



**UNIVERSITI PUTRA MALAYSIA**

***MODIFICATION OF NATURAL WASTE CLAMSHELLS BY  
HYDRATION-DEHYDRATION TECHNIQUE FOR  
TRANSESTERIFICATION REACTION OF PALM  
OIL TO BIODIESEL***

**NURUL ASIKIN BT MIJAN**

**FS 2014 82**



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OIL TO BIODIESEL**

**By**

**NURUL ASIKIN BT MIJAN**

**Thesis Submitted to School of Graduate Studies, Universiti Putra Malaysia, in  
Fulfillment of the Requirement for the Degree of Master of Science**

**June 2014**

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Degree of Master of Science

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**June 2014**

**Chair : Prof. Taufiq Yap Yun Hin, PhD**  
**Faculty: Science**

Utilization of catalyst from waste shell (clamshell) via modification of catalyst via hydration followed by thermal decomposition is not only economic and environmental friendly. The hydration-dehydration method is efficient and easy to manufacture. The clamshell-derived calcium oxide (CS-CaO) from hydration technique shows high basicity as well as high surface area that exhibited higher catalytic activity than CaO of commercial standard. The CS-CaO derived from clamshell was reflux continuously with water for 1,3,6,9 and 12 h and calcined at 600 °C for 3 h to produce heterogeneous catalyst with greater properties (stronger activity and better selectivity relatively due to high surface area and high basicity) that perform better in transesterification reaction. The clamshell was characterized by using X-Ray fluorescence spectroscopy (XRF) and thermogravimetric analysis (TGA). The synthesized catalyst was characterized by using several methods such as X-Ray diffraction (XRD) analysis, N<sub>2</sub> adsorption (BET), temperature-programme desorption of carbon-dioxide (TPD-CO<sub>2</sub>), scanning electron microscopy (SEM). The synthesized biodiesel was characterized using gas chromatography (GC) and atomic absorption (AAS). Furthermore, the catalytic activity of the catalyst derived from clamshell; CS-CaO, CS-CaO<sub>1h</sub>, CS-CaO<sub>3h</sub>, CS-CaO<sub>6h</sub>, CS-CaO<sub>9h</sub> and CS-CaO<sub>12h</sub> were investigated. Elongating the time during refluxing process in water resulted in high basicity of catalyst and surface area which leads to high catalytic activity (CaO<sub>12h</sub>>CaO<sub>9h</sub>>CaO<sub>6h</sub>>CaO<sub>3h</sub>>CaO<sub>1h</sub>). The transesterification activity was greatly influenced by basicity of the active sites on the catalyst. The optimization study for palm-based biodiesel production using CS-CaO, CS-CaO<sub>1h</sub>, CS-CaO<sub>3h</sub>, CS-CaO<sub>6h</sub>, CS-CaO<sub>9h</sub> and CS-CaO<sub>12h</sub> was conducted in this study. The effect of the variables including methanol and oil molar ration (5-17), catalyst loading (0.2-1 wt. %) and reaction time (1-5 h) was investigated. The results shows CS-CaO<sub>9h</sub> catalyst resulted in completed reaction (FAME > 98 %) at optimum condition of 2 h reaction time via catalyst loading equal to 1 wt.% with 9:1 methanol and oil molar ratio. Several physicochemical properties of palm-based biodiesel produced was tested and agreed

to ASTM D6751 (ASTM D445, ASTM D93, ASTM D97, ASTM D2500) and EN 14214 standard.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia  
Sebagai memenuhi keperluan untuk ijazah Master Sains

**PENGUBAHSUAIAN SISA SEMULA JADI CENGKERANG KEPAH  
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TINDAK BALAS TRANSESTERIFIKASI MINYAK SAWIT KEPADA  
BIODISEL**

Oleh

**NURUL ASIKIN BT MIJAN**

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Penggunaan pemangkin dari sisa cengkerang (cengkerang kepah) melalui pengubahsuaian penghidratan diikuti oleh penguraian terma bukan sahaja menjimatkan dan mesra alam sekitar. Kaedah penghidratan-penyahidratan juga efisien dan penghasilannya sangat mudah. Kalsium oksida (CS-CaO) yang diperbuat daripada cengkerang kepah melalui kaedah penghidratan menunjukkan darjah kealkalian dan luas permukaan yang tinggi, ia menunjukkan kadar aktiviti pemangkin yang tinggi lebih daripada pemangkin CaO komersial. CS-CaO daripada cengkerang telah direflukskan di dalam air untuk jangka masa 1,3,6,9, dan 12 jam dan dikalsin pada suhu 600 °C untuk 3 jam bagi menghasilkan pemangkin heterogen dengan ciri-ciri lebih bagus (aktiviti yang lebih aktif dan pemilihan yang lebih baik, disebabkan luas permukaan dan kealkalian yang tinggi), ia akan menyebabkan tindak balas berlaku dengan berkesan. Cengkerang kepah tersebut dianalisa dengan menggunakan sinar-X pendarfluor spektroskopi (XRF) dan termogravimetri analisis (TGA). Pemangkin yang telah disintesis akan dicirikan dengan menggunakan beberapa kaedah seperti analisis belauan sinar-X (XRD), Brunauer-Emmet-Teller (BET), Program suhu peyahjerapan karbon dioksida (TPD-CO<sub>2</sub>), pengimbas mikroskopi elektron (SEM). Biodiesel yang dihasilkan akan dicirikan menggunakan gas chromatogram (GC) dan spektroskopi penyerapan atom (AAS). Seterusnya, aktiviti pemangkin yang diperbuat daripada cengkerang kepah CS-CaO, CS-CaO<sub>1h</sub>, CS-CaO<sub>3h</sub>, CS-CaO<sub>6h</sub>, CS-CaO<sub>9h</sub> dan CS-CaO<sub>12h</sub> disiasat. Pemanjangan tempoh masa semasa proses refluks dalam air akan menyebabkan peningkatan kealkalian dan luas kawasan permukaan yang tinggi sekaligus membawa kepada aktiviti pemangkinan yang tinggi (CS-CaO<sub>12h</sub> > CS-CaO<sub>9h</sub> > CS-CaO<sub>6h</sub> > CS-CaO<sub>3h</sub> > CS-CaO<sub>1h</sub> > CS-CaO). Transesterifikasi aktiviti dipengaruhi oleh kealkalian tapak aktif catalyst. Kajian pengoptimuman biodiesel daripada minyak sawit menggunakan CS-CaO, CS-CaO<sub>1h</sub>, CS-CaO<sub>3h</sub>, CS-CaO<sub>6h</sub>, CS-CaO<sub>9h</sub> dan CS-CaO<sub>12h</sub> telah dijalankan dalam kajian kesan pemboleh ubah termasuk nisbah molar (5-17) metanol dan minyak, kuantiti pemangkin (0.2-1 wt.%) dan masa tindak balas (1-5 h) telah disiasat. Keputusan menunjukkan pemangkin CS-CaO<sub>9h</sub> menghasilkan tindak balas lengkap (FAME > 98 %) di dalam keadaan

optimum masa tindak balas 2 jam , kuantiti pemangkin 1 wt.% dan nisbah methanol dan molar minyak pada 9:1. Beberapa sifat fisikokimia biobahan api biodiesel minyak sawit yang dihasilkan telah diuji dan mematuhi ASTM D6751 (ASTM D445, ASTM D93, ASTM D97, ASTM D2500) dan EN 14214 standard.



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I certify that a Thesis Examination Committee has met on 19 June 2014 to conduct the final examination of Nurul Asikin binti Haji Mijan on her thesis entitled "Modification of Natural Waste Clamshells by Hydration-Dehydration Technique for Transesterification Reaction of Palm Oil to Biodiesel" 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 Master of Science.

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## LIST OF ABBREVIATIONS

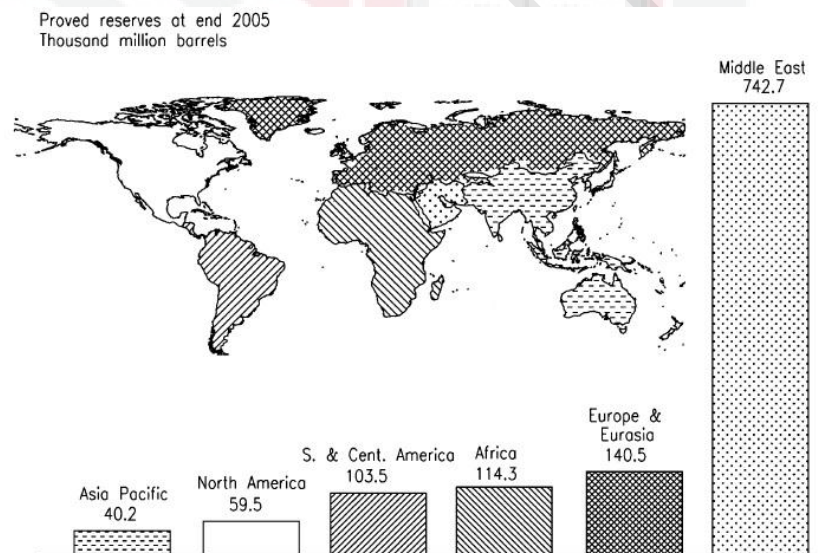
ASTM	American Society for Testing and Materials
EN	European Standard
JCPDS	Joint Committee on Powder Diffraction Standards
MPOB	Malaysian Palm oil Board
R&D	Research And Development
TGA	Thermogravimetry Analysis
XRD	X-Ray Diffraction Analysis
TPD-CO <sub>2</sub>	Temperature Programmed Desorption of Carbon Dioxide
BET	Brennauer-Emmet-Teller
SEM	Scanning Electron Microscopy
XRF	X-ray Fluorescence Spectroscopy
GC	Gas Chromatography
AAS	Atomic Absorption Spectroscopy
FFA	Free Fatty Acid
TCD	Thermal Conductivity Detector
D2	Diesel Fuel
SNI	Shipp Non-ionic
EMA	Engine Manufacturers' Association
TCD	Thermal Conductivity Detector
FAME	Fatty acid methyl ester
CS	Raw fresh powder clamshell
CS-CaO	CaO derived from clamshell
CS-CaO <sub>1 h</sub>	CaO derived from clamshell from 1 h water treatment
CS-CaO <sub>3 h</sub>	CaO derived from clamshell from 3 h water treatment
CS-CaO <sub>6 h</sub>	CaO derived from clamshell from 6 h water treatment
CS-CaO <sub>9 h</sub>	CaO derived from clamshell from 9 h water treatment
CS-CaO <sub>12 h</sub>	CaO derived from clamshell from 12 h water treatment

## CHAPTER 1

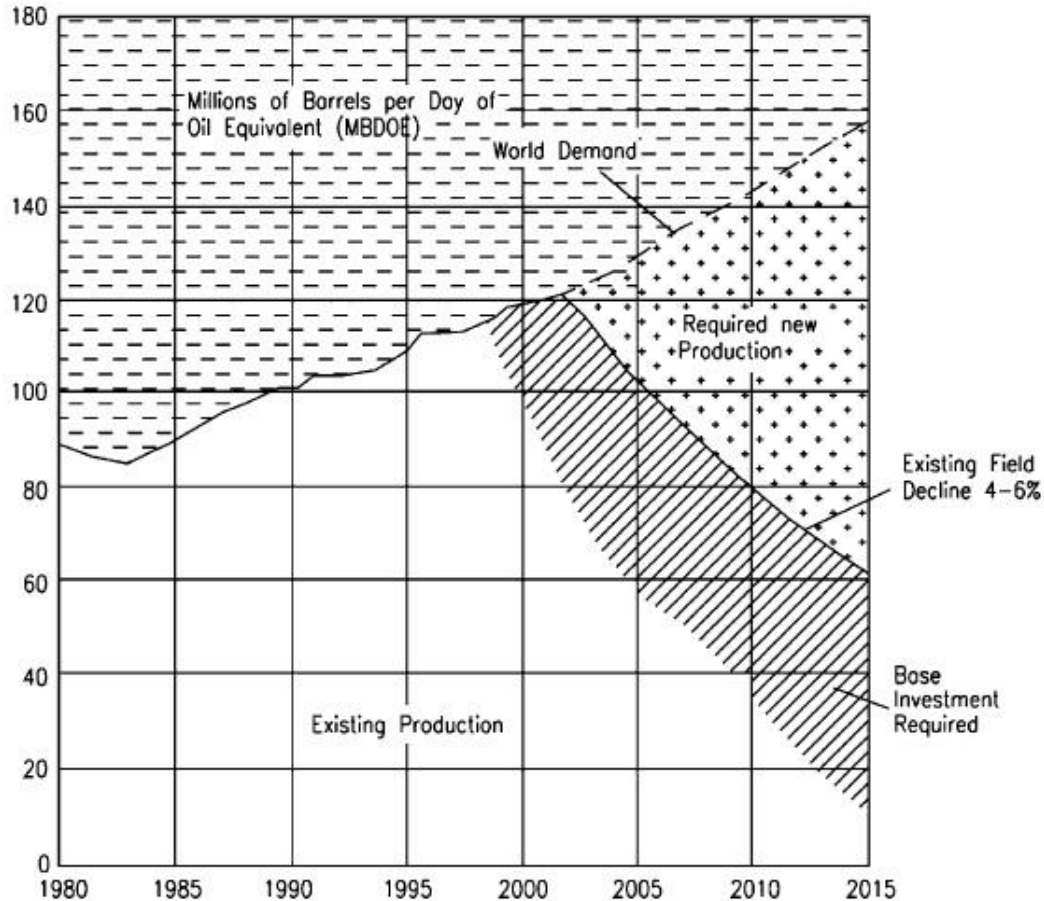
### INTRODUCTION

#### 1.1 Fossil Fuel Energy

The world has recently been in trouble with energy crisis due to the depletion of fossil fuel (Ngamcharussrivichai *et al.*, 2010). This fact also in agreement by Alba-Rubio *et al.*, 2010, which the exhaustion of the fossil source has provoked enormous problem of energy dependency in most countries. The world's oil reserves are located in certain location and extremely irregularly. The specific areas which have suitable geological features and allowed the creation along with accumulation of the oil. Figure 1 shows the current scene of the distribution of the oil reserves around the world. It found, that majority about 65 % of oil reserve possess by Middle East followed by Europe and Eurasia (11.7 %), Africa (9.5 %), Central and South America (8.6 %), North America (5 %) and Asia and The Pacific (3.4 %) (Escobar *et al.*, 2009)



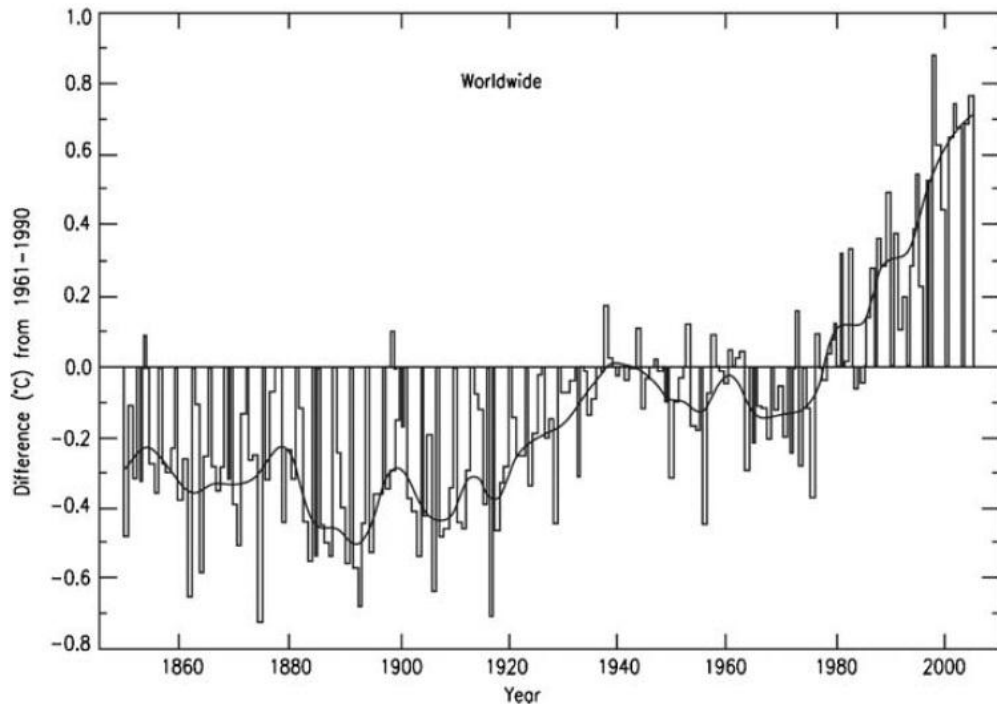
**Figure 1. Current panorama and distribution of the oil reserves in the world**  
(Source: Escobar *et al.*, 2009)



**Figure 2. Projection of the energy demand from (1980-2015) (ExxonMobil)**

Furthermore, Figure 2 shows projection of the world energy demands for near future. The forthcoming reduction of fossil fuel production along with the rapid growth of population and urbanization contributed to the rising of the petroleum derived fuels demand for daily necessities especially in transportation sector. In 2010, Rahman's stated that the growing consumption of energy resulted in the country's increasing dependent on fossil fuels such as coal, oil and gas. But, energy sources are limited and decreasing gradually. Therefore, limitability and unrenewability energy for fossil resources are the main reason to the rising of cost of petroleum-derived fuels. Hence, new energy sources which can contribute towards meeting the demands must be explored.

Application of the petroleum-derived fuels is one of the reasons to the increasing emission of polluted gasses that lead to the global warming effect such as CO<sub>x</sub> and NO<sub>x</sub>. It is terrified that global warming will lead to a serious climatic change and threatening human nature. Global warming is mainly caused by greenhouse gases, particularly CO<sub>2</sub> which are produced during the burning of fossil fuels which results in significant changes in the ecosystem. Over the past century, the atmospheric concentration of CO<sub>2</sub> reached its highest levels. As it can be observed in Figure 3. Escobar's reported, these problems happened due to unsustainable usage of fossil fuels product and the change in the use of land (Escobar *et al.*, 2009).



**Figure 3. The variation of the concentration level of CO<sub>2</sub> in the atmosphere and the rise in the planet's global temperature**  
(source: Escobar *et al.*, 2009).

In 2012, Kouzu and Hidaka reported the constant ascend of the earth's average temperature, threatens millions of people with growing risk of hunger, floods, water shortage and diseases such as malaria. Escobar's group agreed that the decreasing of the resources of the fossil energy and the accumulation of carbon dioxide and other greenhouse gases in the atmosphere are the main explanation for the change in climates, and will result in very bad consequences on human and other living organisms.

Therefore, it is necessary to solve this problem by making great effort in order to reduced the climate change and also reduce the level of greenhouse gas emission. Nowadays, all the developed countries are competing among themselves to create new alternative low cost fuel known as biodiesel which should be sustainable and also friendly to environment.



## 1.2 Problem Statements and Scope of Research

The increasing of crude oil petroleum prices, limited resources of fossil fuels and environmental concern have led to the search for new alternative fuels which are more sustainable, energy conservation, efficiency and environmental friendly. In this present study, biodiesel production from transesterification reaction are focussed by application of heterogeneous catalyst. Heterogeneous catalyst attracted much attention due to the technological problems that are associated with the production of biodiesel when using homogeneous catalyst in which required extra purification or neutralization step. The neutralization step is non-friendly environmental process. It because of neutralization step will produced high amounts of waste water and caused water pollution. In addition utilization of homogeneous catalyst in vegetable oil transesterification, results in soap formation which is an undesirable side-reaction. Since the catalyst is consumed in the reaction, it will make separation process of ester and glycerol becomes very difficult and require more purification process which will lead to higher production cost. Besides, homogenous catalyst cannot be reused or regenerated.

Therefore, heterogeneous catalyst are very important for biodiesel production because it have many advantages over homogeneous catalysts. Generally, they are noncorrosive, environmentally friendly and less disposal problems. Application of heterogeneous catalyst will not cause soaps formation through fatty acid neutralization saponification. Moreover, it also easy to be separated from liquid product, reusable and can be designed to give higher catalytic activity, selectivity and longer catalyst lifetime.

Nowadays, biodiesel researches are directed towards the development of environment friendly and involved lower cost. Therefore, various of heterogeneous catalysts from different natural resources have been reported in previous studies such as eggshell, cockle shell, chicken bone, bovine bone, oyster shell and etc. Most of these waste material derived catalysts are coming from cheap waste resources for CaO production. The CaO is one of the highly effective base catalyst in biodiesel production other than MgO, BaO and SrO. Moreover, it normally show high performance when vegetable oils with high quality is used in the transesterification process. Application of natural CaO from waste materials has been considered as a new trend for biodiesel production. This catalyst considered as strong basic catalyst, it could produce high yield of biodiesel (> 98 %) at lower temperature (60-65 °C). Therefore, application CaO catalysts from waste shell have very high commercial prospects in biodiesel production and will costly effective because involved nominal cost as it coming from waste material.

The waste materials were not important and considered as waste, therefore introducing waste material in biodiesel production will make it competitive with petroleum diesel. This discovery and utilization as a catalyst means a value addition to the recycled waste. The catalysts are reusable for several reaction cycles. These catalysts are considered as green-catalyst which is derived from renewable biomasses and the production of biodiesel is also a promising green-process. Moreover, easy availability, biodegradability and environmental acceptability are other three factors in favour of the catalysts as their large scale use will pose no disposal. In this

research, the heterogeneous catalyst made from waste shell of clamshell from *Meretrix meretrix* sp. like in Figure 4.



**Figure 4. Fresh clamshell (*Meretrix meretrix*)**

The clamshell is non-toxic, biodegradable and environmentally friendly. Generally, application of CaO catalyst will take longer time in transesterification reaction compared to other base catalyst, attempt have been done in order to improve the catalytic activity and selectivity of using CaO catalyst by increasing its surface area and its basicity. Improving these two properties could result in maximum conversion of biodiesel in a shorter time. One of the method is through hydration-dehydration technique. This technique not only simple, easy to handle but also less costly. In the hydration-dehydration technique the CaO were react with hot water. In this research the hydration-dehydration technique were applied in different water treatment in order to investigate the effect of time on formation of hydroxide for increasing the basicity of catalyst.

Chapter 1 gives a brief introduction about fossil energy, problem statement and scope of research. While Chapter 2 is a review of previous literature to with biodiesel topic and background of the research. Chapter 3, it explained more details about materials, instruments and various method of characterizations to produce and characterized the catalysts and biodiesel including all experimental part of this research will be explained. Results is presented and discussed in Chapter 4. Finally is the comprehensive conclusion associates with overall study are in Chapter 5.



### 1.3 Objectives of Research

The objectives of this research are:

1. To synthesize CS-CaO derived from natural  $\text{CaCO}_3$  waste shells from clam shell (*Meretrix meretrix*).
2. To enhance the CS-CaO catalyst by implementing the hydration technique via various time of water treatment process to produce CS-CaO<sub>1 h</sub>, CS-CaO<sub>3 h</sub>, CS-CaO<sub>6 h</sub>, CS-CaO<sub>9 h</sub>, CS-CaO<sub>12 h</sub>.
3. To screen and characterize the derived heterogeneous catalyst using several methods such as Thermogravimetry (TGA) Analysis, X-ray Fluorescence Spectroscopy (XRF), X-Ray diffraction (XRD) Analysis, Temperature programmed desorption of carbon dioxide (TPD-CO<sub>2</sub>), Brunauer-Emmett-Teller (BET) and Scanning electron microscopy (SEM).
4. To optimize the biodiesel production by manipulating its parameters (methanol and oil molar ratio, reaction time period and amount of catalyst).

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