MODIFICATION OF CALCIUM-BASED CATALYST DERIVED FROM NATURAL SOURCES FOR PALM OIL BIODIESEL PRODUCTION

NUR AQLILI RIANA CHE MOHAMAD

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By

NUR AQLILI RIANA CHE MOHAMAD

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

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

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NUR AQLILI RIANA BINTI CHE MOHAMAD

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Chairman : Ernee Noryana Muhamad, PhD
Faculty : Science

In recent years, calcium oxide has gained much interest among researchers in the production of biodiesel due to its high catalytic activity compared to other solid heterogeneous catalysts. Interestingly it also can be produced from natural abundant material that is cheap and readily available. In this study, various types of natural calcium sources such as cockle shells, horned helmet shells, limestone and mud creeper shells were selected and used to synthesize active calcium oxide catalyst for biodiesel production. The catalytic activity of calcined CaO catalyst was further improved by modification using hydration technique. This facile and economical technique was conducted in reflux condition using different medium such as distilled water, ammonia hydroxide solution and sodium hydroxide solution. The physicochemical characteristics of the raw material and synthesized catalysts was investigated using various characterization methods such as X-Ray Fluorescence (XRF), Thermogravimetric analysis (TGA), X-Ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, CO_2-Temperature Programmed Desorption (CO_2-TPD) and Field Emission Scanning Electron Microscopy (FESEM). For catalytic activity, all of the modified and unmodified catalysts were tested for the transesterification of palm oil under reaction condition of 15:1 methanol to oil ratio, 3 wt.% catalyst loading, 5 h reaction time at 338 K reaction temperature. The product (FAME) was analysed by using Gas Chromatography (GC) and Atomic Absorption Spectroscopy (AAS) was used to identify the amount of Ca leaching. As expected, all of the modified catalysts show significantly higher biodiesel conversion compared to that of pure CaO catalysts, while distilled water can be regarded as the best medium for hydration technique compared to ammonia hydroxide solution and sodium hydroxide solution generally. Hydrate limestone (i.e.: in distilled water, HLS) shows the highest biodiesel conversion of 98 %, while the lowest biodiesel conversion of 67 % was recorded when the mud creeper shells was modified in sodium hydroxide solution (OSS). In general, the improvement in the catalytic activity can be attributed to the increase in the basic sites and changes in morphology of the modified catalysts. The evaluation of the fuel properties according to the international standard of EN 14214 and ASTM D 6751 revealed that the produced biodiesel has meet certain requirements for biodiesel (B100) and has a potential to be used as blending fuel.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

PENGUBAHSUAIAN MANGKIN BERASASKAN KALSIUM YANG DIPEROLEHI DARI SUMBER SEMULAJADI UNTUK PENGHASILAN BIODIESEL MINYAK KELAPA SAWIT

Oleh

NUR AQLILI RIANA BINTI CHE MOHAMAD

Mei 2015

Pengerusi : Ernee Noryana Muhamad, PhD
Fakulti : Sains

Dalam beberapa tahun kebelakangan ini, kalsium oksida telah mendapat banyak perhatian di kalangan penyelidik dalam pengeluaran biodiesel kerana aktiviti pemangkinannya yang tinggi berbanding dengan mangkin pepejal heterogen lain. Menariknya, ia juga boleh dihasilkan daripada bahan semula jadi yang banyak, murah dan mudah didapati. Dalam kajian ini, pelbagai jenis sumber kalsium semula jadi seperti kulit kerang, kulit cengkerang bertanduk, batu kapur dan kulit siput sedut telah dipilih dan digunakan untuk mensintesis mangkin kalsium oksida aktif bagi pengeluaran biodiesel. Aktiviti mangkin CaO terkalsin telah ditingkatkan dengan pengubahsuaian menggunakan teknik penghidratan. Teknik yang mudah dan ekonomi ini telah dijalankan dalam keadaan refluks dengan menggunakan medium yang berbeza seperti air suling, larutan ammonia hidroksida dan larutan natrium hidroksida. Ciri-ciri fizikokimia bahan mentah dan mangkin yang telah disintesis ini telah dikaji dengan menggunakan pelbagai kaedah pencirian seperti pendarfluor sinar-X (XRF), analisis termogravimetri (TGA), belauan sinar-X (XRD), analisis luas permukaan Brunauer-Emmett-Teller (BET), penyahjerapan suhu terancang-CO_2 (CO_2-TPD) dan pancaran medan mikroskopi elektron penskanan (FESEM). Untuk aktiviti pemangkinan, semua mangkin yang diubah suai dan tidak diubah suai telah diuji untuk pentransesteran di bawah keadaan tindak balas nisbah molar metanol kepada minyak 15:1, kuantiti mangkin 3 wt.%, masa tindak balas 5 jam dan pada suhu tindak balas 338 K. Produk (FAME) telah dianalisis dengan kromatografi gas (GC) dan spektoskopi penyerapan atom (AAS) telah digunakan untuk mengenal pasti jumlah Ca yang larut lesap. Seperti yang dijangka, semua mangkin yang diubahsuai menunjukkan penukaran biodiesel yang lebih tinggi berbanding dengan mangkin CaO tulen, manakala air suling boleh dianggap sebagai medium terbaik bagi teknik penghidratan berbanding dengan larutan ammonia hidroksida dan larutan natrium hidroksida, umumnya. Batu kapur terhidrat (i.e.: dalam air suling, HLS) menunjukkan penukaran biodiesel tertinggi iaitu 98 %, manakala penukaran biodiesel yang paling rendah 67 % telah dicatatkan oleh kulit siput sedut yang diubah suai dalam larutan natrium hidroksida (OSS). Secara umumnya, peningkatan dalam aktiviti pemangkinan boleh dikaitkan dengan peningkatan tapak bes dan morfologi mangkin yang diubahsuai. Penilaian sifat-sifat bahan api mengikut standard antarabangsa EN 14214 dan ASTM D6751 menunjukkan bahawa biodiesel

yang dihasilkan menepati keperluan tertentu untuk biodiesel (B100) dan mempunyai potensi untuk digunakan sebagai campuran bahan api

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Finally, I would like to express my deepest appreciation to all who directly or indirectly involved in making this thesis a reality. Thank you.

I certify that a Thesis Examination Committee has met on 7 May 2015 to conduct the final examination of Nur Aqlili Riana binti Che Mohamad on her thesis entitled "Modification of Calcium-Based Catalyst Derived from Natural Sources for Palm Oil Biodiesel Production" 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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This is to confirm that;

- The research conducted and the writing of this thesis was under our supervision;
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Signature: ______________________________
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Signature: ______________________________
Name of Member of Supervisory Committee: Irmawati Ramli, PhD

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CO_2-TPD	Temperature Programmed Desorption in Carbon Dioxide
FAEE	Fatty Acid Ethyl Ester
FAME	Fatty Acid Methyl Ester
FESEM	Field Emission Scanning Electron Microscopy
FFA	Free Fatty Acid
MPIC	Ministry of Plantation Industries and Commodities Malaysia
MPOB	Malaysia Palm Oil Board
MPOC	Malaysia Palm Oil Council
S_{BET}	Brunauer-Emmett-Teller Surface Area Measurement
SV	Saponification Value
TGA	Thermogravimetry Analysis
XRD	X-Ray Diffraction Analysis

CHAPTER I

INTRODUCTION

1.1 Energy Demand and Environmental Concerns

Until now, the issues on the world's energy demand and the environmental concern are never ending. In a report published by the International Energy Agency (IEA), fossil fuel, which comprises coal, oil, petroleum and natural gas products account over 80.3 % of the primary energy consumption in the world. From that figure, about 57.7 % is used for the transportation sector. The skyrocketing increment of the fossil energy recorded by the IEA was in the year 2000 to 2008. It is reported that in 1985, total worldwide petroleum consumption was 2807 million tonnes, but in 2008, it reached 3928 million tonnes with an average annual growth rate of almost 1.5 % (British Petroleum, 2009). In other similar report by Pandey *et al.*, (2012) the annual rate of global primary energy demand is estimated to a value of 1.7 % and reach a value of 16,487 Mtoe (million tons of oil equivalent) from 2002 to 2030. Hence, the World Energy Forum predicted that if new oil wells are not found, the fossil oil will be exhausted in less than 10 decades from now (Sharma and Singh, 2009).

The main reasons that caused the fast diminishing of energy resources are due to rapid population and industrial growth globally (Pimentel and Pimentel, 2006). Due to this phenomenon, the era of cheap crude oil no longer exists. Consequently, the price of petroleum will rise steeply, leading to bellicose conflicts and increasing number of undernourished people especially from undeveloped countries. Figure 1.1 presents the prediction of world energy demand in the near future, indicating that there is an urgent need to find more new renewable energy sources to ensure energy security worldwide (Exxon Mobile, 2004). Without any appropriate alternatives to crude oil, the global economy will suffer a dramatic collapse due to exploding oil prices as the demand will continuously rise (Rottig *et al*., 2010).

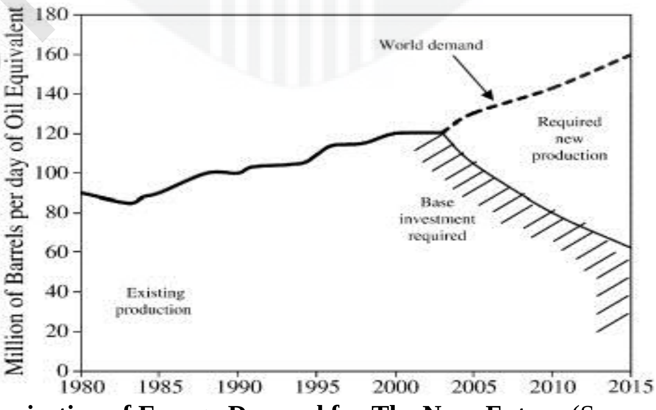

Figure 1.1. Projection of Energy Demand for The Near Future (Source: Exxon Mobile, 2004)

As stated above, the transportation sector worldwide consumed 57.7 % of fossil fuel usages, which directly make one-fifth of global carbon dioxide (CO_2) emissions (Goldemberg, 2008). Moreover, industrialization and deforestation also distinctly contribute to the increasing of the average temperature of the Earth`s surface because of the concentration of heat-trapping greenhouse gases are increasing in the atmosphere. Therefore, concerns over increasing energy demands, continuous global warming effects, declining petroleum reserves, petroleum price hike and scarcities have raised the critical need to search for alternative, renewable and environmentally friendly fuels.

1.2 Importance of Renewable Energy

Renewable energy has been highlighted in the last decade because of its potential to replace fossil fuel especially for transportation. Renewable energy sources such as solar energy, wind energy, hydro energy and energy from biomass and waste have been successfully developed and used by different nations with an aim to limit the use of fossil fuels. Among all sources, the IEA reported that, the energy produced from renewable sources and wastes has the highest potential as shown in Figure 1.2 (International Energy Agency, IEA, 2008).

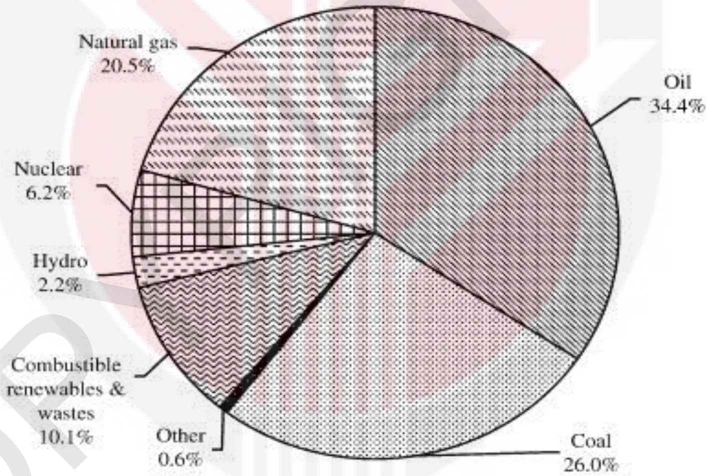

Figure 1.2. The World Total Energy Supply (Source: IEA, 2008)

Recently, struggle against climate change and fossil energy depletion has compelled humanity to decarbonize the economy by minimizing the usage of carbon based power that emits the greenhouse gases (GHG) like CO_2 to the atmosphere. Bueno *et al*. (2012) reported that the global CO_2 emission has to be reduced to at least 85 % by the year 2050 and much higher in developing countries (>95 %). To support these efforts, the target of the European Union target by the year 2020 are to reduce 20 % of GHG emissions, increase the share of renewable energy to 20 % and finally achieve 20 % improvement in energy efficiency (Streimikien *et al*., 2012). Since combustible renewable and waste energy accounted for 10.1 % compared to hydro energy (2.2 %) and others (0.6 %) including geothermal, solar, wind and heat, it is predicted that renewable energy such as biodiesel (i.e.: biofuel) will enter the energy market intensively in future to diversify the global energy sources (IEA, 2008).

Biodiesel is considered as renewable fuels, as they are derived, at least partially from parts of dead organisms such as plants, animals and etc. (Savvanidou *et al.*, 2010). It is non-toxic and environmentally benign since it does not contain sulfur, aromatic hydrocarbons, metals or crude oil residues (Dubei *et al.*, 2007). This is in contrast with conventional diesel, which contains 20-40 wt.% aromatic compounds and as high as 500 ppm sulfur that resulted in black smoke particulate together with SO_2 emissions (Phan and Phan, 2008). A conventional engine that used diesel fuel also contributes to one third of the total GHG emissions (Nas and Berktay, 2007). Thus, the use of biodiesel is believed to able to lower the net greenhouse gas emissions from the transportation sector and reduce the mass and carcinogenicity of particulate matter emissions (Nguyen *et al.*, 2010).

1.3 Advantages of Biodiesel as Fuel

By definition, biodiesel is a sustainable fuel produced from natural biomass such as vegetable oils, cooking waste and animal fats. Chemically, biodiesel is defined as the mono alkyl esters of long chain fatty acids, typically produced through the reaction (i.e.: transesterification) of a vegetable oils or animal fats with methanol or ethanol in the presence of a catalyst to yield methyl or ethyl esters (biodiesel) and glycerol as a by-product (Demirbas, 2002). Many advantages of biodiesel have brought it to be the most competitive alternative fuel to replace petrol-based fuels. Among many outstanding advantages of biodiesel are their high flash point, high lubricity, high cetane number and low viscosity (Zabeti *et al.*, 2009). Furthermore, the calorific value of biodiesel is comparable to conventional diesel, so it can be utilized as fuel in compression ignition engines at various blending ratios with petro-based diesel fuel with little or without any significant modification of the engine (Math *et al.*, 2010). Moreover, some characteristics of biodiesel are superior to conventional diesel for example, in terms of its flash point and oxygen content. Generally, biodiesel contains 11 % oxygen that can lead to smoother combustion (Openshaw M; Waynick, 2005). It also has antifoaming characteristics which enables and ensures fast filling of vehicle without possible foam leaks or overflows. Meanwhile, glycerol, the co-product, is normally used in the food, pharmaceutical and cosmetic industries. Interestingly, glycerol also can be used to synthesize methanol that is used in this reaction as reported in the US patent (Goetsch *et al*., 2008). This finding has opened up an avenue to produce raw material from the by-product itself.

In terms of the exhaust gas emission, biodiesel can lower the emissions of CO_2 caused by the transportation sector by 80 % (Leduc *et al.*, 2009). Utlu and Kocak, (2008) reported that there was a decrease of 14 % for CO_2, 17.1% for CO and 22.5 % of smoke density when using biodiesel that was derived from waste frying oil (WFO) as fuel. According to Morf, (2009), biodiesel does not increase the CO_2 content in the atmosphere simply because the release CO_2 can be recycled by growing plants, which are later being back processed into fuel. The cycle continues and finally causes the CO_2 level in atmosphere to remain constant (Figure 1.3). Thus, biodiesel is a carbon reused transportation fuel that is not a net-emitter of carbon dioxide. Industrially, pure biodiesel (100 %) is indicated as B100, while B20 is a fuel that comprised 20 % of pure biodiesel blended with 80 % of diesel fuel. The fuel properties must reach the requirement of the American Society for Testing Methods ASTM D6751 specifications before it can be used as a diesel engine.

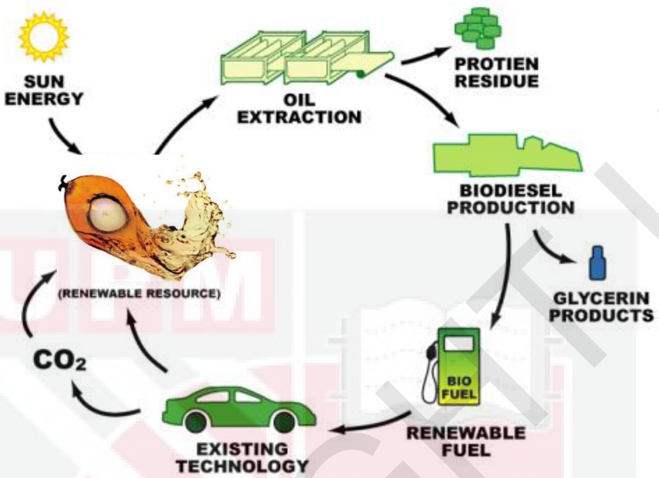

Figure 1.3. Biodiesel Cycle

1.4 Current Status of Biodiesel Production

Nowadays, biodiesel has emerged as the fastest growing industries worldwide, replacing fossil fuel due to its high demand and environmentally benign. Several countries, especially the United State and members of the European Union such as Germany, France and Italy are actively supporting the production of biodiesel from the agriculture sector. Figure 1.4 shows world biofuel production for different countries in 2012. In year 2006, nearly 6.5 billion litres of biodiesel were produced globally as reported by The World Bank (TWB), (2008). However, this number continues to increase year by year owing to substantial support, especially from the European government, such as consumption incentives (fuel tax reduction) and production incentives (tax incentives and loan guarantees). Statistically in 2003, the total production of biofuels in the European Union was 1,434,000 tons (Bendz, 2005) but was increased by 35.7 % to nearly 2 million tons in 2008 (European Biodiesel Board, EBB, 2010). On the other hand, the United States spent around USD 5.5 billion to 7.3 billion a year (TWB, 2008) to accelerate biofuels production. As a result, around 450 million gallons of biodiesel were produced in the United States in the year 2007 compared to only 25 million gallons in 2004 (Thurmond, 2008).

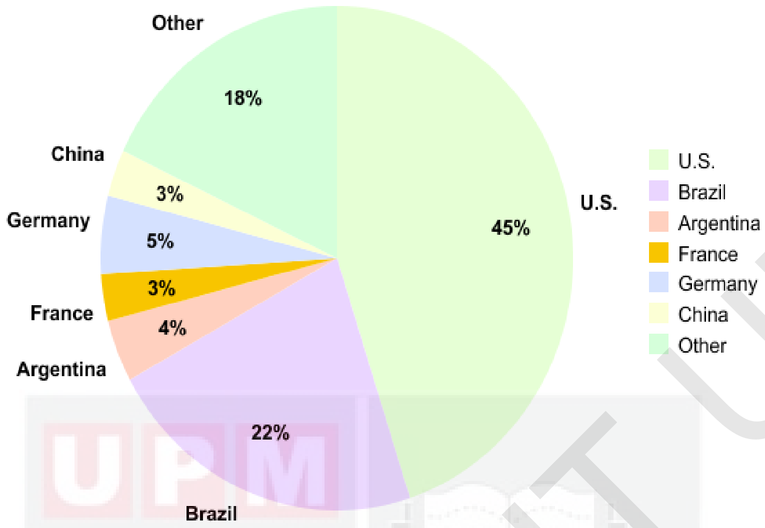

Figure 1.4. 2012 Global Biofuel Productio (Source: BP Statistical Review, 2013)

Typically, the fuel that was produced is used as a diesel blend in the range of 5 to 20 %, but, some producer also produced B100 (100 % biodiesel). For example, some European vehicle manufacturers have approved the use of B100 in certain engines such as Volkswagen and BMW (Mandil, 2009).

Thurmond, (2008) predicted that although the US and EU took the lead in biodiesel production, Brazil, China, India and some South East Asia countries like Malaysia and Indonesia could contribute as much as 20 % to the world biodiesel production by the year of 2020. Currently, Indonesia is dominating the production of palm oil in the world followed by Malaysia, Thailand, Colombia, Nigeria and Equador. Zhou and Thomson, (2009) said that the driving force for the development of biodiesel in these countries are economic, energy and environmental security, improving trade balances and expansion of agriculture sector.

1.5 Development of Biodiesel Production and Challenges in Malaysia

Considering various oil sources, palm oil has become one of the most interesting option biodiesel feedstock particularly in Malaysia and has the capacity to become the largest source of edible oil which was previously dominated by soybean oil. Figure 1.5 represents the world production of palm oil versus other vegetable oils in 2011. Malaysia Palm Oil Council (MPOC, 2008b) in their report stated that palm oil is the most traded oil in the world with a total export of 39.04 million tonnes of which Malaysia alone accounted for about 46 %. Nowadays, Malaysia government is trying to implement energy technology and policy by using palm oil biodiesel as the most eco-friendly source of energy due to availability of feedstock locally. The National Biofuel Policy which was launched in 2006 has implemented the use of B5 in the diesel fuel. B5 is a blend of 5 % palm methyl esters (biodiesel) and 95 % petroleum diesel. The implementation of B5 has been initiated in stages at petrol stations (i.e.: Petronas, Shell and BH petrol) in the Central Region of Peninsular Malaysia involving Putrajaya, Malacca, Negeri Sembilan, Kuala Lumpur and Selangor (Ministry of Plantations Industries and Commodities, MPIC, 2011).

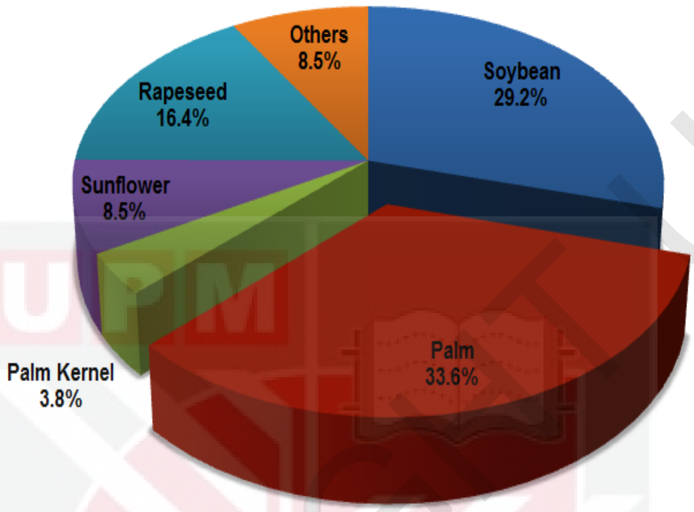

Figure 1.5. World Production of Palm Oil Production versus Other Vegetables Oils in 2010/2011

According to Malaysian Biodiesel Association (MBA), there are 11 active biodiesel plants in the country with total annual biodiesel installed capacity of 1.65 million tonnes (Kheang and May, 2012). Most of the plants are in Johor, Pahang, Perak, Selangor, Negeri Sembilan including Sabah and Sarawak (Table 1.1). The success of palm oil industry in Malaysia is achieved based on highly desirable properties of palm oil trees, careful management by Malaysia Palm Oil Board (MPOB) and more importantly the sustainability of palm oil farming (Abdullah *et al.*, 2009; Lam *et al.*, 2009; Basiron, 2007).

Table 1.1. List of active biodiesel plants in Malaysia as in 2008

No.	Company	Location	Plant capacity (t/year)
1	Carotino Sdn. Bhd.	Pasir Gudang, Johor	200,000
2	Malaysia Vegetable Oil Refinery Sdn. Bhd.	Pasir Gudang, Johor	110,000
3	PGEO Bioproducts Sdn. Bhd.	Pasir Gudang, Johor	100,000
4	Vance Bioenergy Sdn. Bhd.	Pasir Gudang, Johor	200,000
5	Mission Biotechnology Sdn. Bhd.	Kuantan, Pahang	200,000
6	Carotech Bio-Fuel Sdn. Bhd.	Ipoh, Perak	150,000
7	Lereno Sdn. Bhd.	Setiawan, Perak	60,000

8	Golden Hope Biodiesel Sdn. Bhd.	Teluk Panglima Garang, Selangor	150,000
9	Global Bio-Diesel Sdn. Bhd.	Lahad Datu, Sabah	200,000
10	SPC Bio-Diesel Sdn. Bhd.	Lahad Datu, Sabah	100,000

(Source: Lim and Lee, 2010)

Despite the efforts being made by the government to increase the value added of palm oil, several accusations upon palm oil have risen such as the rising production of biodiesel from palm oil is blamed for the gradual increment of palm oil`s price which subsequently has caused in shortage of supply in palm-oil related products in Malaysia. Rumours also said that palm oil are claimed to be unhealthy oil due to its high content in saturated acid normally palmitic (44 %) and stearic (5 %) which can increase the cardiovascular diseases (Palm Oil Truth Foundation**,** POTF, 2007). So, to address all these issues, MPOB which was established on May 1st, 2000 has entrusted by the Malaysia`s government to promote and develop globally competitive and sustainable oil palm industry. Through extensive research, they found out that the major changes in the government policy in Europe regarding the biofuel feedstock (i.e.: rapeseed oil) and shortage of corn oil in the USA have made food manufacturers to utilize palm oil as an alternative source of oils which prompted a substantial increase in palm oil price. Additionally, MPOB along with more than 160 nutritional researches also has successfully proven that palm oil contains an equal amount of both unsaturated (mainly oleic) and saturated (mainly palmitic) fatty acids, which apparently do not elevate cholesterol levels in the normal ranges (MPOC, 2008a).

1.6 Problem Statements

Rapid population and accumulative industrial growth globally had caused fast shrinking of fossil fuel based energy, which subsequently caused the petroleum price rise sharply. Therefore, an alternative is needed to fulfil continuous energy demand as well as to overcome negative outcomes caused by fossil fuel consumption. Biodiesel production industry has gradually grown as an alternative to replace fossil fuel based energy. Unfortunately, the high cost of the production especially for the product separation and purification have become the major obstacles over the years. One of the main factors contributing to this is because of the usage of the homogenous catalyst (i.e.: sodium methoxide) which normally used in industry. Even though sodium methoxide catalyst can produce a high yield of biodiesel in a moderate reaction condition, it requires separation and purification process, which cost a fortune. Therefore, in this research, Ca-based heterogeneous catalysts were developed to overcome problems associated by homogeneous catalyst. On top of that, the Ca-based catalysts used in this study were derived from local sources and waste materials, which give value added as future cost-effective catalyst.

Based on literature survey, since the performance of pure calcium catalyst is not as high as sodium methoxide and normally has a Ca leaching problem, attempts have been experimenting to improve the catalytic activity of catalyst as well as to reinforce its mechanical strength. Thus, hydration method is chosen to increase the performance of the catalyst since it is effective, simple and cheap. Modification of this method is applied upon preparation of modified Ca-based catalysts.

1.7 Scope of This Thesis

In this study, a series of base heterogeneous catalyst synthesized from natural raw calcium material such as cockle shells, horned helmet shells, limestone, and mud creeper shells were prepared for the transesterification of palm oil with methanol for the production of biodiesel. The synthesized calcium oxide catalysts were then treated in reflux condition (i.e.: hydration technique) by using three different hydroxide medium, for instance distilled water, ammonia hydroxide and sodium hydroxide. Prior to the treatment, the raw calcium sources were calcined at different temperature and time according to the TGA (thermogravimetric analysis) data analysis. The composition of the raw material was analysed by using X-Ray fluorescence (XRF) analysis, while the synthesized catalysts were characterized by using X-Ray diffraction (XRD), surface area analysis, scanning electron microscopy (SEM) and temperature programmed desorption of CO_2 (TPD-CO_2). Meanwhile, Gas chromatography (GC) was used for biodiesel characterization. As for reaction study, all catalysts were tested in the transesterification reactions under the same condition for biodiesel production.

The main objective of this thesis is to provide a complete report on the performance of natural calcium sources as potential heterogeneous base catalysts for biodiesel production from palm oil. Chapter 1 gave a brief introduction on biodiesel production and its advantages. Chapter 2 presented literature review and historical background of the research, meanwhile chapter 3 described the materials and methods used in synthesizing the catalyst and the production of biodiesel. This chapter also described various types of characterization techniques that were used in this research. In chapter 4, the results and the analysis data that were obtained from the experiments were discussed. Lastly, complete conclusions which correlate the overall study were presented in Chapter 5.

1.8 OBJECTIVES

The objectives of this research are:

1. To prepare and characterize calcium oxide catalysts from Malaysia natural calcium sources (i.e.: cockle shells, horned helmet shells, limestone and mud creeper shells)
2. To modify and characterize the prepared calcium oxide catalysts via hydration technique by using three different mediums (i.e.: distilled water, ammonium hydroxide solution and sodium hydroxide solution)
3. To evaluate the catalytic activity of unmodified (pure CaO) and modified catalysts for the production of biodiesel from palm oil

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