PREPARATION, CHARACTERIZATION AND MECHANISTIC STUDY OF ALUMINA SUPPORTED CALCIUM OXIDE BASED CATALYSTS IN TRANSESTERIFICATION OF REFINED COOKING OIL

NORHASYIMAH BT MOHD KAMAL

A thesis submitted in fulfilment of the requirements for the award of the degree of Doctor of Philosophy (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

NOVEMBER 2018
A Special Dedication to my beloved family especially to:

My sweetheart Mohd Norhelmi,
My cute little flower Siti Aisyah Humaira,
My sweet mums Habsah and Sepiah
My handsome dads Mohd Kamal and Samsudin
My supportive sisters Ashikin, Aishah and Aini
My loving brothers Firdaus, Fadzil and Fairuz's
My BFF Nur Fatin

For all the love, supports and continues doa to complete this work

“I am the person I am today because of all the people who have shaped me in every way”
ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious, the Most Merciful

Very Special thanks dedicated to my beloved supervisor, Prof. Dr. Wan Azelee Wan Abu Bakar, Dr. Susilawati Toemen and Dr. Rusmidah Ali as my co-supervisors for their time, guidance and encouragement during conducting this research. Without all of them, this work was unable to be accomplished very well.

My deepest gratitude and thanks go to all my friends especially Fatin, Kak Renu and Afiqah who give me all the time, support and being a good listener to all my problems every single day. Million thanks to all the laboratory staffs of Faculty Science, and for their technical cooperation, knowledge, encouragement and guidance throughout this research. I am grateful to Universiti Teknologi Malaysia and Ministry of Science, Technology and Innovation Malaysia for financial support for this research as well as Ministry of Higher Education (MOHE) for MyPhD Scholarship given to me.

Last but not least, I wish to express my sincere appreciation to my husband, Helmi Samsudin and my beauty daughter Aisyah, for standing beside me. My deepest gratitude goes to my beloved parents and my parents in law for their endless prayers, and unconditional love. Thank you all for always being there and being my pillar stone. To those who indirectly contributed in this research, your kindness means a lot to me.
ABSTRACT

Biodiesel synthesized from the transesterification reaction using heterogeneous base catalyst has been extensively studied over the past decades. In this research, a series of alumina-supported catalysts were synthesized utilizing CaO and MgO via impregnation with transition metal oxides of Cu, Zn and Ni. Through the catalyst screening process, Cu/Ni/Ca/Al$_2$O$_3$ and Cu/Zn/Ca/Al$_2$O$_3$ were selected, and further studies were carried out for optimization of several reaction parameters. The optimum calcination temperature of Cu/Ni/Ca/Al$_2$O$_3$ was at 700ºC, while that of Cu/Zn/Ca/Al$_2$O$_3$ was at 800ºC. The ratio of co-catalyst to based for both the catalysts was 3:7:90 wt%, with two times of alumina coatings performed on the samples. Study of the surface morphology by FESEM and TEM revealed the existence of agglomerated platelet-shape particles on the catalysts surface. XRD analysis showed the crystallinity of synthesized catalysts were generally poor, with the particle sizes of less than 50 nm. The Cu/Ni/Ca(3:7:90)/Al$_2$O$_3$ catalyst with BET surface area of 140 m$^2$/g, exhibited a higher amount of weak and moderate basic sites (4.02 mmol/g) when compared to the Cu/Zn/Ca(3:7:90)/Al$_2$O$_3$ catalyst, as obtained from the CO$_2$-TPD data. The optimum conditions were found as reaction temperature of 65ºC, catalyst loading of 4 wt% and oil to methanol molar ratio of 1:16, to achieve 90.12% of biodiesel production for 90 minutes of reaction time, in the transesterification of refined cooking oil over the Cu/Ni/Ca(3:7:90)/Al$_2$O$_3$ catalyst. Meanwhile, the Cu/Zn/Ca(3:7:90)/Al$_2$O$_3$ with 10 wt% catalyst loading underwent 180 minutes of reaction time and subsequent achievement of 82.34% of biodiesel production. The validated data from RSM analysis indicated that the selected model was adequate with a percentage error less than 5%. Mechanistic study of the catalyst surface using FTIR and the GC-FID analysis of the transesterification product showed that both the catalysts obeyed the Langmuir mechanism rule and capable to produce the cis and trans isomers of oleic acid methyl ester. The biodiesel produced complied with the quality standard and specification recommended by the American Society for Testing Materials D6751.
Biodiesel yang disintesis daripada tindak balas transesterifikasi menggunakan mangkin bes heterogen telah dikaji secara meluas sejak berdekad yang lalu. Dalam penyelidikan ini, satu siri mangkin berpenyokong alumina telah disintesis menggunakan CaO dan MgO secara pengisitapan oksida logam peralihan daripada Cu, Zn dan Ni. Melalui proses penyaringan mangkin, Cu/Ni/Ca/Al2O3 dan Cu/Zn/Ca/Al2O3 telah terpilih dan kajian lanjut telah dilakukan untuk pengoptimuman beberapa parameter tindak balas. Suhu pengkalsinan optimum bagi Cu/Ni/Ca/Al2O3 ialah pada 700°C, manakala bagi Cu/Zn/Ca/Al2O3 pada 800°C. Nisbah ko-mangkin kepada asas untuk kedua-dua mangkin adalah 3:7:90 wt% dengan dua kali salutan alumina. Kajian morfologi permukaan menggunakan FESEM dan TEM mendedahkan kewujudan zarah berbentuk platelet yang teraglomerat pada permukaan mangkin. Analisis XRD menunjukkan kehabluran mangkin yang disintesis pada umumnya adalah rendah, dengan saiz zarah di bawah 50 nm. Mangkin Cu/Ni/Ca(3:7:90)/Al2O3 dengan luas permukaan BET 140 m²/g, memperoleh jumlah tapak bes lemah dan sederhana (4.02 mmol/g) yang lebih tinggi apabila dibandingkan dengan mangkin Cu/Zn/Ca(3:7:90)/Al2O3, seperti yang diperoleh dari data CO2-TPD. Keadaan optimum adalah suhu tindak balas 65°C, muatan mangkin 4 wt% dan nisbah molar minyak kepada metanol 1:16, untuk mencapai 90.12% pengeluaran biodiesel bagi masa tindak balas 90 minit, dalam transesterifikasi minyak masak bertapis dengan menggunakan mangkin Cu/Ni(Ca(3:7:90)/Al2O3. Sementara itu, Cu/Zn/Ca(3:7:90)/Al2O3 dengan muatan mangkin 10 wt% menjalani 180 minit masa tindak balas, diikuti dengan pencapaian 82.34% pengeluaran biodiesel. Data yang disahkan daripada analisis RSM menunjukkan bahawa model yang dipilih adalah mencukupi dengan peratus ralat kurang daripada 5%. Kajian mekanistik ke atas permukaan mangkin menggunakan FTIR dan analisis produk menggunakan GC-FID menunjukkan bahawa kedua-dua mangkin mematuhi peraturan mekanisme Langmuir dan boleh menghasilkan isomer cis dan trans metil ester asid oleik. Biodiesel yang dihasilkan telah mematuhi spesifikasi dan piawaian yang diperakukan oleh Persatuan Amerika untuk Bahan Ujian D6751.
TABLE OF CONTENTS

CHAPTER     TITLE                   PAGE

DECLARATION            ii
DEDICATION              iii
ACKNOWLEDGEMENT        iv
ABSTRACT               v
ABSTRAK                vi
TABLE OF CONTENTS      vii
LIST OF TABLES         xviii
LIST OF FIGURES        xxiii
LIST OF ABBREVIATIONS  xxxv
LIST OF APPENDICES     xxxvi

1  INTRODUCTION            1
1.1 Biodiesel as Alternative Energy Resources  1
1.2 Catalysts in Biodiesel Production  5
1.3 Response Surface Methodology (RSM)  7
1.4 Problem Statement  8
1.5 Objectives of the Study  10
1.6 Scope of the Research  11
1.7 Significant of Study  12

2  LITERATURE REVIEW       13
2.1 Introduction  13
2.2 Magnesium oxide as Heterogeneous Base Catalyst in Transesterification Reaction
2.3 Calcium oxide as Heterogeneous Base Catalyst in Transesterification Reaction
2.4 The Influence of Transition Metal oxide over Transesterification Reaction
2.5 Catalyst Support
2.6 Mechanism of catalytic Transesterification Reaction
2.7 Biodiesel Feedstock

3 EXPERIMENTAL
3.1 Introduction
3.2 Chemicals and Reagents
3.3 Catalysts Preparation
3.4 Transesterification Reaction for Screening Process
3.5 Product Analysis
   3.5.1 SP 2560 Capillary Column
   3.5.2 MET-Biodiesel Column
3.6 Optimization Parameters of Potential Catalyst
   3.6.1 Co-Catalysts Ratios to Based Loadings
   3.6.2 Number of Alumina Coatings
3.6.3 Calcination Temperatures of Supported Catalyst 44
3.6.4 Reliability Testing of the Catalyst 44
3.6.5 Reproducibility of the Catalyst 45
3.6.7 Regeneration Activity of the Catalyst 45
3.6.8 Response Surface methodology (RSM) for Potential Catalyst 45

3.7 Characterization of the Potential Catalyst 48
3.7.1 Nitrogen Adsorption (NA) 48
3.7.2 Field Emission Scanning Electron Microscopy (FESEM) 49
3.7.3 Energy Dispersive X-ray (EDX) 49
3.7.4 High Resolution Transmission Electron Microscopy (HRTEM) 50
3.7.5 X-Ray Diffraction Spectroscopy (XRD) 50
3.7.6 X-ray Photoelectron Spectroscopy (XPS) 51
3.7.7 CO₂-Temperature Programmed Desorption (CO₂-TPD) 51
3.7.8 Thermogravimetry Analysis- Differential Thermal Analysis (TGA-DTA)

3.8 Optimization of the Catalytic Conditions Testing

3.8.1 Effect of Time in Transesterification Reaction

3.8.2 Effect of Ratio oil to methanol in Transesterification Reaction

3.8.3 Effect of Catalyst Loading in Transesterification Reaction

3.8.4 Response Surface Methodology (RSM) for Transesterification Reaction

3.9 Mechanistic Study

3.10 Verification Method for Biodiesel Production

3.10.1 Total Acid Number (TAN) Analysis (ASTM D664)

3.10.2 Flash Point (D93)

3.10.3 Kinematic Viscosity (D445)

3.10.4 Density (DMA 4100M)

3.10.5 Pour Point (ASTM D 97)

3.10.6 Cetane Index (ASTM D967-91)

3.10.7 Determination of Total Glycerin
RESULTS AND DISCUSSION 61

CATALYTIC SCREENING OF THE CATALYSTS AND OPTIMIZATION USING RSM

4.1 Introduction 61

4.2 Catalytic Screening of Monometallic and Bimetallic Magnesium Oxide Based Catalysts 62

4.3 Catalytic Screening of Calcium Oxide Based Catalysts 64

4.3.1 Catalytic Screening of Monometallic and Bimetallic Calcium Oxide Based Catalysts 65

4.3.2 Catalytic Screening of Trimetallic Calcium Based Metal Oxides 67

4.4 Catalytic Activity over Cu/Ni/Ca/Al₂O₃ Catalyst 68

4.4.1 Effect of Alumina Coating 69

4.4.2 Effect of Co-catalyst ratio to Based 70

4.4.3 Effect of Calcination Temperatures 72

4.4.4 Optimization of Cu/Ni/Ca (3:7:90)/Al₂O₃ using Response Surface Methodology (RSM) 74
4.4.4.1 Regression Model and Statistical Analysis 75
4.4.4.2 Response Surface and Contour Plots 80
4.4.4.3 Optimization of Response Parameters 84

4.5 Catalytic Activity over Cu/Zn/Ca/Al₂O₃ Catalyst 85
4.5.1 Effect of Alumina Coating 86
4.5.2 Effect of Co-catalyst Ratios to Based 87
4.5.3 Effect of Calcination Temperatures 89
4.5.4 Optimization of Cu/Zn/Ca(3:7:90)/Al₂O₃ using Response Surface Methodology (RSM) 90
4.5.4.1 Regression Model and Statistical Analysis 91
4.5.4.2 Response surface and Contour Plots 95
4.5.4.3 Optimization of Response Parameters 98

5 CHARACTERIZATION OF Cu/Ni/Ca/Al₂O₃ CATALYST AND BIODIESEL OPTIMIZATION 99
5.1 Introduction 99
5.2 X-ray Diffraction Analysis (XRD) over Cu/Ni/Ca/Al$_2$O$_3$ Catalyst
5.2.1 XRD analysis at Different Calcination Temperatures
5.2.2 XRD analysis at Different Co-catalyst Ratios to Based
5.3 Nitrogen Absorption Analysis (NA)
5.4 Transmission Electron Microscopy (TEM)
5.5 X-Ray Photoelectron Spectroscopy (XPS)
5.6 Temperature Programmed Desorption-CO$_2$ (TPD-CO$_2$)
5.7 Field Emission Scanning Electron Microscopy - Energy Dispersive X-Ray (FESEM-EDX)
5.8 X-Ray Fluorescence (XRF)
5.9 Thermogravimetric Analysis (TGA)
5.10 Optimization Study in Transesterification Reaction using Cu/Ni/Ca (3:7:90)/Al$_2$O$_3$ catalyst
5.10.1 Effect of Catalyst loadings
5.10.2 Effect of Methanol to oil Ratio
5.10.3 Effect of Reaction Time
5.10.4 Reusability Testing of Cu/Ni/Ca(3:7:90)/Al$_2$O$_3$ catalyst
5.10.5 Regeneration Testing
Cu/Ni/Ca(3:7:90)/Al$_2$O$_3$ catalyst

5.10.6 Reliability Testing 146

5.10.7 Optimization of Transesterification Reacting using RSM 148

5.10.7.1 Regression Model and Statistical Analysis 148

5.10.7.2 Response surface and Contour Plots 153

5.10.7.3 Optimization of Response Parameters 155

6 CHARACTERIZATION OF Cu/Zn/Ca/Al$_2$O$_3$ CATALYST AND BIODIESEL OPTIMIZATION 157

6.1 Introduction 157

6.2 X-ray Diffraction Analysis (XRD) over Cu/Zn/Ca/Al$_2$O$_3$ Catalyst 157

6.2.1 XRD analysis at Different Calcination Temperatures 158

6.2.2 XRD analysis at Different Co-catalyst Ratios to Based 162

6.3 Nitrogen Absorption Analysis (NA) 165

6.4 Temperature Programmed Desorption-CO$_2$ (TPD-CO$_2$) 172

6.5 Transmission Electron Microscopy (TEM) 175
6.6 Field Emission Scanning Electron Microscopy - Energy Dispersive X-Ray (FESEM-EDX)

6.7 X-Ray Fluorescence (XRF)

6.8 Thermogravimetric Analysis (TGA)

6.9 Optimization Study in Transesterification Reaction using 
Cu/Ni/Ca (3:7:90)/Al₂O₃ catalyst

   6.9.1 Effect of Catalyst loading
   6.9.2 Effect of Oil to Methanol Ratio
   6.9.3 Effect of Oil to Reaction time
   6.9.4 Reusability Testing of 
      Cu/Ni/Ca (3:7:90)/Al₂O₃ catalyst
   6.9.5 Regeneration Testing of 
      Cu/Ni/Ca(3:7:90)/Al₂O₃ catalyst
   6.9.6 Reliability Testing
   6.9.7 Optimization of Transesterification Reacting using RSM

      6.9.7.1 Regression Model and Statistical Analysis
      6.9.7.2 Response surface and Contour
7 \hspace{1em} MECHANISTIC STUDY AND SPECIFICATION

ANALYSIS OF BIODIESEL

7.1 Introduction \hspace{1em} 207

7.2 Mechanistic Study over Cu/Ni/Ca (3:7:90)/Al$_2$O$_3$ Catalyst

7.2.1 Product Analysis of Cu/Ni/Ca(3:7:90)/Al$_2$O$_3$ Catalyst \hspace{1em} 208

7.2.2 Mechanism on Surface Cu/Ni/Ca(3:7:90)/Al$_2$O$_3$ Catalyst \hspace{1em} 211

7.3 Mechanistic Study of Cu/Zn/Ca(3:7:90)/Al$_2$O$_3$ Catalyst

7.3.1 Product Analysis of Cu/Zn/Ca(3:7:90)/Al$_2$O$_3$ Catalyst \hspace{1em} 214

7.3.2 Mechanism on Surface Cu/Zn/Ca(3:7:90)/Al$_2$O$_3$ Catalyst \hspace{1em} 218

7.4 Proposed Mechanism for Transesterification of Triolein using Cu/Ni/Ca (3:7:90)/Al$_2$O$_3$ and Cu/Zn/Ca (3:7:90)/Al$_2$O$_3$ Catalyst \hspace{1em} 220
7.5 Specification Analysis for Biodiesel Product in Transesterification of Refined cooking Oil using Cu/Ni/Ca (3:7:90)/Al₂O₃ Catalyst

8 CONCLUSION AND RECOMMENDATIONS

8.1 Conclusion 227
8.2 Recommendations 230

REFERENCES 231

Appendices A-H 252-261
<table>
<thead>
<tr>
<th>TABLE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Parameter programmed for FAME identification</td>
<td>41</td>
</tr>
<tr>
<td>3.2</td>
<td>Parameter programmed for Triglycerides identification using GC-FID</td>
<td>42</td>
</tr>
<tr>
<td>3.3</td>
<td>Independents variables and factor level use in optimization of the potential catalyst</td>
<td>47</td>
</tr>
<tr>
<td>3.4</td>
<td>Independents variables and factor level use in optimization for biodiesel production</td>
<td>55</td>
</tr>
<tr>
<td>4.1</td>
<td>Biodiesel production over mono and bimetallic alumina supported magnesium oxide based catalyst calcined at 800ºC for 5 hours, one time alumina coating at 65ºC of reaction temperature, 3 hours of reaction time, 1:16 of ratio oil to methanol and 6 wt% of catalyst loadings</td>
<td>62</td>
</tr>
<tr>
<td>4.2</td>
<td>Production of biodiesel over monometallic and bimetallic alumina supported calcium oxide based catalysts calcined at 800ºC for 5 hours, one time alumina coating at 65ºC of reaction temperature, 3 hours of reaction time, 1:16 of ratio oil to methanol and 6 wt% of catalyst loading.</td>
<td>65</td>
</tr>
</tbody>
</table>
4.3 Production of biodiesel over trimetallic alumina supported calcium oxide based catalyst calcined at 800ºC for 5 hours, one time alumina coating at 65ºC of reaction temperature, 3 hours of reaction time, 1:16 of ratio oil to methanol and 6 wt% of catalyst loading.

4.4 The coded level of the independent variables over Cu/Ni/Ca/Al$_2$O$_3$

4.5 ANOVA results of the response surface quadratic model for biodiesel production over Cu/Ni/Ca/Al$_2$O$_3$

4.6 The optimum parameter conditions for maximum biodiesel production

4.7 The coded level of the independent variables

4.8 ANOVA results of the response surface quadratic model for biodiesel production

4.9 The optimum parameter condition for biodiesel production using Cu/Zn/Ca(3:7:90)/Al$_2$O$_3$ catalyst

5.1 Crystallite size of Cu/Ni/Ca(3:7:90)/Al$_2$O$_3$ catalysts calcined at different calcination temperatures for 5 hours with two times of alumina coatings

5.2 Crystallite size over Cu/Ni/Ca/Al$_2$O$_3$ calcined at 700ºC with different Co-catalyst ratios to based
5.3 Surface area, average pre diameter and pore volume for Cu/Ni/Ca/Al₂O₃ at different calcination temperatures and deferent co-catalyst loading and calcined for 5 hours with two times alumina coatings

5.4 Binding energy elements species obtained over Cu/Ni/Ca(3:7:90)/Al₂O₃ catalysts calcined at 600ºC, 700ºC and 800ºC for 5 hours

5.5 CO₂ desorbed temperature and basic sites amount of Cu/Ni/Ca(3:7:90)/Al₂O₃ catalysts at different calcination temperatures and co-catalyst loading with two times alumina coatings

5.6 Elemental composition by EDX analysis of Cu/Ni/Ca/Al₂O₃ catalyst calcined at different calcination temperature and co-catalyst loadings

5.7 XRF data for calculated and as prepared catalyst (actual detected by XRF) for Cu/Ni/Ca(3:7:90)/Al₂O₃ with two times alumina coatings

5.8 The coded level of the independent variables

5.9 Summarize of ANOVA analysis data for independent and dependant variables

5.10 The optimum parameter condition for biodiesel production using Cu/Ni/Ca(3:7:90)/Al₂O₃ catalyst calcined at 700ºC for 5 hours with two times alumina coatings

6.1 Crystallite size over Cu/Zn/Ca(3:7:90)/Al₂O₃
catalysts at different calcination temperatures for 5 hours with two times alumina coatings

6.2 Crystallite size over Cu/Zn/Ca/Al₂O₃ catalysts calcined at 800ºC, two times alumina coatings and in different co-catalyst ratios to based

6.3 Surface areas, average pre diameter and pore volume for Cu/Zn/Ca/Al₂O₃ at different calcination temperatures and deferent co-catalyst loadings calcined for 5 hours with two times alumina coatings

6.4 The amount of CO₂ desorbed temperature and basic sites amount of Cu/Zn/Ca/Al₂O₃ catalysts at different calcination temperatures and co-catalyst loadings calcined for 5 hours with two times alumina coatings

6.5 Elemental composition by EDX analysis of Cu/Zn/Ca (3:7:90)/Al₂O₃ at different calcination temperature for 5 hours with two times alumina coatings

6.6 XRF data for element presence between nominal and actual (identified by XPS) for Cu/Zn/Ca(3:7:90)/Al₂O₃ catalyst

6.7 BBD matrix of three independent variables along with experimental and predicted response over Cu/Zn/Ca(3:7:90)/Al₂O₃ catalyst

6.8 Summarize of ANOVA analysis data for independent and dependent variables over Cu/Zn/Ca(3:7:90)/Al₂O₃ catalyst
6.9 The optimum parameter condition for biodiesel production using Cu/Zn/Ca(3:7:90)/Al₂O₃ catalyst

7.1 Percentage production of oleic acid methyl ester (FAME) and peak identification using Cu/Ni/Ca(3:7:90)/Al₂O₃ catalyst calcined at 700°C for 5 hours with two times alumina coatings

7.2 Percentage production of oleic acid methyl ester (FAME) and peak identification using Cu/Zn/Ca(3:7:90)/Al₂O₃ catalyst calcined at 800°C for 5 hours with two times alumina coatings

7.3 Specification analysis of biodiesel in transesterification of refined cooking oil using Cu/Ni/Ca(3:7:90)/Al₂O₃ calcined at 700°C for 5 hours and two times alumina coatings
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE NO.</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Reflux and distillation processes in a transesterification reaction</td>
<td>40</td>
</tr>
<tr>
<td>4.1</td>
<td>Effect of alumina coatings for Cu/Ni/Ca(3:7:90)/Al₂O₃ catalyst calcined at 800°C for 5 hours, at 65°C of reaction temperature, 3 hours of reaction time, 1:16 of ratio oil to methanol and 6 wt% of catalyst loading.</td>
<td>69</td>
</tr>
<tr>
<td>4.2</td>
<td>Effect of dopant and co-dopant ratios to based for Cu/Ni/Ca/Al₂O₃ calcined at 800°C for 5 hours, two times alumina coatings at 65°C of reaction temperature, 3 hours of reaction time, 1:16 of ratio oil to methanol and 6 wt% of catalyst loading.</td>
<td>71</td>
</tr>
<tr>
<td>4.3</td>
<td>The effect of calcination temperatures over Cu/Ni/Ca(3:7:90)/Al₂O₃ calcined for 5 hours with two times alumina coatings at 65°C of reaction temperature, 3 hours of reaction time, 1:16 of ratio oil to methanol and 6 wt% of catalyst loading.</td>
<td>73</td>
</tr>
</tbody>
</table>
4.4 Fit plot of regression model for biodiesel production from the experimental design over Cu/Ni/Ca/Al\textsubscript{2}O\textsubscript{3}

4.5 3D and 2D plot for a) and b) interaction between calcination temperature and co-catalyst ratio to based c) and d) interaction between calcination temperature and numbers of alumina coating, e) and f) interaction between co-catalyst ratio to based and numbers of alumina coating

4.6 Effect of alumina coatings over Cu/Zn/Ca(3:7:90)/Al\textsubscript{2}O\textsubscript{3} catalyst calcined at 800\textdegree C, at 65\textdegree C of reaction temperature, 3 hours of reaction time, 1:16 of ratio oil to methanol and 6 wt\% of catalyst loading

4.7 Effect of co-dopant, dopant to based for Cu/Zn/Ca(3:7:90)/Al\textsubscript{2}O\textsubscript{3} catalyst calcined at 800\textdegree C for 5 hours with two times alumina coatings at 65\textdegree C of reaction temperature, 3 hours of reaction time, 1:16 of ratio oil to methanol and 6 wt\% of catalyst loading

4.8 Effect of calcination temperatures on Cu/Zn/Ca(3:7:90)/Al\textsubscript{2}O\textsubscript{3} catalyst calcined for 5 hours with two times alumina coatings at 65\textdegree C of reaction temperature, 3 hours of reaction time, 1:16 of ratio oil to methanol and 6 wt\% of catalyst loading
4.9 Fit plot of regression model for biodiesel production from the experimental design

4.10 3D and 2D plot for a) and b) interaction between calcination temperature and co-catalyst ratio to based c) and d) interaction between calcination temperature and numbers of alumina coating, e) and f) interaction between co-catalyst ratio to based and numbers of alumina coatings

5.1 XRD diffractograms of Cu/Ni/Ca(3:7:90)/Al₂O₃ catalysts at different calcination temperatures of a) 600°C; b) 700°C, c) 800°C and 1000°C for 5 hours with two times alumina coatings

5.2 XRD diffractograms of Cu/Ni/Ca/Al₂O₃ catalysts at different co-catalyst ratios to based a) Cu/Ni/Ca(2:8:90), b) Cu/Ni/Ca(3:7:90) and c) Cu/Ni/Ca(4:6:90) at calcination temperature of 700°C for 5 hours with two times alumina coatings

5.3 Pore size distribution plot for Cu/Ni/Ca(3:7:90)/Al₂O₃ at calcination temperature of a) 600°C, b) 700°C, c) 800°C and d) 1000°C calcined for 5 hours with two times alumina coatings

5.4 Isotherm linear plots at different for Cu/Ni/Ca(3:7:90)/Al₂O₃ at calcination temperature of a) 600°C, b) 700°C, c) 800°C
and d) 1000°C calcined for 5 hours with two times alumina coatings

5.5 Pore distribution plots for Cu/Ni/Ca/Al$_2$O$_3$ calcined at 700°C for 5 hours with different co-catalyst loadings of a) 2:8:90, b)3:7:90 and c) 4:6:90 with two times alumina coatings

5.6 Isotherm linear plots for Cu/Ni/Ca/Al$_2$O$_3$ at different co-catalyst loading at calcination temperature 700°C calcined for 5 hours with two times alumina coatings

5.7 TEM images of Cu/Ni/Ca(3:7:90)/Al$_2$O$_3$ catalyst calcined at a) 600°C, b)700°C and c) 800°C for 5 hours with two times alumina coatings

5.8 HRTEM image of Cu/Ni/Ca (3:7:90)/Al$_2$O$_3$ catalyst calcined at 600°C, for 5 hours, a) Al$_2$O$_3$ (400), b) CaO (200) and c) NiO (200) with two times alumina coatings

5.9 HRTEM image of Cu/Ni/Ca (3:7:90)/Al$_2$O$_3$ catalyst calcined at 700°C, for 5 hours with two times alumina coatings, a) Al$_2$O$_3$ (400), b) CaO (200) and c) NiO (200) with two times alumina coatings

5.10 HRTEM image of Cu/Ni/Ca (3:7:90)/Al$_2$O$_3$ catalyst calcined at 800°C, for 5 hours with two times alumina coatings, a) Al$_2$O$_3$ (400), b) CaO (200) and c) NiO (200) d) CaAl$_4$O$_7$ (243) calcined for 5 hours with two times
alumina coatings.

5.11 Wide Scan XPS spectrum for Cu/Ni/Ca/Al₂O₃ catalysts calcined at a) 600°C, b) 700°C and c) 800°C for 5 hours with two times alumina coatings

5.12 XPS results for different types of elements (Al, O, Ca, Ni and Cu) obtained over Cu/Ni/Ca(3:7:90) Al₂O₃ catalyst calcined at a) 600°C, b) 700°C and c) 800°C for 5 hours with two times alumina coatings

5.13 CO₂-TPD curves for Cu/Ni/Ca (3:7:90)/Al₂O₃ catalyst at calcination temperatures of a) 600°C, b) 700°C and c) 800°C for 5 hours with two times alumina coatings

5.14 CO₂-TPD curves for Cu/Ni/Ca/Al₂O₃ catalyst at co-catalyst loading of a) Cu/Ni/Ca (2:8:90)/Al₂O₃, b) Cu/Ni/Ca(3:7:90)/Al₂O₃ and c) Cu/Ni/Ca(4:6:90)/Al₂O₃ calcined at 700°C for 5 hours with two times alumina coatings

5.15 FESEM micrograph of catalyst a) Cu/Ni/Ca(3:7:90)/Al₂O₃ calcined at 600°C, b) Cu/Ni/Ca(3:7:90)/Al₂O₃ calcined at 700 °C, c) Cu/Ni/Ca(3:7:90)/Al₂O₃ calcined at 800°C, d) Cu/Ni/Ca(2:8:90)/Al₂O₃ calcined at 700°C and e) Cu/Ni/Ca(4:6:90)/Al₂O₃ calcined at 700°C

xxvii
5.16 EDX mapping image of Cu/Ni/Ca (3:7:90)/Al₂O₃ catalyst calcined at 700°C for 5 hours. ((a: alumina compound), (b: oxygen compound), (c: calcium species), (d: copper species) and (e: Nickel species)

5.17 TGA analysis of as prepared Cu/Ni/Ca(3:7:90)/Al₂O₃ catalyst with two times alumina coatings

5.18 Effect of catalyst loading on biodiesel production (%) in the presence of Cu/Ni/Ca (3:7:90)/Al₂O₃ catalyst calcined at 700°C with oil to methanol molar ratio of 1:16, reaction temperature of 65°C and reaction time of 60 minutes

5.19 Effect of oil to methanol ratio in the presence of Cu/Ni/Ca(3:7:90)/Al₂O₃ catalyst calcined at 700°C with 4 wt% catalyst loading, reaction temperature of 65°C and reaction time of 60 minutes

5.20 Effect of reaction time in the presence of Cu/Ni/Ca (3:7:90)/Al₂O₃ catalyst calcined at 700°C for 5 hours, two times alumina coating with 4 wt% catalyst loading, reaction temperature of 65°C and 1:16 molar ratio oil to methanol

5.21 Reusability testing of Cu/Ni/Ca (3:7:90)/Al₂O₃ catalyst calcined at 700°C, two times alumina coatings with 4 wt%
catalyst loading, reaction temperature of 65°C, 1:16 molar ratio oil to methanol and 90 minutes reaction time

5.22 Reliability testing of Cu/Ni/Ca(3:7:90)/Al₂O₃ catalyst calcined at 700°C with 4 wt% catalyst loading, reaction temperature of 65°C, 1:16 molar ratio oil to methanol and 90 minutes reaction time

5.23 Fit plot of regression model for biodiesel production from the experimental design

5.24 3D and 2D surface contour plots of the relation between dependant and independent variable over Cu/Ni/Ca/Al₂O₃

6.1 XRD diffractograms of Cu/Zn/Ca(3:7:90)/Al₂O₃ catalysts at different calcination temperatures of a) 700°C, b) 800°C, c) 900°C and d) 1000°C for 5 hours with two times alumina coatings

6.2 XRD diffractograms of Cu/Zn/Ca/Al₂O₃ catalysts at 800°C with different co-catalyst ratios to based calcined for 5 hours with two times alumina coatings

6.3 Pore size distribution plot of Cu/Zn/Ca(3:7:90)/Al₂O₃ at calcination temperatures of a) 700°C; b) 800°C; c) 900°C and d) 1000°C, calcined for 5 hours with two times alumina coatings
6.4 Isotherm linear plots of Cu/Zn/Ca(3:7:90)/Al₂O₃ at calcination temperatures of a) 700°C; b) 800°C; c) 900°C and d) 1000°C, calcined for 5 hours with two times alumina coatings.

6.5 Pore size distribution plots calcined at 800°C co-catalyst with co-catalyst loading of a) Cu/Zn/Ca(2:8:90)/Al₂O₃; b) Cu/Zn/Ca(3:7:90)/Al₂O₃ and c) Cu/Zn/Ca(4:6:90)/Al₂O₃ calcined for 5 hours with two times alumina coatings.

6.6 Isotherm linear plots of Cu/Zn/Ca/Al₂O₃ calcined at 800°C with co-catalyst loadings of a) Cu/Zn/Ca(2:8:90)/Al₂O₃; b) Cu/Zn/Ca(3:7:90)/Al₂O₃ and c) Cu/Zn/Ca(4:6:90)/Al₂O₃ calcined for 5 hours with two times alumina coatings.

6.7 CO₂-TPD curves at different calcination temperatures and co-catalyst ratios to based of a) Cu/Zn/Ca(3:7:90)/Al₂O₃(700°C), b) Cu/Zn/Ca(3:7:90)/Al₂O₃(800°C), c) Cu/Zn/Ca(3:7:90)/Al₂O₃(900°C), d) Cu/Zn/Ca(2:8:90)/Al₂O₃(800°C) and e) Cu/Zn/Ca(3:7:90)/Al₂O₃(800°C).

6.8 TEM images (50 nm scale) of Cu/Zn/Ca(3:7:90)/Al₂O₃ catalyst calcined at a) 700°C, b) 800°C and c) 900°C for 5 hours with two times alumina coating.
6.9 TEM images of Cu/Zn/Ca(3:7:90)/Al\(_2\)O\(_3\) catalyst calcined at 700\(^\circ\)C, for 5 hours with two times alumina coatings; a) Al\(_2\)O\(_3\) (4,0,0) plane and b) CaO (2,0,0) plane

6.10 TEM images of Cu/Zn/Ca (3:7:90)/Al\(_2\)O\(_3\) catalyst calcined at 800\(^\circ\)C, for 5 hours with two times alumina coatings; a) Al\(_2\)O\(_3\) (4,0,0), and b) CaO (2,0,0)

6.11 TEM images of Cu/Zn/Ca (3:7:90)/Al\(_2\)O\(_3\) catalyst calcined at 900\(^\circ\)C, for 5 hours with two times alumina coatings; a) Al\(_2\)O\(_3\) (400) plane, b) CaO (200) plane, c) CaAl\(_2\)O\(_19\) (108) plane and d) ZnAl\(_{94}\)O\(_{144}\) (103) plane

6.12 FESEM micrograph of catalyst a) Cu/Zn/Ca(3:7:90)/Al\(_2\)O\(_3\) calcined at 700\(^\circ\)C with two times alumina coatings, b) Cu/Zn/Ca(3:7:90)/Al\(_2\)O\(_3\) calcined at 800\(^\circ\)C, c) Cu/Zn/Ca(3:7:90)/Al\(_2\)O\(_3\) calcined at 900\(^\circ\)C for 5 hours.

6.13 EDX mapping image of Cu/Zn/Ca (3:7:90)/Al\(_2\)O\(_3\) catalyst calcined at 800\(^\circ\)C for 5 hours with two times alumina coatings; a: alumina compound; b: oxygen compound; c: calcium species; d: zinc species and e copper species

6.14 TGA analysis for Cu/Zn/Ca(3:7:90)/Al\(_2\)O\(_3\) catalyst (as prepared) with two times alumina coatings
6.15 Effect of catalyst loading on biodiesel production (%) in the presence of Cu/Zn/Ca (3:7:90)/Al₂O₃ catalyst calcined at 800°C with oil to methanol molar ratio of 1:16, reaction temperature of 65°C and the reaction time of 60 minutes.

6.16 Effect of oil to methanol ratio in the presence of Cu/Zn/Ca(3:7:90)/Al₂O₃ catalyst calcined at 800°C with 10 wt% catalyst loading, reaction temperature of 65°C and reaction time of 60 minutes.

6.17 Effect reaction time in the presence of Cu/Zn/Ca(3:7:90)/Al₂O₃ catalyst calcined at 800°C, two times alumina coatings with 10 wt% catalyst loading, reaction temperature of 65°C and 1:16 molar ratio of oil to methanol.

6.18 Reusability testing of Cu/Zn/Ca(3:7:90)/Al₂O₃ catalyst calcined at 800°C with 10 wt% catalyst loading, the reaction temperature of 65°C, 1:16 molar ratio oil to methanol and 180 minutes of reaction time.

6.19 Reliability testing of Cu/Zn/Ca(3:7:90)/Al₂O₃ catalyst calcined at 800°C, two times alumina coatings with 10 wt% catalyst loading, the reaction temperature of 65°C 1:16 molar ratio of oil to methanol and 180 minutes reaction time.
6.20 Fit plot of the regression model for biodiesel production from the experimental design over Cu/Zn/Ca/Al₂O₃ catalyst

6.21 3D and 2D surface contour plots of the relation between dependent and independent variables over Cu/Zn/Ca/Al₂O₃ catalyst

7.1 GC chromatogram of cis and trans oleic acid methyl ester using Cu/Ni/Ca(3:7:90)/Al₂O₃ catalyst calcined at 700°C for 5 hours with two times alumina coating.

7.2 FTIR spectra for transesterification reaction of triolein and methanol in the presence of Cu/Ni/Ca (3:7:90)/Al₂O₃ catalyst calcined at 700°C for 5 hours with two times alumina coating.

7.3 GC chromatogram of cis and trans oleic acid methyl esters using Cu/Zn/Ca(3:7:90)/Al₂O₃ catalyst calcined at 800°C for 5 hours with two times alumina coating.

7.4 FTIR spectra for transesterification reaction of triolein and methanol in the presence of Cu/Zn/Ca(3:7:90)/Al₂O₃ catalyst calcined at 800°C for 5 hours with two times alumina coating.
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANOVA</td>
<td>Analysis of Variance</td>
</tr>
<tr>
<td>2D</td>
<td>Two Dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three Dimensional</td>
</tr>
<tr>
<td>BBD</td>
<td>Box-Behnken Design</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmet-Teller</td>
</tr>
<tr>
<td>c</td>
<td>cubic</td>
</tr>
<tr>
<td>FESEM-EDX</td>
<td>Field Emission Scanning Electron Microscope - Energy Dispersive X-Ray</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>h</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standard</td>
</tr>
<tr>
<td>RSM</td>
<td>Response Surface Methodology</td>
</tr>
<tr>
<td>TAN</td>
<td>Total Acid Number</td>
</tr>
<tr>
<td>TGA-DTA</td>
<td>Thermogravimetry Analysis-Differential Thermal Analysis</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature Programmed Desorption</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>NA</td>
<td>Nitrogen Adsorption</td>
</tr>
<tr>
<td>RSM</td>
<td>Response Surface Methodology</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
</tbody>
</table>
# LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Conceptual and Operational Research Framework</td>
<td>252</td>
</tr>
<tr>
<td>B</td>
<td>Calculation for catalyst preparation</td>
<td>253</td>
</tr>
<tr>
<td>C</td>
<td>Calculation for oil to methanol molar ratio</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Peaks assignment in the XRD patterns over Cu/Ni/Ca(3:7:90)/Al₂O₃ catalyst calcined at 600°C, 700°C, 800°C and 1000°C for 5 hours with two times alumina coatings</td>
<td>255</td>
</tr>
<tr>
<td>E</td>
<td>Peaks assignment in the XRD patterns of Cu/Ni/Ca/Al₂O₃ catalyst at various co-catalyst ratios to based and calcined at 700°C, for 5 hours with two times alumina coatings</td>
<td>257</td>
</tr>
<tr>
<td>F</td>
<td>Peaks assignment in the XRD patterns over Cu/Zn/Ca(3:7:90)/Al₂O₃ catalyst calcined at 700°C, 800°C, 900°C and 1000°C calcined for 5 hours with two times alumina coatings</td>
<td>258</td>
</tr>
<tr>
<td>G</td>
<td>Peaks assignment in the XRD patterns over Cu/Zn/Ca/Al₂O₃ catalyst calcined at 800°C with different co-catalyst ratio to based</td>
<td>260</td>
</tr>
<tr>
<td>H</td>
<td>Publications and Presentation</td>
<td>261</td>
</tr>
</tbody>
</table>
1.1 Biodiesel as Alternative Energy Resources

Fossil fuel was naturally produced from organic matter that decays deep in the earth over the course of millions years (Droege et al., 2002). Since the industrial development was started, a large quantity of fossil fuel was utilized to drive the economy to huge number of people (Shafiee et al., 2009). From the data analysis in global energy statistical 2017, petroleum oil is one of the most fossil fuel resources that are widely used in Malaysia especially in transportation. Thus, it is estimated that world crude oil reserves will vanish at the rate of 4 billion tons a year and it has become increasingly evident that humanity faces a number of unprecedented challenges in terms of future energy resources and consumption (Atabani et al., 2012).

On the other hand, the usage of petroleum based fossil fuel (petro diesel) may leads to the several disadvantageous. The combustion of petro diesel may releases the greenhouse gases to the environmental surrounding and contributes to the global warming. The emission from the combustion can produce nitrogen oxide (NO$_x$), sulphur oxide (SO$_x$) and aromatic particulates which harmed the human health (Zhong et al., 2017). Therefore, several researches
were conducted to solve this critical issue by searching new alternative energy resources which were technically feasible, economically competitive, environmentally acceptable, and readily available. Above all, biodiesel is one of the best renewable energy resources to substitute the petro diesel and contribute more advantageous due to environmentally benign.

Biodiesel which are derived from vegetable oil and animals fats through transesterification reaction has become one of the renewable energy resources that have similar properties as petro diesel. The reaction takes place when one mole of triglycerides (contain in vegetable oil and animal fats) reacted with 3 mole of methanol in the presence of catalyst (heterogeneous or homogeneous acid, basic or enzymatic) to produced three mole of methyl ester (biodiesel) and 1 mole of glycerol. The overall reaction is presented as in Equation 1.1.

\[
\text{Triglyceride} + 3\text{CH}_3\text{OH} \rightarrow 3\text{CH}_3\text{COOR} + \text{CH}_2\text{OH} \text{(Glycerol)}
\]

Biodiesel is a liquid fuel usually stated as B100 was in un-homogenised form. Like petroleum diesel, biodiesel was used as fuel in compression ignition engines. It has frequently used as a blend with regular diesel fuel and can be used in several diesel vehicles.
without any engine modification. The most common biodiesel blend is B20, which was the combination of 6% to 20% biodiesel blended with petroleum diesel. Meanwhile, B5 (5% biodiesel, 95% diesel) was commonly used in fleets.

There were several advantageous of using biodiesel as petro diesel substitution. For example, it can improve the fuel lubricity and raises the cetane number of the fuel. The diesel engines depend upon the lubricity of the fuel to stay moving components from wearing untimely. Besides that, the emissions from the biodiesel were better than regular diesel and produced less NOx gases. In addition, it is also easy to use and less vehicle modification or any fuelling equipment was needed. Moreover, from environmental side of view, biodiesel is helping in reducing pollution and improve health by lowering the emission of CO$_2$ thus may reduces the effect of global warming. Moreover, it is also safer to handle due to less toxic and easy to be stored compared to petro diesel.

In producing biodiesel, the feedstock was the major reactant that has to be taken into account before the transesterification reaction takes place. There were several feedstocks that have been used in order to produce high quality of biodiesel. Previous study proved that the biodiesel can be synthesize from palm oil, canola oil, sunflower oil, corn oil, rice bran oil and rapeseed oil (Canakci et al., 2008). However, the production of biodiesel from first generation vegetable oil has a limitation issues. The crisis was raised up due to the competing with arable land culture and human food supply. Due to this problem, the idea of using non edible feedstock (second
Synthesized of biodiesel from non edible feedstock or known as second generation biodiesel was becoming a new idea to solve this crucial crisis (Mardhiah et al., 2017). The biodiesel was synthesis from the whole plant matter, agricultural residue and processing waste has become the main attention among researchers. For example, there were studies that use microalgae plants as the feedstock to produce biodiesel (Chiaramonti et al., 2017). Besides that, the use of rise husk, oil palm leave, palm kernel and Jatropha Curcas was also reported to have a potential in producing a biodiesel (Karmakar et al., 2010). However, the production was not reached the industrial scale especially for commercialization due to the source limitation.

Along with that, feedstock from waste cooking oil has been generating a new idea to produce biodiesel. It was due to the large quantities of waste cooking oils and animal fats generated throughout the country (Sudhir et al., 2007). Management of oils and fats was a significant challenge due to the disposal problems which leads to the contamination of the water and land resources (Chhetry et al., 2008). Even though some of this waste cooking oil is used for soap production, a major part of it was being discharged into the environment. Therefore in this study, refined cooking oil was introduced as the feedstock to produce biodiesel and offers
significant advantages due to the reduction in environmental pollution and lowers in production cost.

1.2 Catalysts in Biodiesel Production

In transesterification reaction, the process involved both endothermic and reversible reaction. It can be carried out either in catalytic or non catalytic approach. It has been recognised that the catalyst acts by reducing the activation energy along the reaction pathway. The lower the activation barrier, the faster the reaction will takes place. Thus, the usage of catalyst was necessary in order to increase the production rate and saving the production time. In normal reaction, the catalyst was required to shift the equilibrium to the right and produce high production of biodiesel. Various catalysts were used in transesterification reaction such as heterogeneous, homogeneous and enzymatic catalyst. In addition, the catalyst can also be basic or acidic depends on the catalytic reaction and the mechanism pathway might be different (Atadashi et al., 2013)

Homogeneous catalyst was widely used especially in industrial development due to the better performance with lower FFA content in the feedstock. Large amount of FFA (>1%) in the system may neutralized the basic catalyst and leads to the formation of soap and water (Ramachandran et al., 2013). In addition, homogeneous base catalysts mainly dissolved in glycerol and alcohol after the reaction was completed. It cannot be recycled for
the following batches and the purification process with water was needed. Thus, it may leads to the waste water problem which was harmful to the environmental (Thanh et al., 2012).

Since the homogeneous catalyst leads to the several crises, thus heterogeneous catalyst was synthesis to substitute the using of homogeneous catalyst. Heterogeneous catalyst can be categorized as basic and acidic depends on the nature of the catalyst itself. In previous studies, heterogeneous catalyst such as metal oxide, zeolite and hydrotalcites catalyst was extensively used due to the ability to be separated from the final product and can be reused back in the next transesterification reaction (Kiakalaieh et al., 2013). Most of these catalysts were alkaline metal oxides supported on materials with a large surface area and have high basicity (Wittoon et al., 2014). Similar properties to homogeneous catalyst, solid base-catalysts are more active as compared to solid acid-catalysts.

In this study, the performance of bimetallic and trimetallic alumina supported basic catalyst was evaluated in transesterification of refined cooking oil to produce biodiesel. The catalyst was prepared via wetness impregnation method by incorporating the transition metal elements like copper (Cu), Nickel (Ni) and zinc (Zn) as dopant and co dopant. Meanwhile, calcium (Ca) and magnesium (Mg) was selected as the based and supported on gamma alumina. The development of this catalyst was rarely explored especially in transesterification reaction. Thus, it may become the advantage for this research to synthesis new catalyst which was lower in production cost and more environmental friendly.
1.3 **Response Surface Methodology (RSM)**

In this study, the experimental was done to determine the optimum condition of the catalyst prepared and transesterification reaction condition to produce high biodiesel production. Thus, in order to validate this optimization study, another tools was used which is called response surface methodology (RSM) analysis. RSM is defined as a collection of mathematical and statistical techniques for empirical model building. The objective is to optimize a response (output variable) which was influenced by several independent variables (input variables). An experiment is a series of tests, called runs, in which changes are made in the input variables in order to identify the reasons for changes in the output response. There are two popular experimental designs that generally applied which are the central composite design (CCD) and the Box-Behnken design (BBD). Both designs are built up from simple factorial or fractional factorial designs.

RSM had been extensively used by many researchers in a wide variety of fields for process optimization. However, there still lack of research in the study of RSM on the trimetallic catalyst in the transesterification reaction of biodiesel. Thus, in this study, RSM was applied in order to check the suitability of the technique to optimize the catalytic performance of trimetallic alumina supported catalyst reaction and the transesterification reaction condition was evaluated using BBD. The BBD was selected since it is an economical design with high efficiency and requires only three levels for each factor (the optimum conditions for each variable). It
was used in RSM and validates the optimal conditions obtained from laboratory experiments.

1.4 Problem Statement

Biodiesel was one of the renewable energy resources that gave a better substitution from the usage of petro diesel. However, there were several challenges that have been noticed in the production of biodiesel like type of feedstock, catalyst used in the biodiesel synthesis and quality of biodiesel due to the leaching effect of the metal. Thus, this limitation leads to the research to be conducted in order to find the solution for the crisis that has been faced.

As mention earlier, previous research has synthesized the biodiesel using edible oil from vegetable and animal fats which leads to the competition with food consumption for human supply. Therefore, employing refined waste feedstock or non edible oil was become the main idea to overcome this crisis. Thus, in this study refined cooking oil (refined from the used cooking oil) was selected as feedstock to produce biodiesel in the presence of heterogeneous basic catalyst. Besides it can solve the competition with food supply, it also may lower down the production cost as compared from using edible oil.
Currently, many type of heterogeneous catalysts such as monometallic alkaline earth metal oxides supported on alumina have been reported to be catalyzing in transesterification reactions. However, the monometallic based metal oxides may cause leaching effect of metal into the reaction systems and reduce the quality of the biodiesel. Besides that, the basicity of the single oxide was lower and leads to the low biodiesel production. Thus, in order to solve these issues, the bimetallic and trimetallic supported catalyst was synthesize by using calcium (Ca) and magnesium (Mg) as based and incorporated with nickel (Ni), copper (Cu) and zinc (Zn). The modification of the catalyst may reduce the leaching effect due to the strong interaction between metal oxides and increase the degree of basicity for the catalyst that leads to the increasing of biodiesel production.

On the other hand, the usage of support in synthesizing the heterogeneous catalyst was an important for the catalyst to perform at the highest potential. In previous, zeolites present severe limitations when engage with the large molecules of reactant. It has a narrow and uniform micropore size distribution due to their crystallographically defined pore system (Taguchi and Schuth, 2005). In order to overcome the existing problem, the pursuit of solid base catalyst has been recently focused on mesoporous gamma alumina supported catalyst due to very high surface area, uniformity in pore size and high thermal stability which promise great opportunity for application as catalysts and catalytic supports. Thus in this study, series of alumina supported mixed metal oxide was
synthesis and used in transesterification of refined cooking oil to produce high quality of biodiesel.

1.5 Objectives of the Study

The main goal of this research was to develop a new heterogeneous basic catalyst that can be used in transesterification reaction of refined cooking oil effectively at optimum conditions. The objectives of this research were:-

1. To synthesize the alumina supported calcium and magnesium oxides based catalysts for transesterification of refined cooking oil.
2. To screening and optimize the performance of prepared catalysts in transesterification reaction under normal reflux condition.
3. To characterize the catalysts in order to understand the chemical and physical properties of the catalysts.
4. To study the mechanistic reaction involve over potential catalysts and verified the biodiesel obtained according to American Standard Testing Material (ASTM) using potential catalyst
1.6 Scope of the Research

This research was focused on synthesis higher biodiesel production from refined cooking oil using alumina supported calcium (Ca) and magnesium (Mg) oxides based catalysts while, copper (Cu), nickel (Ni) and zinc (Zn) as dopants and co-dopants. The catalyst was prepared using nitrate salt via wetness impregnation method. After that, all the catalysts were screening in the transesterification reaction using refined cooking oil and methanol as reactant to produce methyl ester and glycerol and measured by gas chromatography-flame ionization detector (GC-FID) analysis. From the screening process, the highest potential catalyst and less potential catalyst was selected and were optimized according to the number of alumina coating, co-catalyst loading and calcination temperatures, reliability, reusability and regeneration testing. The optimum conditions over the two catalysts were validated by response surface methodology (RSM) via Box-Behnken design (BBD). It were then characterized by using various techniques in order to understand the physical properties of the catalysts such as X-ray diffraction (XRD) analysis for bulk structure, field emission scanning electron microscope-energy dispersive X-ray (FESEM-EDX) for morphology and elemental composition study, transmission electron microscopy (TEM) for particle size, nitrogen adsorption (NA) for pore texture and surface area of the catalyst. Meanwhile, thermal gravimetric analysis (TGA) was also performed to study the mass loss of the catalyst during temperature change while, the active surface components and reducibility of the catalysts were investigated using X-ray photoelectron spectroscopy.
(XPS) and CO$_2$-temperature programmed desorption (CO$_2$-TPD). Furthermore, the mechanistic study occurred in product and on the surface of the catalyst was evaluated using GC-FID and FTIR-ATR. Lastly, the biodiesel produce using the best catalyst was selected and verified to study the properties of the biodiesel according to the American Standard Testing Material (ASTM).

1.7 Significance of Study

Biodiesel can be synthesized from edible and non edible oil of vegetable and animal fats. However, in order to solve the competition with human food supply this research was conducted using refined cooking oil as feedstock which were more easily obtained and more feasible to be employed in large scale production. Besides that, the catalyst prepared for this study was categorized as heterogeneous basic catalysts which were more stable, low in production cost and can be recycled. Thus this study was significant to be conducted and the novelties of this research study could be listed as follows:

1. The development of highly basic metal oxide catalysts from transition metal (Cu, Ni and Zn) and alkaline earth metal (Ca and Mg) as based catalysts.
2. The usage of refined cooking oil as feedstock in producing biodiesel
3. The postulated mechanism deduced from the most potential catalyst.
REFERENCES


Chumuang, N. and Punsuvon, V. (2017). Response Surface Methodology for BiodieselProduction Using Calcium


Ghozatloo, A., Hajjar, Z., Niassar, M.S. and Rashidi, A.M. (2015). Application of Box Behnken Design to Optimize the


Teo, S.H., Yap, Y.H.T. and Ng, F.I. (2014). Alumina supported/unsupported mixed oxides of Ca and Mg as heterogeneous catalysts for transesterification of


Thomas J. Davison, a Chinedu Okoli, d Karen Wilson, b Adam F. Lee, b Adam Harvey, c Julia Woodford, b and Jhuma Sadhukhan. (2013). Multiscale modelling of heterogeneously catalysed transesterification reaction process: an overview. RSC Advances. 3:6226-6240.


