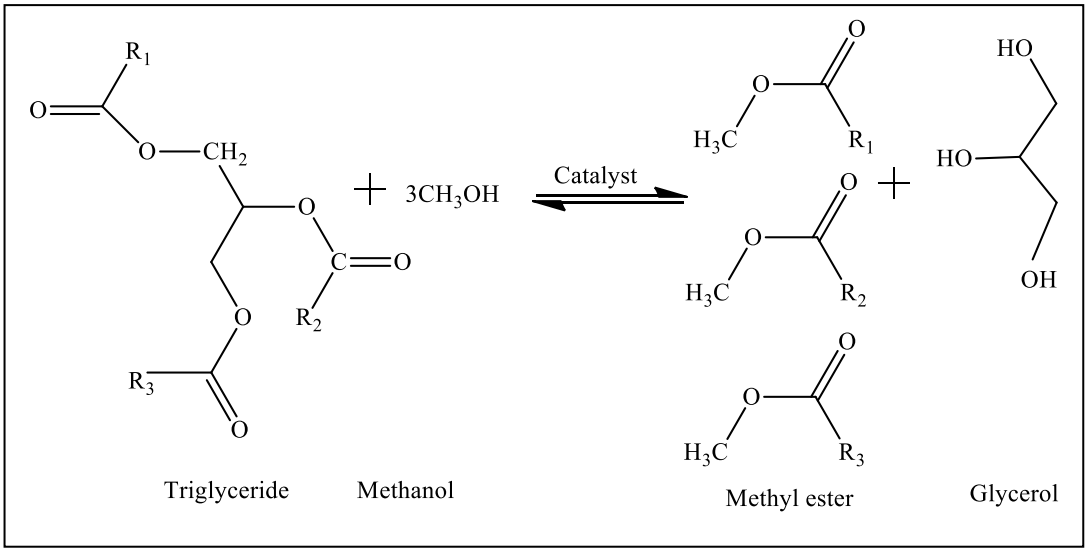

Figure 1.2 Catalytic transesterifications of triglyceride (Borges and Díaz, 2012)

Transesterification reaction can be catalyzed by either acid-catalyzed, base-catalyzed or enzymatic. They were then generally categorized into homogeneous and heterogenous catalysts. Advantages and disadvantages of each type of catalysts are summarized in Table 1.3. According to Issariyakul and Dalai, (2014), the heterogeneous catalyst has gained much attention and concern nowadays from various biodiesel researchers as compared to the homogeneous catalyst. This is due to the fact that heterogeneous catalyst can be regenerated and could be operated in continuous processes for oil transesterification reaction.

Table 1.3: Comparison between homogeneous and heterogenous catalyst (Issariyakul and Dalai, 2014)

Characteristics	**Homogeneous**	**Heterogenous**
Thermal stability	Low	High
Catalyst separation	More wastewater from neutralization	Easily separation
Cost of catalyst	High	Low
Catalyst recycling	Non-recyclable	Recyclable
Presence of free fatty acids and water	High sensitivity	Less sensitivity
Example	NaOH, KOH, H_2SO_4, HCl, HF and H_3PO_4	CaO, alumina/silica supported, zeolite

Therefore, this research, the usage of different lanthanide oxides as co-catalysts of is mainly focused on catalytic transesterification reaction. Lanthanide oxides such as cerium oxide (Ce), lanthanum oxide (La) and praseodymium oxide (Pr) are used. Lanthanide metals is used as the alternative catalysts to produce biodiesel since it offers high efficiently in reaction, as well as increases the percent yields of biodiesel. Similarly, the use of refined cooking palm oil could benefit the disposal of waste which will then reduce pollution.

1.2 Problem Statement

As the world is rapidly urbanized, the use of energy is also growing but the supplies of non-renewable fossil fuels were exhausted. The limited reserve of fossil fuels is getting depleted at an alarming rate. Unfortunately, relying too much on the fossil fuels gives several undesirable side effects to the environment, economic and human health. Excessive consumption of fossil fuel would lead to severe increase in global warming occurs when the atmosphere traps too much carbon dioxide. In order to solve these issues and raise awareness of environmental pollution from petroleum fuel emissions, the biomass has become the worldwide focus as one of the excellent promising substitutes for petroleum-based fuel. It is anticipated that biodiesel obtained from renewable feedstock such as vegetable oil and animal fats will be one of the perfect biomass-based options to replace fossil fuel.

Several conventional base-catalyzed transesterification reactions can be carried out and catalyzed by either acid or base catalysts. In the homogeneous base catalysts, reactions is mainly catalyzed by alkaline metal hydroxides, sodium or potassium (Paulo *et al*., 2016). However, the use of this conventional process has several major drawbacks, such as difficulties to separate the catalyst from the glycerine phase and sensitive to the presence of water and free fatty acid. The homogeneous base catalyst is completely dissolved in the reaction mixture. Thus, a large amount of wastewater is produced to effectively separate the biodiesel and glycerol products. On the other hand, these base catalysts also react with free fatty acids which leads to soap formation. Soaps formation consumes the catalyst and deactivates the catalyst.

Therefore, the biodiesel production proceeds at lower yield with tedious purification steps.

The acid-catalyzed transesterification reaction often uses hydrochloric acid (HCl), phosphoric acid (H_3PO_4) and sulphuric acid (H_2SO_4) as catalyst *(Koh et al*., 2011; Othman *et al*., 2017; Vyas *et al*., 2010). However, acid-catalyzed is not recommended due to it longer reaction time, high cost and high molar ratio of methanol to oil requirement. Moreover, the acid catalysts are highly corrosive as compared to basic catalyst. The transesterification reaction was explored using several solid base catalysts in the biodiesel production including alkaline earth metal oxides, rare earth oxides, transition metal oxides and basic zeolite (Kamal *et al*., 2017; Maleki *et al*., 2017; Nasreen *et al*., 2016; Santório *et al*., 2016). Despite its higher catalytic activity than acid catalyst, solid base catalyst still unfavorable for high free fatty acid content of raw oil. The solid base catalyst gets deactivated when in contact with water and air which enhances the possibility of soap formation. Therefore, in this study, the heterogeneous base catalyst was used in biodiesel production reaction under mild transesterification conditions. The biodiesel production using heterogeneous catalyst are expected to have minimal environmental impact and low production cost.

This study focused on the mixed metal oxides catalyst prepared by combining calcium oxides with the incorporation of lanthanide oxides as co-catalyst supported on alumina for transesterification reaction of refined cooking oil in biodiesel production. The supported catalyst can be directly applied in most modern engines due to its great chemical stability, which can allow for the high reuse ability of the supported catalyst for a few times (Musa, 2016). The great advantage of this mixed metal oxides catalysts is relatively high surface areas and small particle sizes (Refaat, 2011). The biodiesel production with mixed metal oxides renders lower leaching of components into the reaction media (Hwei *et al*., 2016).

Nizah *et al*. (2014) reported that biodiesel production involved a two-step catalytic transesterification reaction. However, the shortcoming of this method requires washing step and separation, which could increase the production cost of biodiesel. To tackle the shortcomings, a single step can be used to separate the glycerol

from biodiesel products. Another factor that affects the production cost of biodiesel depends on the cost of raw materials as feedstocks. Animal fats such as white grease or tallow as feedstocks are economically crucial, but these raw materials will never be able to satisfy the worldwide demand for transport fuels due to the restricted quantity of animal fats available. In addition, animal fats become solid wax at room temperature, which makes it difficult to produce biodiesel as compared to vegetable oil.

Most of the biodiesel production that has been extensively used include edible vegetable oils like canola, palm, walnut, corn, rapeseed, soybean, sunflower, sesame, olive pomace, cotton seed and coconut (Carvalho *et al*., 2018; Knothe and Razon, 2017; Lim and Teong, 2010; Nasreen *et al*., 2016; Sajjadi *et al*., 2016). The usage of edible oil can cause direct competition with food consumption and hence can adversely affect the price of biodiesel production. In this research, refined cooking oil can be used effectively for biodiesel production due to its abundant availability. Besides that, the problems of food and biodiesel production can be circumvented with the use of refined cooking oil as raw materials.

1.3 Objectives of the Study

The main aim of this research is to develop a potential catalyst that can catalyze transesterification reaction of refined cooking oil at optimum conditions. The specific objectives of this research are:-

1. To synthesize alumina supported calcium oxides based nano-catalysts with the addition of lanthanide oxides as co-catalysts for transesterification reaction of biodiesel.
2. To test and optimize the preparation of the catalyst as well as the transesterification reaction in order to maximize the catalytic activity condition for the prepared catalysts.
3. To characterize the selected prepared catalysts in order to investigate the chemical and physical properties of the catalysts.

1.4 Scope of the Research

This research was emphasized on converting the refined cooking oil into value added products of biodiesel through catalytic transesterification by using alumina supported calcium oxide (CaO) based catalysts with the cerium (Ce), lanthanum (La) and praseodymium (Pr) oxides as co-catalysts. First, the nitrate salt was used as precursor for preparing a catalyst. All the catalysts were prepared via wetness impregnation method. The optimization of the catalyst was done on the different amount of based loadings (5:95, 10:90, 20:80 and 30:70 wt.%) and calcination temperatures of catalysts (700-1000ºC). Next, the catalytic activity of the prepared catalysts was evaluated by gas chromatography-flame ionization detector (GC-FID) to determine the percentage conversion of triglycerides. In addition, optimization condition of transesterification reaction was done on the various amount of oil to methanol ratios (1:6, 1:12, 1:18, 1:20 and 1:24 wt.%) and reaction times (1-6 hours). Finally, the potential catalyst was characterized by using various techniques in order to understand the physical properties of the catalysts such as field emission scanning electron microscope-energy dispersive X-ray (FESEM-EDX) and transmission electron microscopy (TEM) for morphology and elemental composition study, X-ray diffraction (XRD) analysis for bulk structure, nitrogen adsorption (NA) for pore texture and surface area of the catalyst, thermal gravimetric analysis (TGA) to study the mass loss of the catalyst during temperature change, X-ray fluorescence (XRF) for chemical state and elemental composition of the catalysts. Besides, temperature programmed reduction-desorption (CO_2-TPRD) was also performed to study the basicity of the catalysts.

1.5 Significance of Study

Catalytic transesterification of refined cooking oil is a promising method in biodiesel production. The production of biodiesel is the potential alternatives that can substitute diesel since it offers many advantages such as renewable energy source, sustainable, non-toxic, biodegradable and economic. Besides, the emission of CO, CO_2, SO_x, particle matter, soot and hydrocarbons, as well as NO_x in optimized diesel-

fuelled engines, can be significantly decreased by promoting switching from fossil fuel to biodiesel. Hence, through this technique, the harmful emission can be reduced together with the effect of global warming. Thus, biodiesel capable of meeting increasing energy demand worldwide and reduce global dependence on the fossil fuel source.

Substituting fossil fuels by biodiesel not only presents economic advantages, but also represents a promising approach for a more sustainable raw material for future generation. Biodiesel consists organic substance which has high molecules like ether, ketones, phenols and alcohols (Adewale *et al*., 2015; Carvalho *et al*., 2018; Chen *et al*., 2018). Biodiesel has low density as compared to water. Therefore, it can be stored in a stable form for a longer period (Noor *et al*., 2018; Sajjadi *et al*., 2016; Veljkovi *et al*., 2018). Furthermore, biodiesel has lower sulphur content than diesel. Besides, it does not have aromatic hydrocarbons. Therefore, emission from biodiesel production generate less not toxic to human health and environment. Biodiesel also has a reduced amount of cetane than diesel fuel, which promotes increases engine performance and combustion properties (Geng *et al*., 2017; Othman *et al*., 2017).

The selection of the best feedstock is a crucial endeavor in maintaining the biodiesel production at low cost. Because using the feedstock from the refined cooking oil, which is abundantly available of renewable resources at no cost or very low cost, it will not only solve the environmental pollution crisis, but it can also offer an economically promising way to convert refined cooking oil into a valuable source as fuel.

In this research, the application of heterogeneous catalyst in biodiesel production has many advantages such as simple separation, prevent saponification during the reaction, regenerated, good reusability as well as high conversions with minimal side products. In addition, the catalyst is typically non-corrosive at longer lifetime. Moreover, the catalyst is easier and safe to handle due to its low temperature requirement. The addition of co-catalyst is one of the alternatives for the catalysts in order to avoid soap formation which can modify the acid-base and redox properties of a catalyst.

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