BASE HETEROGENEOUS CATALYTIC TRANSESTERIFICATION OF RICE BRAN OIL TO BIODIESEL USING CALCIUM OXIDE NANOSTRUCTURED

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Science (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

AUGUST 2013

Dedicated to my beloved parents,
Sulaiman Bin Ahmad and Foziah Binti Jusoh @ Mohd Yusoff ,
to my siblings and family,
to special person, Mohamad Helmi Bin Abd Mubin,
to my friends,
thank you so much,
for their patience, support, love and encouragement.

ACKNOWLEDGEMENT

In the name of Allah s.w.t, the most gracious and the most merciful

Firstly, I wish to express my sincere appreciation to my supervisor, Prof. Dr. Abdul Rahim Bin Yacob for giving me an opportunity for this research. I am also grateful for the support, guidance, patient and imparting his knowledge for me. Writing this thesis is a remarkable accomplishment, thanks for his lots of advices.

Furthermore, I would also like to thank to all lecturers and lab assistants from the Department of Chemistry especially to Physical Chemistry Lab II for their help and advice during this research. I am also grateful to my supervisor and Universiti Teknologi Malaysia for the financial support through the GUP vote.

Besides that, I would like to show my appreciation to my research team, Kak Ekin, Abg Asyraf, Abg Ad, Kak Nurul, Syima, Shera, Alin, Pia and Kak Ayu and also my friends for their supports, ideas and information for me to complete this research. Lastly, I would like to express my gratitude to my beloved family members, my father, Sulaiman Bin Ahmad, my mother, Foziah Binti Jusoh, my siblings, Mohd Shafarulazhar, Mohd Syafiq, Nur Farrah, Nurul Najwa and Nur Amani and to special person in my life, Mohamad Helmi Bin Abd Mubin. Thanks for all the love, support and encouragement.

PREFACE

This thesis is the results of my work carried out in Department of Chemistry, Universiti Teknologi Malaysia between December 2010 and October 2012 under the supervision of Prof. Dr. Abdul Rahim Bin Yacob. Part of my work described in this thesis has been sent for exhibition participations and reported in the following publications:

1. Abdul Rahim Yacob, Nur Fatin Sulaiman, Hidayah Mohd Aziz, Noor Idayu Masrom and Mohd Khairul Asyraf Amat Mustajab. (2011). Effect of Hydration-Dehydration Activation on the Basic Strength of Nano Structured Alkaline Earth Metal Calcium Oxide. *2011 International Conference on Manufacturing Science and Technology (ICMST 2011).* 16-18 September 2011 in Singapore.

2. Abdul Rahim Yacob, Nur Fatin Sulaiman, Nadjiah Patimi Bt Noordin and Mohd Khairul Asyraf Amat Mustajab. (2011). Single Step Transesterification of Palm Oil Using Prepared Calcium Oxide. *Journal of Materials Science and Engineering A 1*. Published: 10 November 2011.

3. Abdul Rahim Yacob, and Nur Fatin Sulaiman. (2012). Hydration Dehydration Effect on Morphology and Basic strength of Nano-Calcium Oxide. *2012 International Conference on Manufacturing and Industrial Engineering (ICMIE 2012).* 26-28 February 2012 in Singapore.

4. Abdul Rahim Yacob, Nur Fatin Sulaiman, Noor Idayu Masrom and Norhasyimah Binti Mohd Kamal. (2012). Biokerosene by Microwave Induced and Catalytic Cracking of Palm Oil. *Industrial Art and Technology Exhibition (INATEX 2012)*. Bronze Medal Award. Universiti Teknologi Malaysia.

5. Abdul Rahim Yacob, Nur Fatin Sulaiman, Norhasyimah Binti Mohd Kamal and Noor Idayu Masrom. (2013). Biokerosene by Microwave Induced and Catalytic Cracking of Palm Oil. *24th International Invention, Innovation And Technology Exhibition, ITEX 2013*. Gold Medal Award. Kuala Lumpur, Malaysia.

ABSTRACT

Biodiesel or fatty acid ester is commonly produced by transesterification of vegetable oil or animal fat. Commercially, biodiesel was synthesized using homogeneous base catalysts such as NaOH and KOH. However, homogeneous base catalyst adsorped into the vegetable oil or animal fat. Thus, a large amount of water is required to clean the biodiesel and might lead to saponification or soap formation. As a result, this will lower the biodiesel quality and makes the biodiesel production becomes difficult, producing waste water, expensive and complicated. This research focused on the use of heterogeneous base catalyst, calcium oxide (CaO), an alkaline earth metal oxide that make the biodiesel easily separated, low cost and environmental friendly. The aim of this research is to investigate the potential of commercial calcium carbonate, CM-$CaCO_3$ to be transformed to nanostructured CaO and used as a heterogeneous base catalyst for single step transesterification of rice bran oil to biodiesel. The CaO samples were prepared by calcination at 100°C to 700°C under vacuum at 10^{-3} mbar. The prepared CaO nanostructured was characterized by thermogravimetric analysis-differential thermal analysis (TGA-DTA), Fourier transform infrared (FTIR) spectroscopy, X-ray powder diffraction (XRD), nitrogen gas adsorption analysis (NA), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX). The basicity of the prepared CaO nanostructured was determined via back titration method. TGA-DTA result showed that the calcination temperature for CM-$CaCO_3$ to form CaO must be higher than 600°C. This was supported by FTIR results which indicated the complete formation of CaO at 700°C. XRD showed that at this temperature, the rhombohedral $CaCO_3$ and hexagonal $Ca(OH)_2$ were totally disappeared leaving only crystalline cubic CaO. CaO obtained at 700°C (CaO-700) showed the highest BET surface area of 11.49 m^2g^{-1}. FESEM image showed the spherical particles coagulated to form agglomeration with nanoparticle size. The EDX further supported the formation of CaO and indicated to contain 53.56% of oxygen and 46.44% of calcium. It was found that CaO-700 has the highest basicity with 1.959 mmol/g. After optimization process, the prepared nanostructured CaO-700 was selected and applied for single step transesterification reaction of rice bran oil to produce biodiesel. The biodiesel produced was characterized using FTIR, NMR and GC-FID. The catalytic activity was further studied on the effect of time of reaction, percentage catalyst loading and a mechanism reaction was proposed. FTIR and NMR results further confirmed that biodiesel was successfully formed. In this study, the optimum reaction conditions to produce the highest biodiesel of 89% was at 60 minutes reaction time with 1.0% catalyst loading.

ABSTRAK

Biodiesel atau ester asid lemak kebiasaannya dihasilkan oleh transesterifikasi minyak sayuran atau lemak haiwan. Secara komersial, biodiesel disintesis dengan menggunakan mangkin bes homogen seperti NaOH dan KOH. Walau bagaimanapun, mangkin bes homogen terlarut ke dalam minyak sayuran atau lemak haiwan. Oleh itu, sejumlah besar air diperlukan untuk membersihkan biodiesel dan akan membawa kepada proses saponifikasi atau pembentukan sabun. Akibatnya, akan mengurangkan kualiti biodiesel dan membuatkan pengeluaran biodiesel menjadi sukar, menghasilkan air sisa, mahal dan rumit. Kajian ini memberi tumpuan kepada penggunaan mangkin bes heterogen, kalsium oksida (CaO) iaitu oksida logam bumi beralkali yang membolehkan biodiesel ini mudah dipisahkan, kos yang rendah dan mesra alam. Tujuan kajian ini adalah untuk mengkaji potensi kalsium karbonat komersial, CM-$CaCO_3$ untuk ditukarkan kepada CaO berstruktur nano dan digunakan sebagai mangkin bes heterogen dalam transesterifikasi satu langkah bagi minyak sekam padi kepada biodiesel. Sampel CaO telah disediakan melalui proses pengkalsinan pada 100°C sehingga 700°C dalam keadaan vakum 10^{-3} mbar. CaO yang telah disediakan dianalisis menggunakan analisis termogravimetri-analisis berbeza terma (TGA-DTA), spektroskopi inframerah transformasi Fourier (FTIR), pembelauan serbuk sinar-X (XRD), analisis penjerapan gas nitrogen (NA), mikroskopi elektron pengimbas medan pemancaran (FESEM) dan serakan tenaga sinar-X (EDX). Kebesan CaO berstruktur nano ditentukan melalui kaedah pentitratan semula. Data TGA-DTA menunjukkan suhu pengkalsinan untuk CM-$CaCO_3$ membentuk CaO perlu dilakukan lebih tinggi daripada 600°C. Keputusan ini disokong oleh keputusan FTIR yang menunjukkan pembentukan lengkap CaO berlaku pada 700°C. Analisis XRD menunjukkan bahawa pada suhu ini struktur rombohedral $CaCO_3$ dan heksagon $Ca(OH)_2$ telah hilang meninggalkan hanya kubus kristal CaO. CaO yang dihasilkan pada 700°C (CaO-700) mempunyai luas permukaan BET tertinggi dengan nilai 11.49 m^2g^{-1}. Imej FESEM menunjukkan zarah sfera berbentuk gumpalan dan bersaiz nano. Data EDX menyokong pembentukan CaO dengan kandungan oksigen 53.56% dan kalsium 46.44%. CaO-700 didapati menunjukkan kebesan tertinggi dengan nilai 1.959 mmol/g. Selepas proses pengoptimum, CaO-700 berstruktur nano telah dipilih dan digunakan untuk tindak balas transesterifikasi satu langkah minyak sekam padi untuk menghasilkan biodiesel. Biodiesel dianalisis menggunakan FTIR, NMR dan GC-FID. Seterusnya, aktiviti sebagai pemangkin dikaji terhadap kesan masa tindak balas, peratusan mangkin yang digunakan dan mekanisma tindak balas juga dicadangkan. Keputusan FTIR dan NMR seterusnya mengesahkan bahawa biodiesel telah berjaya dihasilkan. Dalam kajian ini, keadaan optimum tindak balas untuk menghasilkan biodiesel tertinggi iaitu 89% adalah pada masa 60 minit dengan peratusan muatan mangkin 1.0%.

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LIST OF ABBREVIATIONS

CM-CaO	-	Commercial Calcium Oxide
CM-$CaCO_3$	-	Commercial Calcium Carbonate
BET	-	Brunauer-Emmett-Teller
DTA	-	Differential Thermal Analysis
EDX	-	Energy Dispersive X-Ray
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared
GC-FID	-	Gas Chromatography-Flame Ionization Detector
NA	-	Nitrogen Gas Adsorption Analysis
NMR	-	Nuclear Magnetic Resonance
TGA	-	Thermogravimetric Analysis
XRD	-	X-Ray Power Diffraction
FAME	-	Fatty Acid Methyl Ester

LIST OF SYMBOLS

°C	-	Degree Celcius
g	-	Gram
h	-	Hours
min	-	Minutes
mg	-	Milligram
mL	-	Mililitre
mA	-	Miliampere
cm	-	Centimeter
nm	-	Nanometer
rpm	-	Rotation per Minute
kV	-	Kilovolt
Eq.	-	Equation
%	-	Percentage
θ	-	Half Angle of Diffraction Beam
β	-	Beta
α	-	Alpha
λ	-	Wavelength

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

Physicochemical properties of solid base catalyst are dependent on their preparation methods, pretreatment process and the way of handling the catalyst itself. There are numbers of preparation methods for producing solid base catalyst such as hydration dehydration method (Yacob *et al.,* 2011; Yacob *et al.,* 2010; Murphy *et al.,* 1999), sol gel (Yamamura *et al.,* 1995), thermal decomposition (Tang *et al.,* 2008) and chemical vapor deposition (CVD) methods (Knozinger *et al.,* 2000). Physicochemical properties such as morphology, surface area, particle size and basicity normally can influence any catalytic activity. The importance of solid base catalysts has come to be known also for their environmentally friendly qualities. Much significant progress has been made over the past two decades in catalytic materials and solid base-catalyzed reactions (Hattori, 2001).

In this study, alkaline metal oxide will be prepared and the physicochemical properties modified. It was reported by Hattori, (2001) and Yacob *et al.,* (2011), a strong basic strength can be formed after a high temperature treatment applied in order to obtain a carbonate free metal oxide surface. Surface defect which can be detected using surface area analysis display the significant sites for heterogeneous catalysis that can change the reactivity of any reaction (Jackson and Hargreaves, 2009). Thus, the higher the surface area indicates higher reactivity.

This research alkaline metal, magnesium oxide will be studied. Reported by Krylov *et al.*, (1965), three types of basic centers at the surface of partially dehydrated magnesium hydroxide were recognized, which are the strongly basic O^{2-} center, the mixture of strong basic centers derives O^{2-} ions adjacent to ^{-}OH ions, and the weaker surface ^{-}OH ions basic center (O^{2-} >> O^{2-} + ^{-}OH >> ^{-}OH). Malinowski *et al.*, (1964) studies show that more O^{2-} basic centers formed on the oxide surfaces if the samples were heated at temperatures higher than 600°C. Yacob *et al.*, (2010) also supported the previously study that the basic strength for MgO lies on the method of higher temperature of preparation.

From the studies of Murphy *et al.*, (1999) and Collucia *et al.*, (1979), the surface defect of alkaline metal oxides was found with several ion pairs and also different coordination numbers. Ion pairs of the lowest coordination numbers exist at the corners, followed by edges and surfaces. The study suggested that there are three expected surface defects, pores and cavities, comprising of 3, 4 and 5 coordination based on ^{1}H-NMR data respectively. This is illustrated by Figure 1.1.

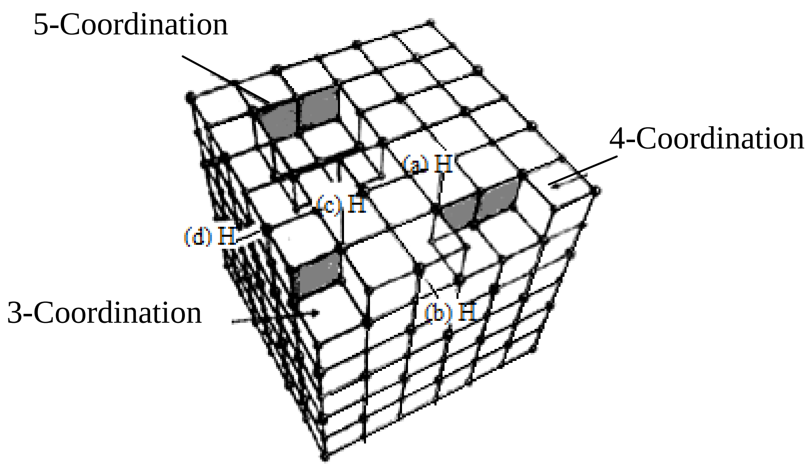

Figure 1.1: Surface model of alkaline metal oxide proposed by Murphy *et al.* (1999).

Alkaline earth metals such as calcium oxide, CaO have basic properties because their oxides give basic alkaline solutions when dissolved in water. The proton is transferred from water to basic oxide during the conversion of basic oxide to hydroxides. Otherwise, the solid basic oxides donate its electron pair to the reactants. Here, the alkaline earth metal oxide acts as a Brönsted base while the water acts as a Brönsted acid. Transesterification is the most recurrently studied and alkaline earth metal oxide is used in solid base catalyst reactions (Kawashima *et al.*, 2009; Benjapornkulapong *et al.*, 2009; Cho *et al.*, 2009).

Biodiesel refers to renewable energy that is produced from vegetable oil or animal fat. It consist of mixture of long-chain alkyl esters such as methyl esters which can be used as an alternative for petroleum diesel without modification to the diesel engine. Biodiesel is commonly used in standard diesel engines and it is different from the vegetable oils used to fuel converted diesel engines. Otherwise, it can also be used as a low carbon alternative to heating oil. Fuels produced from renewable biomass can reduce in greenhouse gas emissions, pollution, deforestation and the rate of biodegradation. Biodiesel is free of sulphur and aromatics as it is non-toxic and biodegradable that can produce lower exhaust emissions (Albuquerque *et al.*, 2008).

Biodiesel or fatty acid ester is usually produced by transesterification reaction of vegetable oil or animal fat feedstock. There are several methods for carrying out this transesterification reaction including common batch process, supercritical processes, ultrasonic methods and microwave methods. Transesterification is a process where triglyceride reacts with an alcohol to give ethyl ester of fatty acids and glycerol as shown in Figure 1.2. The alcohol that is commonly used in this transesterification process is methanol or ethanol that will produce fatty acid methyl ester (FAME) or fatty acid ethyl ester (FAEE) respectively which is deprotonated with a base to make it a stronger nucleophile.

This research work had focused on the preparation of CaO nano structured from commercial calcium carbonate, CM-$CaCO_3$ by thermal decomposition method at 100°C to 800°C respectively under vacuum atmosphere of 10^{-3} mbar. The basicity of CaO nano structured was analyzed by back-titration method. The relationship between basicity and calcinations temperature was also studied. Then, the prepared CaO nano structured was used as a heterogeneous base catalyst for transesterification of rice bran oil to biodiesel. Rice bran oil was selected because it is non-conventional, inexpensive and low-grade vegetable oil that does not have much competition for food requirement.

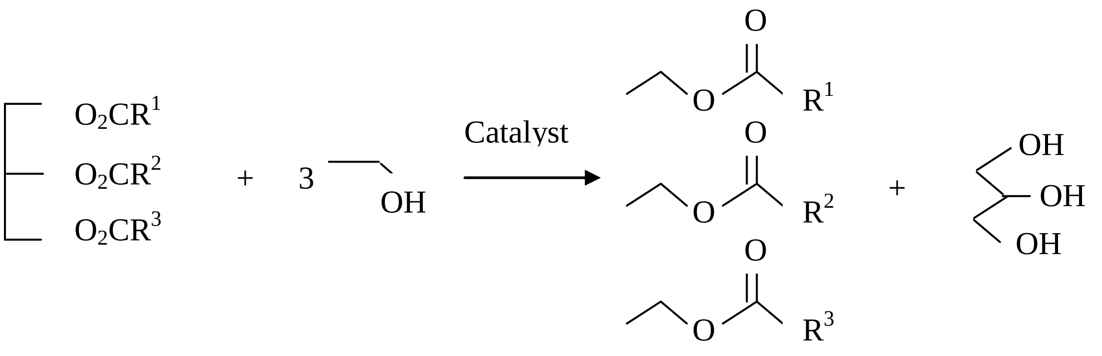

Figure 1.2: Transesterification Reaction.

1.2 Problem of Statement

Biodiesel is commercially synthesized in the presence of homogeneous catalysts such as sodium hydroxide and sodium methoxide (Bak *et al.,* 1996). Homogeneous base catalyst however was dissolved into the vegetable oil or animal fat. Thus, a large amount of waste water was required to remove the homogeneous base catalyst that can make the soap formation. As a result, the saponification can lower the biodiesel quality and makes the biodiesel production becomes difficult, time consuming, expensive and complicated. Therefore, in this study, heterogeneous catalytic reaction was introduced in biodiesel production. Recently, much interest has been taken in alkaline earth metal oxide, calcium oxide due to its economical advantages.

From the previous study, double steps transesterification reaction of palm oil to biodiesel was conducted successfully by using prepared magnesium oxide (Yacob *et al.,* 2009). In this method however, single step transesterification reaction using prepared calcium oxide was introduced, subtracting the double steps which took long time and unfavorable for industries. In the reaction, transesterification converts vegetable oil to fatty acid methyl esters (FAME) directly and can be fed into any conventional diesel engine without the needs of modification. Recent global production of vegetable oils and animal fats is not sufficient for human consumption, therefore, this research used rice bran oil as an alternative for replacing vegetable oils and animal fats. Rice bran oil also can act as a substitute for raw materials because it does not have much competition for food necessity.

1.3 Objectives of Research

The main objective of this research is to investigate the potential of CaO nanostructured as a heterogeneous base catalyst for transesterification process. Therefore, the research objectives are to:

i) Synthesize heterogeneous base catalyst, CaO from $CaCO_3$.
ii) Characterize and optimize the prepared CaO nanostructured.
iii) Produce biodiesel from rice bran oil by using prepared CaO nanostructured as a heterogeneous base catalyst by single step transesterification process.
iv) Optimize the catalytic activity parameters including time of reaction, percentage loading and the proposed mechanism.
v) Characterize the prepared biodiesel.

1.4 Significance of Research

The significance of the study is to prepare and characterize the heterogeneous base catalyst, calcium oxide, CaO from calcium carbonate, $CaCO_3$. Heterogeneous catalyst has several advantages including easier operational procedures, effortless catalyst separation and reduction of environmental pollutions. In the production of biodiesel, this research focused on the single step transesterification of rice bran oil as a reacting lipid. Rice bran oil is a non-conventional, inexpensive and low-grade vegetable oil that make the production of biodiesel becomes economical and affordable.

1.5 Scope of Research

The scope of this research can be divided into four major aspects. The first aspect was to prepare CaO nanostructured from $CaCO_3$. The starting material, $CaCO_3$ powder was heated at 100^{o}C to 800^{o}C in vacuum atmosphere, at least 10^{-3} mbar in order to produce higher surface area of CaO.

The second aspect was to characterize the prepared CaO nanostructured. The Thermogravimetric Analysis–Differential Thermal Analysis (TGA-DTA) was used to study the decomposition of $CaCO_3$ to CaO by using inert nitrogen gas flows. Fourier Transform Infrared (FTIR) and X-Ray Powder Diffraction (XRD) techniques were used to identify the functional groups present in $CaCO_3$ and the prepared CaO samples. The surface characteristics of the prepared CaO catalyst were characterized using Nitrogen Gas Adsorption Analysis (NA), Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-Ray (EDX). The basicity of the prepared CaO nanostructured was determined via back titration method.

The third aspect was to apply the prepared CaO nanostructured in single step transesterificaton of rice bran oil to produce biodiesel. In this reaction, the higher basicity of the prepared CaO nanostructured was chosen as a catalyst. The percentage conversion of biodiesel was determined by Gas Chromatography – Flame Ionization Detector (GC-FID). The biodiesel was characterized using Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR). The last part in this research was to optimize the catalytic activity parameters. The percentage catalyst loading and time of reaction versus conversion of biodiesel were studied. This research was also focused on the proposed mechanism of transesterification process of rice bran oil to biodiesel.

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