UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF CALCIUM OXIDE-BASED CATALYST DERIVED FROM WASTE SHELL FOR BIODIESEL PRODUCTION FROM Nannochloropsis oculata OIL AND PALM FATTY ACID DISTILLATE

NUR SYAZWANI BINTI OSMAN

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By

NUR SYAZWANI BINTI OSMAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

June 2017

DEDICATION

Special Dedication to:

My Loving Husband :

Mohd Faiz bin Ismail

&

My Beloved Parents:

Osman Bin Husin & Jemilah bt Jaafar

And My Family

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor Philosophy

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Chairman: Prof. Taufiq Yap Yun Hin, PhD
Faculty: Science

Excessive use of petroleum in transportation and industry, leads to acceleration of greenhouse gas emissions and the depletion of petroleum reserves worldwide. In order to reduce the environmental issues, research on alternative fuel which can replace the dependency on non-renewable petroleum based fuel is crucial. In this research, calcium oxide, (CaO) derived from three different waste shells (Angel Wing, Etok and Green Mussel) were used as catalyst for transesterification of microalgae oil, *Nannochloropsis oculata.* The microalgae oil was extracted after cultivating and harvesting for several weeks. Calcined angel wing shell (CAWS) at 900 ˚C shows highest FAME yield (84.11%) at oil:methanol molar ratio 1:150 and catalyst loading of 9 wt.% in 1 h reaction and can be reused for more than three times.

In order to reduce cost production of biodiesel, low cost feedstock such as palm fatty acid distillate (PFAD) was also used by using sulfated CAWS catalysts. CAWS precursor was sulfated using different sources of SO_4^{2-} ions with varied concentration at ambient temperature. All the catalysts were characterized by using thermogravimetric analysis (TGA), X-ray diffraction spectroscopy (XRD), Fourier transforms infrared spectroscopy (FT-IR), temperature programmed desorption of carbon dioxide (TPD-CO_2), temperature programmed desorption of ammonia (TPD-NH_3), BET surface area and variable pressure scanning electron microscope (VPSEM).

In addition, esterification reaction of PFAD by using a conventional reflux with the presence of $CAWS_{(7)}$-H_2SO_4 catalyst shows 98% of FAME yield at 1:15 PFAD/ methanol molar ratio, 5 wt.% of catalyst loading at 80 ˚C for 3 h reaction. The catalyst also can be reused at least two times with 98% of FAME yield without further treatment. The reused or spent catalyst was analyzed to determine the deactivation mechanism of the reused catalyst. Besides, esterification of PFAD in supercritical methanol reaction produced 97.9% of FAME yield with PFAD/methanol molar ratio

1:6, 2 wt.% of catalyst loading at 290˚C for 15 minutes. The CAWS-$_{(7)}H_2SO_4$ catalyst can be reused up to seven cycles with FAME yield more than 80 %.

The fuel properties were also investigated by using ASTM and European standard method and it was found that the PFAD methyl ester was met the biodiesel quality standard and has almost similar property with petrol fuel. As a conclusion, both CAWS and CAWS$_{(7)}$-H_2SO_4 show outstanding performance as low cost heterogeneous basic and acid catalyst, respectively for biodiesel production from either low or high FFA feedstocks.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

PEMBANGUNAN MANGKIN BERASASKAN KALSIUM OKSIDA TERBITAN SISA CENGKERANG UNTUK PENGHASILAN BIODIESEL DARIPADA MINYAK *Nannochloropsis oculata* DAN SULINGAN ASID LEMAK SAWIT

Oleh

NUR SYAZWANI BINTI OSMAN

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Penggunaan petroleum yang berlebihan dalam pengangkutan dan industri, membawa kepada peningkatan pembebasan gas rumah hijau dan pengurangan rizab petroleum di seluruh dunia. Bagi mengurangkan isu alam sekitar, kajian untuk menghasilkan bahan bakar alternatif yang boleh menggantikan kebergantungan bahan api berasaskan petroleum yang tidak boleh diperbaharui adalah penting. Dalam kajian ini, kalsium oksida, CaO berasal daripada tiga sisa cengkerang yang berbeza telah digunakan sebagai mangkin dalam transesterifikasi minyak mikroalga, *Nannochloropsis oculata*. Minyak mikroalga diekstrak selepas proses menanam dan menuai selama beberapa minggu. Sisa Angel Wing (CAWS) yang dikalsin pada suhu 900˚C menunjukkan hasil FAME tertinggi (84.11%) pada nisbah molar minyak:metanol 1:150 dan muatan berat mangkin sebanyak 9% dalam 1 jam masa tindak balas dan ia boleh digunakan semula lebih daripada tiga kali.

Untuk mengurangkan kos pengeluaran biodiesel, bahan mentah kos rendah seperti sulingan asid lemak sawit (PFAD) telah digunakan dengan menggunakan mangkin sulfat CAWS. CAWS prekursor telah disulfat menggunakan pelbagai sumber ion SO_4^{2-} dengan kepekatan yang divariasikan pada suhu ambien. Semua mangkin dicirikan dengan menggunakan analisis terma gravimetri (TGA), pembelauan sinar-X (XRD), Fourier mengubah inframerah spektroskopi (FT-IR), program-suhu-nyahjerapan karbon dioksida (TPD-CO_2), program-suhu-nyahjerapan ammonia (TPD -NH_3), analisis luas permukaan BET dan tekanan ubah mikroskop imbasan elektron (VPSEM).

Di samping itu, tindak balas pengesteran PFAD dengan menggunakan refluks konvensional dengan kehadiran mangkin $CAWS_{(7)}$-H_2SO_4 menunjukkan hasil 98% FAME pada 1:15 PFAD nisbah molar metanol, berat mangkin 5 wt.% pada 80 ˚C selama 3 jam masa tindak balas. Mangkin ini juga boleh digunakan semula sekurang-kurangnya dua kali dengan 98% hasil FAME tanpa rawatan selanjutnya. Mangkin

digunakan semula dianalisis untuk menentukan mekanisme penyahaktifan yang pemangkin digunakan semula. Selain itu, pengesteran PFAD dalam reaksi superkritikal metanol menghasilkan 97.9% hasil FAME dengan nisbah molar PFAD: metanol 1:6, 2 wt. % berat mangkin pada 290˚C selama 15 minit. Mangkin $CAWS_{(7)}$-H_2SO_4 boleh digunakan semula sehingga tujuh kitaran dengan hasil FAME lebih daripada 80%.

Sifat-sifat bahan api juga telah dikaji dengan menggunakan ASTM dan kaedah piawai Eropah dan didapati PFAD metil ester memenuhi kualiti piawaian biodiesel dan mempunyai sifat yang hampir sama dengan minyak petrol. Kesimpulannya, CAWS and $CAWS_{(7)}$-H_2SO_4 menunjukkan prestasi cemerlang sebagai mangkin heterogen bes dan asid kos rendah dalam penghasilan biodiesel daripada sumber minyak rendah atau tinggi kandungan FFA.

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I certify that a Thesis Examination Committee has met on 5 June 2017 to conduct the final examination of Nur Syazwani binti Osman on her thesis entitled “Development of Calcium Oxide-Based Catalyst Derived from Waste Shell for Biodiesel Production from *Nannochloropsis oculata* Oil and Palm Fatty Acid Distillate” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AOAC	Association of Official Analytical Chemist
ASTM	American Society for Testing and Materials
ATR-FTIR	Attenuated Total Reflection-Fourier Transform Infrared
AV	Acid Value
BET	Brunauer-Emmett-Teller
CHNS	Carbon, Hydrogen, Nitrogen, Sulfur element analysis
CO_2-TPD	Temperature Programmed Desorption CO_2
CAWS	Calcined Angel Wing Shell
CES	Calcined Etok Shell
CGMS	Calcined Green Mussel Shell
Com-$CaSO_4$	Commercial Calcium Sulfate
CP	Cloud Point
DGs	Diglycerides
EDX	Energy Dispersive X-ray
EN	European Standard
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full-Width Half Maximum
GC-FID	Gas Chromatography- Flame Ionization Detector
GC-MS	Gas Chromatography- Mass Spectrometer
GHG	Life-cycle Greenhouse Gas
H_2SO_4	Sulfuric acid
MGs	Monoglycerides
MPOB	Malaysian Palm Oil Board
NH_3-TPD	Ammonia-Temperature Programmed Desorption
NO_x	Nitrogen dioxide
PFAD	Palm Fatty Acid Distillate
PP	Pour Point
SEM	Scanning Electron Microscopy
SV	Saponification Value
TGs	Triglycerides

CHAPTER 1

INTRODUCTION

1.1 Research Background

The world is struggling to confront with the double crisis of fossil fuels declination and environmental pollution. The indiscriminate extraction and extremely high consumption of oil based fuel every year have led to a reduction in petroleum reserves and increment of greenhouse gasses (GHG) emissions. This phenomenon's will change the global climate and continuously lead to unsustainable environment. Figure 1.1 shows the world total liquid oil consumption and production from 1990 to 2035 (BP Energy Outlook 2035, 2015). Generally, both of total oil consumption and production are directly proportional to rapid growth population over the years since 1990 to date. The trends envision to be increasing until 2035 (Figure 1.1). Furthermore, oil consumption is expected to be high demand compared to the oil production in 2020 to 2035.

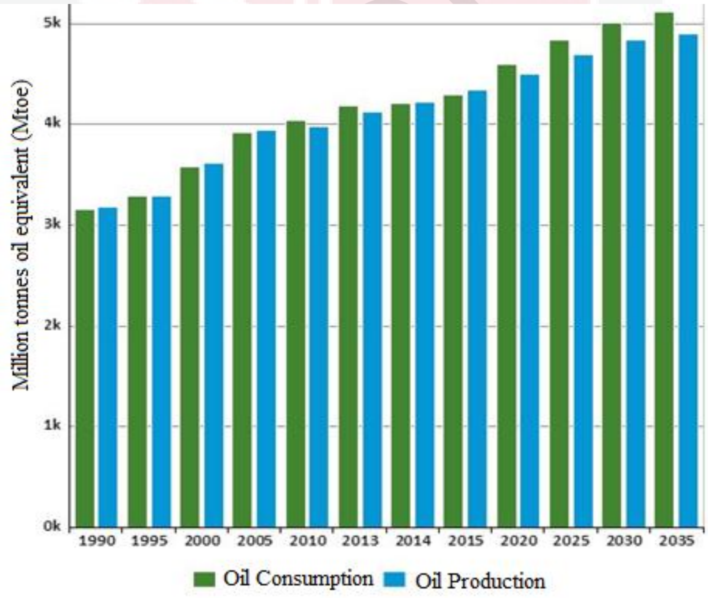

Figure 1.1: The world's total oil consumption and production from 1990 to 2035 (BP Energy Outlook 2035, 2015).

Unfortunately, fossil fuels are non-renewable source that will diminish later and burning fossil fuels significantly contribute towards global warming by emissions of GHG (Demirbas, 2011). Le Quere et al. (2014) investigated assessment of anthropogenic carbon dioxide (CO_2) emissions to study global carbon cycle. As demonstrated in Figure 1.2, emissions of CO_2 increase rapidly since 1990. In addition, the global atmospheric CO_2 concentration reached 392.52±0.10 ppm averaged over

2012. From estimations, the CO_2 concentration will increase about 2.1% to 9.9±0.5 GtC in 2013, 61% above emissions in 1990.

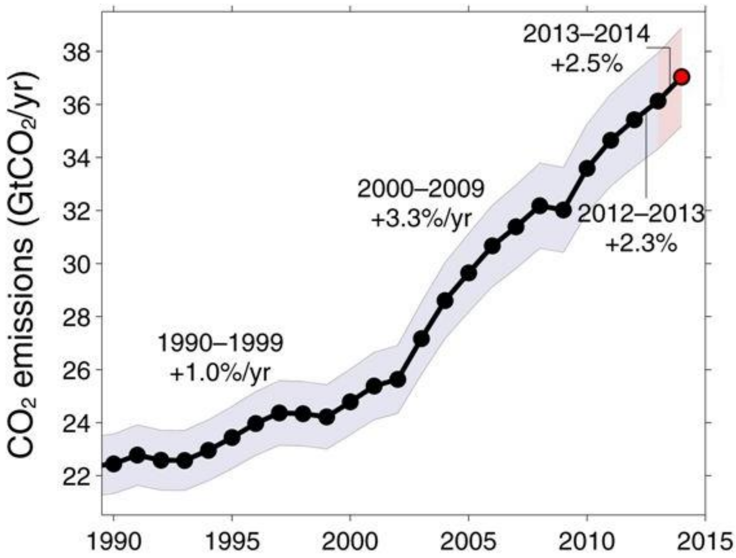

Figure 1.2: Global fossil fuel and cement emissions from 1990 to 2013 adapted from (Le Quéré et al., 2014).

Due to these scenarios, there are vital to find alternative fuels to replace the petroleum based fuel in order to fulfill the high demand of energy and provide sustainable environment. Liquid biofuel, which consists of bioethanol and biodiesel has a potential to replace the non-renewable energy without causing harm to human and environment. Both biofuel can be derived from natural renewable resources. However, in this work, only biodiesel has been focused and investigated as the alternative fossil fuel replacement.

1.2 Biodiesel and its Advantages

Biodiesel or mono alkyl ester of long chain fatty acids is a promising alternative fuel which has similar properties as fossil fuels in terms of the chemical structure and energy content (Lam and Lee, 2011). Moreover, since it can be produced from renewable resources, it is also one of renewable energy. According to Atabani et al.,(2012), biodiesel is highly biodegradable and has minimal toxicity, that could replace petroleum fuel in various applications without major modifications. Besides, biodiesel also non-flammable and produces lower GHG emissions (CO_2, HC, SO_x, and NO_x) compared to fossil fuels (Shahabuddin et al., 2012), leads to the complete combustion and reduced emission due to have a lot of free oxygen (Atabani et al., 2012).

Biodiesel can be used as a pure fuel (B100) or blended with petroleum in any percentage. It offers full blending potential with conventional diesel where a high cetane number giving improved combustion in compression ignition engines, and low emissions of sulphur and particulates. For instance, there are B20 (a blend of 20 percent by volume biodiesel with 80 percent by volume petroleum diesel), B2 (a blend of 2 percent by volume biodiesel with 98 percent by volume petroleum diesel), and B5 (a blend of 5 percent by volume biodiesel with 95 percent by volume petroleum diesel) which are common fuel blends used today (Szybist et al., 2007).

1.3 Catalyst in Biodiesel Production

To be general, biodiesel can be produced from transesterification or esterification reaction of vegetable oils/animal fats which can be done in the presence of enzymes or catalysts (acids or bases) with alcohol (methanol and ethanol). Utilization of homogeneous catalysts in the reaction process has disadvantages due to complexity in purification step for biodiesel production (Granados et al., 2007). The catalyst cannot be recovered and must be neutralized and separated from the methyl ester phase at the end of the reaction, with the consequent generation of a large volume of wastewater. The method for the removal of the catalyst after reaction is technically difficult which increase the overall cost of the process. As a consequence, the total cost of the biodiesel production based on homogeneous catalysis, is not yet sufficiently competitive as compared to the cost of diesel production from petroleum.

Thus, heterogeneous catalysts were used for biodiesel production as they have many benefits such as easily separated, non-corrosive, can be reused and regenerated (long catalyst lifetimes) and economical friendly (Liu et al., 2008). Heterogeneous catalysts also give high purity of glycerol and do not produce soap through free fatty acid neutralization and triglyceride saponification (Refaat, 2010).

1.4 Problem Statement/Hypothesis

Due to highly abundant waste shells which are one of the sources of calcium oxide, CaO, it was widely used for biodiesel production as heterogeneous base catalyst. CaO obtained from different sources gives different physico-chemical properties. Screening of CaO derived from the different waste shells is important to produce highly active catalyst, hence increase biodiesel yield. However, utilization of highly basic metal oxide of CaO is not suitable for high free fatty acid (FFA) oil such as PFAD since it will cause an unfavour saponification reaction.

Recently, microalgae oil has gained research interest as third generation biodiesel feedstock. This is due to its high grow roots and lipid content. In fact, microalgae do not compete for arable land with food crops and other products since it can be grown in various environments that are not suitable for growing other crops for instance, salt water, non arable land, fresh, brackish and also wastewater (Sharma et al., 2012).

Hence, utilization of microalgae as biodiesel feedstock was expected to bring more sustainable environment.

Highly cost biodiesel production makes the biodiesel not compatible in the global market. It has been found that the cost of feedstocks accounts for 75% of the total cost of biodiesel fuel (Atabani et al., 2012). Thus, consumption of palm fatty acid distillate (PFAD) which easily available and known as low-cost feedstock for biodiesel production can reduce the production cost, but it is only suitable for acid catalyst instead of basic catalyst since consist of high free fatty acid (FFA) value.

Basically, esterification reaction of PFAD , high FFA feedstock were performed by using homogeneous acid catalyst such as sulfuric acid, H_2SO_4 (Chongkhong et al., 2009; Rahmi, 2013), phosphoric acid, H_3PO_4 (Metre and Nath, 2015) and methanesulfonic acid (Aranda et al.,2008) while sulfated transition metal oxide for instance sulfonated mesoporous $ZnAl_2O_4$ (Soltani et al., 2016) and sulfonated carbon-based such as sulfonated-glucose (Lokman et al., 2015) was used as heterogeneous acid catalyst. However, these catalysts were expensive and needs complex catalyst synthesis process. Thus, modification of CaO derived from the waste shell by a simple sulfation process with sulfate group, SO_4 to activate the acid site of the catalyst is expected to produce low cost solid acid catalyst which suitable to be used in esterification of high FFA feedstocks.

The esterification reaction was carried out by using the common conventional reflux at mild condition and the effect of the reaction in supercritical methanol was investigated. Basically, supercritical methanol reaction was performed in non-catalytic reaction for biodiesel production. However, it consumes very high temperature and large amount of methanol (Saka and Kusdiana, 2001). Thus, the main idea was to introduce the presence of heterogeneous acid sulfated CaO catalyst in the supercritical methanol reactor to generate the reaction at low reaction temperature in shorter time.

1.5 Objectives

This dissertation aims to synthesize and modify calcium oxide catalysts derived from waste shell. This study also concerned with the physical and chemical properties of synthesized catalysts and the feasibility of biodiesel production from microalgae oil and PFAD through transesterification and esterification reaction with methanol. In order to achieve the main aim, there are six research objectives have been addressed as follows:

1. To synthesize, screen and characterize calcium oxide derived from different waste shells.
2. To optimize the condition for transesterification reaction of microalgae oils by using CaO derived from the waste shell catalysts.
3. To synthesize and investigate physico-chemical characteristics of sulfated CaO derived from waste shell.
4. To optimize the parameter condition for esterification of PFAD.

5. To investigate the effect of supercritical temperature on esterification of PFAD.
6. To determine and evaluate the properties of PFAD biodiesel.

1.6 Scope of Research

This research involved the synthesis and sulfation of CaO derived from waste shells of Angel Wing as heterogeneous acid catalysts for biodiesel production from PFAD. Prior to the sulfation process, the CaO was synthesized from three different waste shells (Angel Wing, Etok and Green Mussel). The suitable calcination temperature for CaO synthesis was investigated and characterized by using TGA, XRF, XRD, FT-IR, TPD-CO_2, TPD-NH_3, BET and SEM. Then, the best calcined shell catalyst was chosen for optimization study by using crude microalgae oil synthesized after cultivation, harvest and extraction process. The condition of the transesterification reactions of microalgae oil was also studied by investigating the effect of variable parameters such as methanol to oil weight ratio, catalyst loading, and reaction time. The reusability of the CaO catalyst was determined and the leaching of calcium species into the reaction product was confirmed by using atomic absorption spectroscopy (AAS) elemental analysis.

Next, the calcined shell (CaO) was sulfated and the effect of catalyst preparation *i.e*, sulfate agent, and concentration of sulfate agent in catalyst performance was investigated. The physico-chemicals properties of sulfated catalysts were performed by using several methods (XRD, FT-IR, TPD-CO_2, TPD-NH_3, BET and SEM). The basicity and acidity properties of the modified catalysts were evaluated in terms of numbers and strength of the basic and the acidic site through CO_2 and NH_3-temperature programmed desorption techniques. In addition, the structural characteristics and the surface properties of the modified catalyst was carried out using XRD and BET surface area, respectively.

The performance of the sulfated catalysts was carried out in esterification reaction of PFAD in two reaction systems: conventional reflux and supercritical methanol. The relationship between concentration of sulfate agent and acidity of the catalyst was discussed. The entire biodiesel product in the reaction was analyzed and the FAME yield was calculated by using gas chromatography (GC-FID). Additionally, the spent catalyst analysis also performed to investigate deactivation of catalyst after reused. The leaching of Ca and sulfur content was also analyzed by using AAS and CHNS, respectively. Lastly, the biodiesel fuel standard quality properties were determined by using ASTM D6751 and European 14212 standard specifications.

1.7 Organization of the Thesis

This thesis contains ten chapters. **Chapter One** introduces research background, the advantages of biodiesel and catalysts involved in biodiesel production. It also consists of problem statement and hypothesis, the objectives and scope of the proposed research. **Chapter Two** reveals a comprehensive literature review relating to the past and current status of biodiesel as one of transportation fuel, the generations of biodiesel feedstocks, biodiesel production by using heterogeneous basic and acid catalyst as well as the reports on utilizing CaO derived from waste shell in biodiesel production. Moreover, recent technologies in biodiesel production also were discussed. **Chapter Three** is the methodology section which covers all issues associated with catalyst preparation, the characterizations and the experimental setup along with the transesterification/esterification reaction and the cultivation, harvest and extraction method of microalgae oil. The characterization of feedstocks and biodiesel also was considered. **Chapter Four** screen and present the characterization of CaO derived from Angel Wing shell, Etok shell and Green Mussel shell. **Chapter Five** shows the optimization result for transesterification of microalgae oil by using CAWS900 catalyst as well as the reusability and leaching of the catalyst. **Chapter Six** present the characterization of sulfated CAWS by using sulfuric acid and chlorosulfonic acid. Moreover, the characterization of sulfated CAWS with different concentration of sulfuric acid also was presented. **Chapter Seven** and **Eight** explain the optimization of PFAD esterification by using conventional reflux and supercritical methanol, respectively. The deactivation of the spent catalyst also is described. **Chapter Nine** shows the PFAD biodiesel fuel properties analysis according to EN14121 and ASTM D6751. **Chapter Ten** summarizes, highlights and concludes the contribution and the main findings of this research study along with the recommendations for future research.

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(ISO) International Organization for Standardization. (n.d.).

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APPENDICES