



UNIVERSITI PUTRA MALAYSIA

***SYNTHESIS AND CHARACTERIZATION OF CALCIUM-BASED
CATALYSTS FOR TRANSESTERIFICATION OF JATROPHA CURCUS L.
AND NANNOCHLOROPSIS OCULATA OILS TO BIODIESEL***

TEO SIOW HWA

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By

TEO SIOW HWA

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*Special Dedicated To My Precious Parents Who Always
Give Me Fabulous Love, Spectacular Care And Continued
Support.*

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirements for the degree of Doctor of Philosophy

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April 2015

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Faculty: Science**

Catalyst plays an important role in biodiesel production. The current transesterification technology using homogeneous liquid catalysts in biodiesel production process is uneconomical, largely due to liquid catalyst is corrosive, difficult to be separated and regenerated in order to reuse. Additionally, the high price of biodiesel is largely due to feedstock prices. Therefore, biodiesel price can be reduced by utilizing non-edible oil feedstock and heterogeneous solid catalysis on transesterification reaction for biodiesel production. The use of heterogeneous catalysis on the other hand, prevents the undesirable saponification, allows process simplification and offers reduction in the processing cost.

In this study, fatty acid methyl ester (FAME) was synthesized by transesterification of *Jatropha curcas* L. crude oil with methanol using calcium based heterogeneous catalysts. The initial part of this project was to synthesize the catalysts and followed by characterized the prepared catalysts *i.e.* calcium lanthanum ($\text{CaO-La}_2\text{O}_3$), calcium cerium (CaO-CeO_2), calcium nickel (CaO-NiO_2), calcium neodymium ($\text{CaO-Nd}_2\text{O}_3$) and calcium methoxide ($\text{Ca}(\text{OCH}_3)_2$). The optimization of the transesterification of *J. curcas* crude oil using different heterogeneous calcium based catalysts was evaluated. The relative order of effectiveness on transesterification was $\text{Ca}(\text{OCH}_3)_2 > \text{CaO-CeO}_2 > \text{CaO-La}_2\text{O}_3 > \text{CaO-NiO}_2 > \text{CaO-Nd}_2\text{O}_3$. The TPD results demonstrated that mixed metal oxides that prepared by co-precipitation method, showed an extremely high FAME yield (85~95%) due to the presence of stronger basic strength on the catalytic site of catalysts. Moreover, all catalysts can be regenerate and reuse. The produced FAME is met ASTM D6751 and European 14214 international biodiesel standards.

In the second part of investigation, cultivation, extraction and methanolysis of crude microalga's (*Nannochloropsis oculata*) oil were carried out. Catalytic screening was performed on $\text{Ca}(\text{OCH}_3)_2$ and mixed oxide catalysts, where $\text{Ca}(\text{OCH}_3)_2$ catalyst revealed to be the superior performance in fast conversion of microalgae derived crude oil to FAME using transesterification technique. $\text{Ca}(\text{OCH}_3)_2$ was prepared via hydrothermal route, resulted in a catalyst with surface area, total pore volume and average pore diameter of $30.5 \text{ m}^2 \text{ g}^{-1}$, $0.21 \text{ cm}^3 \text{ g}^{-1}$ and 31.97 nm , respectively. Photoautotrophic cultivated *N. oculata*, then followed by transesterification of extracted crude oil with methanol in the presence of $\text{Ca}(\text{OCH}_3)_2$ catalyst, gave a FAME yield of 95.78 %. It was observed that methanol volume and catalyst concentration were the important factors attributed to high yield of biodiesel from crude microalgae oil. The experiment results showed that catalytic transesterification technique has the potential to provide energy-efficient routes for biodiesel production from algae biomass.

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

**SINTESIS DAN PENCIRIAN MANGKIN BERASASKAN KALSIUM UNTUK
TRANSESTERIFIKASI MINYAK *JATROPHA CURCUS* L. DAN
NANNOCHLOROPSIS OCULATA KEPADA BIODIESEL**

Oleh

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Mangkini memainkan peranan yang penting dalam penghasilan biodiesel. Teknologi transesterifikasi yang sedia ada dengan menggunakan mangkini cecair homogen dalam process penghasilan biodiesel adalah tidak berekonomik disebabkan oleh mangkini yang manghakis, sukar untuk dipisahkan dan diperbaharui untuk tujuan digunapakai semula. Di samping itu, biodiesel yang berharga tinggi sebahagian besarnya adalah akibat daripada harga bahan mentah yang mahal. Oleh sebab itu, harga biodiesel boleh dikurangkan dengan menggunakan bahan mentah daripada sumber minyak yang tidak boleh dimakan dan pemangkinan pepejal heterogen pada tindak balas transesterifikasi untuk penghasilan biodiesel. Sebaliknya, penggunaan pemangkinan heterogen telah mengelakkan saponifikasi yang tidak diingini, mempermudah proses dan mengurangkan kos pemprosesan.

Dalam kajian ini, asid lemak metil ester (FAME) telah disintesis melalui transesterifikasi minyak mentah *Jatropha curcas* L. dengan metanol menggunakan mangkini heterogen berasaskan kalsium. Bahagian awal projek ini adalah untuk mensintesis mangkini dan diikuti dengan pencirian ke atas mangkini yang disediakan, iaitu kalsium lanthanum ($\text{CaO-La}_2\text{O}_3$), kalsium serium (CaO-CeO_2), kalsium nikel (CaO-NiO_2), kalsium neodimium ($\text{CaO-Nd}_2\text{O}_3$) and calcium metoksida ($\text{Ca}(\text{OCH}_3)_2$). Pengoptimuman transesterifikasi daripada minyak mentah *J. curcas* L. telah dinilai dengan menggunakan mangkini heterogen berasaskan kalsium yang berbeza. Susunan relatif bagi keberkesanan transesterifikasi ialah $\text{Ca}(\text{OCH}_3)_2 > \text{CaO-CeO}_2 > \text{CaO-La}_2\text{O}_3 > \text{CaO-NiO}_2 > \text{CaO-Nd}_2\text{O}_3$. Keputusan TPD menunjukkan bahawa campuran oksida logam yang disediakan dengan kaedah mendakan bersama, menghasilkan FAME yang tinggi (85~95%) disebabkan oleh kehadiran alkali kuat yang lebih kukuh pada tapak pemangkin. Tambahan pula, kesemua mangkini ini boleh diperbaharui dan digunapakai semula. FAME yang dihasilkan telah memenuhi piawaian biodiesel ASTM D6751 dan European 14214 diperingkat antarabangsa.

Dalam bahagian kedua penyelidikan, pengkulturan, pengekstrakan dan metanolisis minyak mentah microalga (*Nannochloropsis oculata*) telah dijalankan. Pemeriksaan ke atas mangkin telah dilakukan ke atas $\text{Ca}(\text{OCH}_3)_2$ dan mangkin-mangkin campuran oksida, dimana mangkin $\text{Ca}(\text{OCH}_3)_2$ didapati menunjukkan prestasi yang unggul dalam penukaran yang cepat minyak mentah hasilan microalga kepada FAME dengan menggunakan teknik transesterifikasi. $\text{Ca}(\text{OCH}_3)_2$ yang disediakan melalui cara sintesis hidroterma ini mempunyai luas permukaan, jumlah isipadu liang dan purata diameter liang masing-masing sebanyak $30.5 \text{ m}^2 \text{ g}^{-1}$, $0.21 \text{ cm}^3 \text{ g}^{-1}$ dan 31.97 nm . Pengkulturan *N. oculata* secara fotoautotrofik, kemudian diikuti oleh transesterifikasi minyak mentah dengan metanol dalam kehadiran mangkin $\text{Ca}(\text{OCH}_3)_2$, memberi hasilan FAME sebanyak 95.78%. Ini dapat diperhatikan dengan isipadu metanol dan kepekatan mangkin merupakan factor yang penting dalam penyumbangan kepada hasilan tinggi biodiesel daripada minyak mentah microalgae. Keputusan-keputusan eksperimen telah menunjukkan bahawa kaedah pemangkin transesterifikasi adalah berpotensi untuk memberi langkah yang cekap tenaga bagi penghasilan biodiesel daripada algae biomass.

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I certify that a Thesis Examination Committee has met on 30 April 2015 to conduct the final examination of Teo Siow Hwa on his thesis entitled “Synthesis and Characterization of Calcium-Based Catalysts for Transesterification of *Jatropha curcas* L. and *Nannochloropsis oculata* Oils to Biodiesel” in accordance with the Universities and University College 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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Ca(OCH₃)₂ and (b) CaO catalysts

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LIST OF SYMBOLS

v	Adsorbed gas quality
P	Actual gas pressure
V	Adsorbed gas quality
$MW_{\text{fatty acid}}$	Average molecular weight of fatty acid
MW_{glycerol}	Average molecular weight of glycerol
M	Average molecular weight of <i>J. curcas</i> crude oil
MW_{oil}	Average molecular weight of microalga's crude oil
MW_{water}	Average molecular weight of water
c	BET constant
R_1, R_2, R_3	Carbon chain of fatty acid
C_{IS}	Concentration of the internal standard
Cu	Copper
t	Crystallite size for (<i>hkl</i>) phase in nm
β_{hkl}	Full width at half maximum (FWHM) at (<i>hkl</i>) peak in radian
A_{IS}	Internal standard peak area
T_{max}	Maxima temperature
R	Mixture of fatty acid chain
v_m	Monolayer adsorbed gas quality
k_f	Rate reaction from forward reaction
k_f'	Rate reaction from backward reaction
T	Reaction temperature
t	Reaction time
P	Reaction pressure
P/P_0	Relative pressure
$\sum A$	Total peak area of fatty acid methyl esters

S_{BET}	Total surface area
P_o	Vapour pressure
V_{IS}	Volume of the internal standard



LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AOAC	Association of Official Analytical Chemist
ATR-FTIR	Attenuated Total Reflection-Fourier Transform Infrared
AV	Acid Value
BET	Brunauer-Emmer-Teller
BJH	Barrett-Joyner-Halenda
CFPP	Cold Filter Plugging Point
CO ₂ -TPD	Temperature Programmed Desorption in Carbon Dioxide
CP	Cloud Point
DG	Diglyceride
DHA	Docosahexaenoic Acid
EDX	Energy Dispersion X-ray
EN	European
EPA	Eicosapentaenoic Acid
FA	Fatty Acid
FAAE	Fatty Acid Alkyl Ester
FAEE	Fatty Acid Ethyl Ester
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FID	Flame Ionization Detector
FIP	French Institute of Petroleum
FP	Flash Point
FWHM	Full-Width at Half Maximum
GCMS	Gas Chromatography Mass Spectroscopy
HT	Hydrotalcite

ICP–AES	Inductively Coupled plasma-atomic emission spectrometric
ICDD	International Centre for Diffraction Data
IR	Infrared
JCOME	<i>Jatropha curcus</i> Oil Methyl Ester
JCPDS	Joint Committee on Powder Diffraction Standards
LED	Light Emitted Diod
MG	Monoglyceride
MPOB	Malaysian palm Oil Board
n.d.	Not detected
n.r.	Not reported
OS	Oxidative Stability
PET	Polyethylene terephthalate
PME	Palm Oil Methyl Ester
PP	Pour Point
ppm	Parts per million
psi	Pounds per square inch
SCM	Supercritical Methanol
SD	Standard Deviation
SEM	Scanning Electron Microscopy
SFA	Saturated Fatty Acid
SME	Soybean Methyl Ester
SV	Saponification Value
SunMe	Sunflower Oil Methyl Ester
TCD	Thermal Conductivity Detector
TEM	Transmission Electron Microscopic

TG/DTA	Thermogravimetric and Differential Thermal Analysis
TG	Triglyceride
tr	Trace Amount
TW/y	Terawatt per year
USFA	Unsaturated Fatty Acid
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence



CHAPTER 1

INTRODUCTION

1.1 Research Background

Petroleum has been the most main fuel needs for current vehicular fuel; the global consumption of petroleum diesel is 934 million tonnes per year (Kulkarni and Dalai, 2006). Diesel-powered vehicles represent approximately one-third of vehicles sold in Europe and United States (Jayed *et al.*, 2009). However, there has been increasing concern about energy security high oil prices caused by prospective petroleum depletion.

Instead, biofuels and biomass based energy have prospective to develop into a major contribution of energy in the next century. For instance, biomass has been recognized by worldwide to be the only sustainable source for generate liquid fuels (Klass, 1988; Huber *et al.*, 2006). Apart from that, biodiesel and bioethanol account for the major proportion of biofuels produced from crops and biomass. Approximately 90% of the biofuels which use in road vehicles is imprisoned by biodiesel and bioethanol (Juan *et al.*, 2011).

Triglycerides, which are mainly from vegetable oils and animal fats, consist of three long chain fatty acids esterifies to a glycerol structure, are highly-density energy liquid molecules with different physical and chemical properties. Transesterification reaction or also known as alcoholysis, is a main catalyzed chemical reaction for biodiesel production between triglycerides and alcohol *i.e.* methanol or ethanol to produce fatty acid methyl ester (FAME) and glycerol as a by-product (Vasudevan and Briggs, 2008) depicted in Figure 1.1.

Generally, transesterification reaction can proceed without or with the presence of catalyst. The reaction is proceeding in an extremely slow rate without any catalysts due to the two phase nature of oil and alcohol (Marchetti *et al.*, 2007). On the other hand, transesterification of triglycerides also can take place without a catalyst at high temperature (573-623 K) and high pressure (about 50 MPa) (warabi *et al.*, 2004a; Saka *et al.*, 2006). However, these intense reaction conditions are not economically. In order to solve the problems, catalysts such as homogeneous, heterogeneous or enzymatic are added to the reaction system with aim of enhance the reaction rate and increase the yield of biodiesel.

Homogeneous transesterification reaction can be either catalyzed by acidic or alkaline. Industrially, sulfuric acid, hydrochloric acid, sodium (or potassium) hydroxide or methoxide are most often used homogeneous catalysts in the conventional commercial plants producing biodiesel from vegetable oils. Homogeneous base catalysts are preferred because they much more active and less corrosive to the processing equipment than the homogeneous acid catalysts. However, the main disadvantage of homogeneous-base catalyzed reaction is that the formation of an unwanted soap by-product in the presence of water and free acid (FFA).

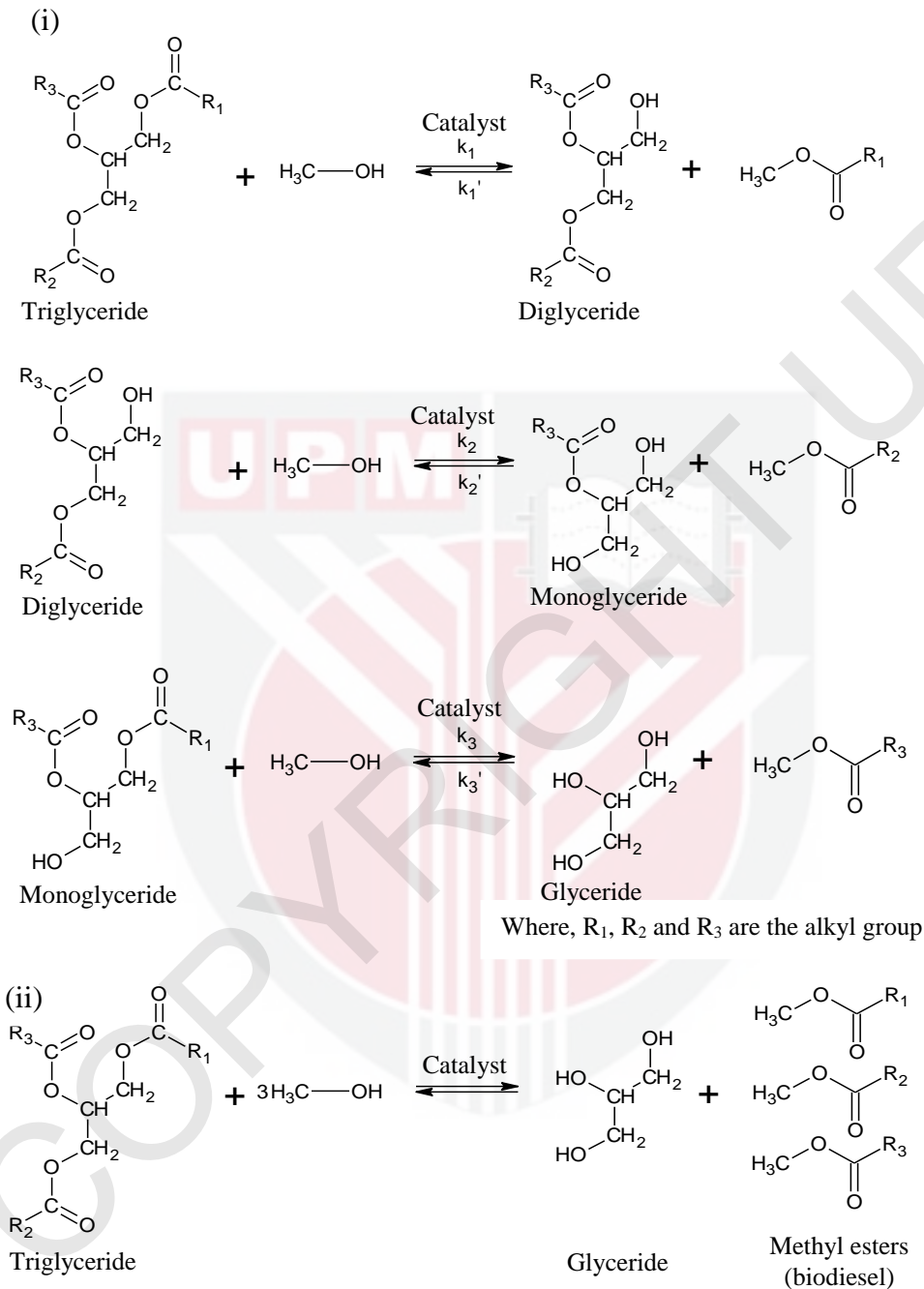


Figure 1.1 Stepwise (i) and overall transesterification (ii) reactions (Adapted from Lakhya *et al.*, 2014; Islam *et al.*, 2014)

For industry viewpoint, homogeneous catalysts are corrosive, use only once with difficulty separation process of biodiesel and catalyst, and generated a massive amount of waste water which eventually increase the overall biodiesel production cost and being not environmentally benign (Fukuda *et al.*, 2001; Van, 2005; Lam *et al.*, 2010; Shajaratun *et al.*, 2014). Next, one of the main attempts to solve drawbacks mentioned above is to replace homogeneous and enzymatic catalysts by heterogeneous catalysts towards a more sustainable industry. Developing an effective heterogeneous catalyst for biodiesel production would be beneficial, since heterogeneous catalysts offer many advantages than homogeneous catalysts in both of economic and environmental protection point of view such as (i) easy to carry and storage, (ii) simplify the separation of catalyst from product (iii) elimination of washing step (iv) long lifetimes, (v) higher efficiency and profitability of the process and (vi) lowering the production cost. Hence, using heterogeneous catalysts catalyzed biodiesel production has high potential to be eco-friendly process and promising alternative to the chemical process.

1.2 Problem Statement/ Hypothesis

Catalyst plays an important role in biodiesel production. In the chemical process industries, utilized homogeneous catalysts in biodiesel production process are ultimately wasted. In fact, alkali-catalysed transesterification reaction results in difficult to remove the liquid form catalyst from biodiesel product. Additional step is necessary to remove the alkaline catalyst that markup the biodiesel cost production. Moreover, waste is also associated with the use of acids to neutralize the reaction after product formation, and wastewater generated from 'washing' the biodiesel product result in loss of homogeneous catalyst.

Sustainable biodiesel production has now focused on production efficiency with minimal waste generation to enhance resource productivity. The need to minimize materials and energy consumption by development of a suitable heterogeneous catalyst and discovery other potential biodiesel feedstocks will be the major crucial in making biodiesel. Nevertheless, a stable catalyst that can be recycled and reused to simplify the product separation and purification steps remains inadequately addressed. Therefore, it is compulsory to discover a suitable and flexible catalyst for transesterification of plant derived oil *Jatropha curcas* (*J. curcas*) and *Nannochloropsis oculata* (*N. oculata*)).

The first approach on catalyst development is to prepare the calcium-based mixed oxides ($\text{CaO-La}_2\text{O}_3$, CaO-CeO_2 , CaO-NiO and $\text{CaO-Nd}_2\text{O}_3$) via co-precipitation process using highly basic precipitate. Overall, this process had been optimized by varies the synthesis parameter such as molar ratio of metal compositions and pH value of precipitation. The second approach of calcium-based catalyst focused on bulk type whereby the structure and morphology of $\text{Ca}(\text{OCH}_3)_2$ catalyst were determined in order to optimize the synthesis parameter prior to the production of nano-architectures $\text{Ca}(\text{OCH}_3)_2$ catalyst.

For comparison of catalytic activity on biodiesel production, *J. curcas* crude oil and extracted *N. oculata* crude oil were used as potential triglycerides source in transesterification reaction. Physico-chemical properties mixed metal oxide catalysts were characterized and also applied for transesterification *J. curcas* crude oil with methanol. Whereas, nano particle $\text{Ca}(\text{OCH}_3)_2$ catalyst was tested for transesterification reaction and its performance in biodiesel production from two different feedstocks: the

J. curcas and the *N. oculata* microalgae crude oils were evaluated in term of FAME yield and catalyst reusability. The overall process flow of research is shown in Figure 1.2.

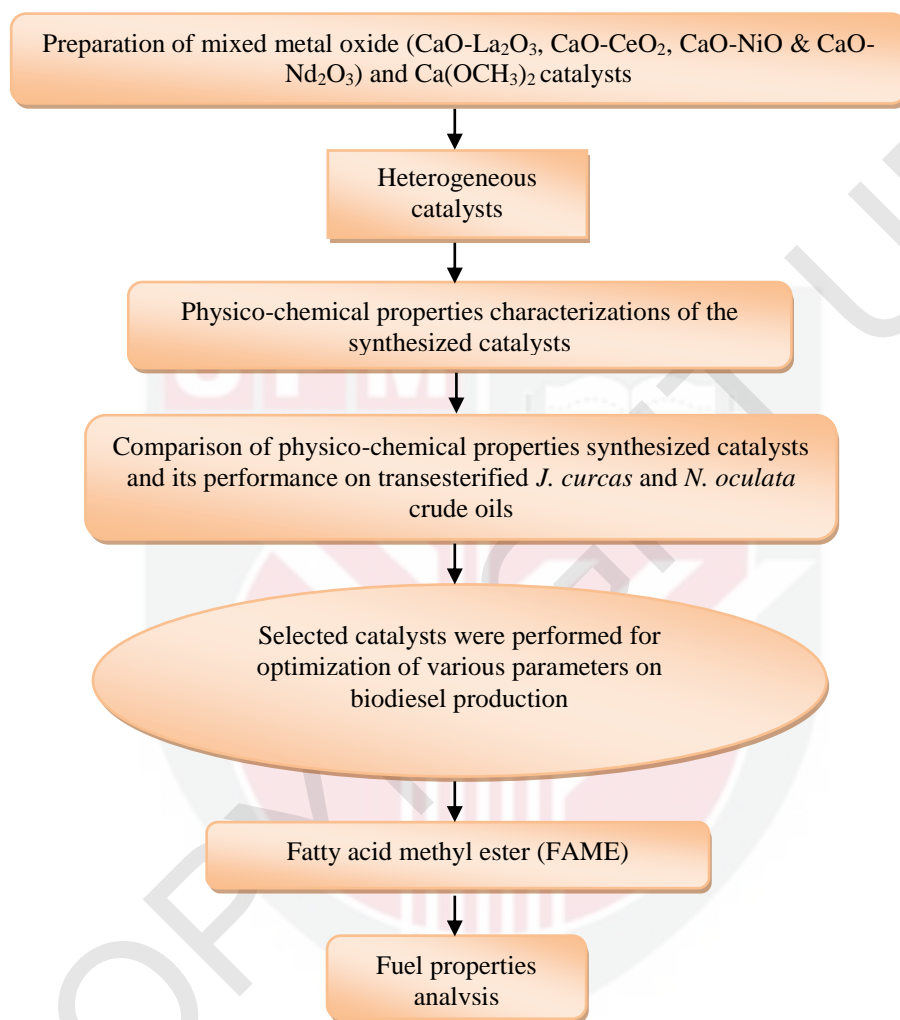


Figure 1.2 Overall diagram of research activities

1.3 Scope of Research

This studies involved synthesis of mixed metal oxide and $\text{Ca}(\text{OCH}_3)_2$ heterogeneous catalysts for biodiesel production from vegetable (*J. curcas*) and microalgae (*N. oculata*) crude oils with methanol. The effect of catalyst preparation condition *i.e.* molar ratio of metal oxide and pH value to synthesis in catalyst performance was investigated. The physic-chemicals characteristics of catalysts were carried out by using several methods (TGA, XRD, BET, FTIR, XRF, TPD, SEM and TEM). The surface properties of the supported catalysts were analyzed using N_2 adsorption/desorption isotherms and the basicity properties, evaluated in terms of

number and strength of basic sites, were analyzed using CO₂-temperature-programmed reduction (CO₂-TPD) techniques. In addition, the structural characteristic of the synthesized catalysts was carried out using XRD. The condition of the transesterification reactions of *J. curcas* crude oil was also studied by investigating the effect of variable transesterification parameters on biodiesel production such as catalyst concentration, methanol/ oil molar ratio, reaction temperature and time. The reusability of the catalyst was determined and the leachate of catalyst into the reaction product was verified by inductively coupled plasma-atomic emission spectrometric (ICP–AES) and absorption spectroscopy (AAS) elemental analysis. The relationship between the basicity of the catalyst and their catalytic activity in the transesterification of *J. curcas* crude oil is also discussed. Next, the selected Ca(OCH₃)₂ was used as catalyst and evaluated its performance in transesterification reaction of *N. oculata* crude oil with methanol at 60 °C in batch process in terms of biodiesel yield and catalyst reusability. The composition of biodiesel was evaluated by the gas chromatography method. In addition, the fuel properties characterization of biodiesel produced from transesterification of *J. curcas* crude oil with methanol was performed according to the ASTM D6751 and European 14214 standard specifications.

1.4 Objectives

This dissertation is aimed to develop calcium-based mixed oxide and calcium methoxide (Ca(OCH₃)₂) catalysts. This study also concerned with the physical and chemical properties of synthesized catalysts and the feasibility of biodiesel production from *J. curcas* and *N. oculata* through transesterification reaction with methanol. Various characterization techniques have been carried out. In order to achieve the main aim, a total of six research objectives have been addressed as follow:

1. To synthesize binary oxide calcium-based heterogeneous catalysts by co-precipitation method.
2. To prepare Ca(OCH₃)₂ heterogeneous catalyst using hydrothermal route.
3. To investigate the physico-chemical characteristics of catalysts.
4. To optimize the condition of the transesterification reactions of jatropha and microalgae oils by investigate the transesterification variables.
5. To characterize the jatropha and FAME product of its quality as diesel substitute.
6. To determine the reusability of the catalysts.

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