

**BIODIESEL PRODUCTION FROM PALM OIL USING
CaO-ZnO CATALYSTS**



Sirichai Chantara-arpornchai

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University, and Institut Français du Pétrole
2012


128014289

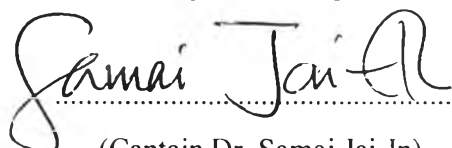
Thesis Title: Biodiesel Production from Palm Oil using CaO–ZnO Catalysts
By: Sirichai Chantara-arpornchai
Program: Petrochemical Technology
Thesis Advisors: Assoc. Prof. Apanee Luengnaruemitchai
Captain Dr. Samai Jai-In

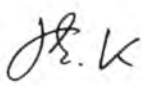
Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.



..... College Dean
(Asst. Prof. Pomthong Malakul)

Thesis Committee:


.....
(Assoc. Prof. Apanee Luengnaruemitchai)


.....
(Captain Dr. Samai Jai-In)


.....
(Dr. Sarawut Kaewtathip)


.....
(Assoc. Prof. Pramoch Rangsunvigit)

ABSTRACT

5371021063: Petrochemical Technology Program
Sirichai Chantara-arpornchai: Biodiesel Production from Palm Oil
Using CaO–ZnO Catalysts
Thesis Advisors: Assoc. Prof. Apanee Luengnaruemitchai and
Captain Dr. Samai Jai-In 97 pp.
Keywords: Transesterification/ Biodiesel/ Heterogeneous catalyst/ CaO/ ZnO

The production of biodiesel from transesterification of palm oil with methanol was studied by using CaO–ZnO prepared by incipient-wetness impregnation (IWI) and co-precipitation (CP) methods as a heterogeneous base catalyst. The optimum conditions—15:1 molar ratio of methanol to oil, a catalyst amount of 6 wt%, reaction temperature of 60 °C, and reaction time of 8 h—were suggested to obtain a biodiesel yield of 79.62 % and 78.88 % for the catalyst prepared by IWI and CP techniques (Ca:Zn atomic ratio of 1:3 and calcination temperature of 800 °C), respectively. During the three cycles of the catalyst's durability observation, the durability of the CaO–ZnO catalyst prepared by IWI technique was much better than that of catalyst prepared by CP technique because the higher amounts of CaO remaining on the IWI catalyst attributed to less CaO leaching during the reaction, evidenced by XRD results of the spent catalysts.

บทคัดย่อ

ศิริชัย จันทอรกรณ์ชัย : การผลิตไบโอดีเซลจากน้ำมันปาล์มโดยใช้แคลเซียมออกไซด์-สังกะสีออกไซด์เป็นตัวเร่งปฏิกิริยา (Biodiesel Production from Palm Oil Using CaO-ZnO Catalysts) อ. ที่ปรึกษา : รศ. ดร. อาภาณี เหลืองนฤมิตชัย และ นาวาเอก ดร. สมัย ใจอินทร์ 97 หน้า

ในงานวิจัยนี้ได้ศึกษาการผลิตไบโอดีเซลจากปฏิกิริยาทรานส์เอสเตอริฟิเคชันของน้ำมันปาล์มกับเมทานอลโดยใช้แคลเซียมออกไซด์-สังกะสีออกไซด์ (CaO-ZnO) ที่เตรียมโดยวิธี incipient-wetness impregnation (IWI) and วิธี co-precipitation (CP) เป็นตัวเร่งปฏิกิริยาแบบวิวิธพันธ์ จากผลการทดลองพบว่า อัตราส่วนโดยโมลระหว่างเมทานอลกับน้ำมันเท่ากับ 15:1 ปริมาณตัวเร่งปฏิกิริยาร้อยละ 6 โดยน้ำหนัก อุณหภูมิในการเกิดปฏิกิริยาที่ 60 องศาเซลเซียส และ เวลาที่ใช้ในการทำปฏิกิริยา 8 ชั่วโมง เป็นปัจจัยที่เหมาะสมที่ให้ผลผลิตไบโอดีเซลร้อยละ 79.62 และ 78.88 จากตัวเร่งปฏิกิริยาที่เตรียมโดยวิธี IWI และ CP ในอัตราส่วนอะตอมเท่ากับ 1:3 และ อุณหภูมิในการเผาที่ 800 องศาเซลเซียส ตามลำดับ ในระหว่าง 3 รอบของการสังเกตความทนทานของตัวเร่งปฏิกิริยาพบว่า ความทนทานของตัวเร่งปฏิกิริยา CaO-ZnO ที่เตรียมโดยวิธี IWI ดีกว่าของตัวเร่งปฏิกิริยาที่เตรียมโดยวิธี CP เพราะปริมาณของแคลเซียมออกไซด์ที่มากที่สุดที่เหลืออยู่บนตัวเร่งปฏิกิริยา IWI ประกอบกับการหลุดออกของแคลเซียมออกไซด์ที่น้อยในระหว่างการทำปฏิกิริยา ซึ่งดูได้จากผล XRD ของตัวเร่งปฏิกิริยาที่ผ่านการใช้แล้ว

ACKNOWLEDGEMENTS

This thesis work would have never been completely finished without the assistance and supporting from the following individuals and organizations:

First of all, I would like to thank The Petroleum and Petrochemical College, and The Center of Excellence on Petrochemical and Materials Technology, Thailand for funding of this thesis work.

I would like to express my sincere gratitude to Assoc. Prof. Apanee Luengnaruemitchai, my advisor, and Captain Dr. Samai Jai-In, my co-advisor, for their invaluable guidance, understanding, and constant encouragement throughout the course of this research.

I would like to express special thanks to Dr. Sarawut Kaewththip and Assoc. Prof. Pramoch Rangsunvigit for kindly serving on my thesis committee. Their sincere suggestions and comments are definitely imperative for accomplishing my thesis.

I would like to take this opportunity to thanks my senior, Pisitpong Intarapong, Natthida Numwong, Chinchanon Pojanavaraphan, and Chesta Jindavat, for their assistance and support. I also would like to give an appreciation to thanks all member and staffs of the Petroleum and Petrochemical College, Chulalongkorn University, for all their kind assistance and cooperation.

I would like to extend my thanks to all my graduate friends for their friendly cheerfulness and encouragement.

Finally, I really would like to express my sincere gratitude to my parents and my family for their support, love, understanding, and cheering.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	x
CHAPTER	
I INTRODUCTION	1
II LITERATURE REVIEW	3
III EXPERIMENTAL	19
3.1 Materials	19
3.2 Equipment	19
3.2.1 Gas Chromatograph (GC)	19
3.2.2 High Performance Liquid Chromatograph (HPLC)	19
3.2.3 Temperature-Programmed Reduction (TPR)	19
3.2.4 X-ray Diffraction (XRD)	19
3.2.5 Scanning Electron Microscopy (SEM)	19
3.2.6 Fourier Transform Infrared Spectrophotometer (FTIR)	19
3.2.7 X-ray Fluorescence (XRF) Spectrometry	19
3.2.8 Condenser	19
3.2.9 Magnetic Stirrer	19
3.2.10 Stirring Plate	19

CHAPTER	PAGE
3.2.11 Hot Plate	19
3.2.12 Thermometer	20
3.2.13 Temperature Controller	20
3.2.14 500-ml Three-necked Flask	20
3.3 Methodology	20
3.3.1 Catalyst Preparation	20
3.3.2 Transesterification of Vegetable Oil using CaO–ZnO Catalyst	21
3.4 Biodiesel Analysis	22
3.4.1 Gas Chromatograph (GC)	22
3.4.2 High Performance Liquid Chromatography (HPLC)	23
3.5 Catalyst Characterization	24
3.5.1 Fourier Transform Infrared Spectrophotometer (FT-IR)	24
3.5.2 Scanning Electron Microscope (SEM)	24
3.5.3 Temperature–Programmed Reduction Technique (TPR)	24
3.5.4 X-ray Diffraction (XRD)	24
3.5.5 X-Ray Fluorescence (XRF)	25
3.5.6 Titration Method	25
3.5.7 Hammett Indicator	25
IV RESULTS AND DISCUSSION	26
4.1 Catalyst Characterization	26
4.1.1 X-ray Fluorescence Spectroscopy (XRF)	26
4.1.2 X-ray Diffraction (XRD)	29
4.1.3 Temperature–Programmed Reduction (TPR)	37
4.1.4 Scanning Electron Microscope (SEM)	43

CHAPTER	PAGE
4.1.5 Hammett Indicator	51
4.1.6 Fourier Transform Infrared Spectrophotometer (FT-IR)	54
4.2 Transesterification Reaction	56
4.2.1 Effect of Reaction Time	56
4.2.2 Effect of Calcination Temperature	57
4.2.3 Effect of Ca:Zn atomic Ratio	59
4.2.4 Effect of Catalyst's Durability	60
V CONCLUSIONS AND RECOMMENDATIONS	63
5.1 Conclusions	63
5.2 Recommendations	63
REFERENCES	64
APPENDIX Biodiesel Analysis	68
CURRICULUM VITAE	97

LIST OF TABLES

TABLE		PAGE
2.1	Chemical composition of vegetable oils	4
2.2	Typical fatty acid composition (%) for different common oil sources	5
2.3	Technical properties of biodiesel	6
2.4	Some fuel properties of six methyl ester biodiesels	7
4.1	Chemical compositions of the fresh catalysts by using XRF measurement	27
4.2	Comparison between the chemical compositions of the fresh and spent catalysts by using XRF measurement	28
4.3	Chemical-physical properties of the CaO–ZnO fresh catalysts	35
4.4	Mean crystallite sizes of the spent CaO–ZnO catalysts	36
4.5	Summarization of basic strength, basicity, and Ca leaching of the fresh and spent catalysts	53
A1	Raw data of CaO–ZnO (1:3, CP) catalyst from HPLC	90
A2	Raw data of CaO–ZnO (1:3, IWI) catalyst from HPLC	92

LIST OF FIGURES

FIGURE		PAGE
2.1	Formation of triglyceride	3
2.2	Transesterification reaction of triglyceride with alcohol	9
2.3	The transesterification reactions of vegetable oil with alcohol to esters and glycerol	10
2.4	Mechanism of the base-catalyzed transesterification of vegetable oils	11
2.5	Saponification of fatty acid alkyl ester	12
2.6	Mechanism of the acid-catalyzed transesterification of vegetable oils	13
4.1	XRD patterns of ZnO and Ca–Zn mixed oxides catalysts with the various Ca:Zn atomic ratios: a) CP and b) IWI techniques	32
4.2	XRD patterns of Ca ₁ Zn ₃ catalysts at different calcination temperatures: a) CP and b) IWI techniques	33
4.3	XRD patterns of Ca ₁ Zn ₃ catalysts after durability testing: a) CP and b) IWI techniques	34
4.4	TPR profiles of ZnO and Ca–Zn mixed oxides with the various Ca:Zn atomic ratios: a) CP and b) IWI techniques	39
4.5	TPR profiles of Ca ₁ Zn ₃ catalysts with different calcination temperatures: a) CP and b) IWI techniques	42
4.6	SEM images of ZnO and Ca–Zn mixed oxides catalysts with various Ca:Zn atomic ratios	43
4.7	SEM images of CaO–ZnO (Ca:Zn = 1:3) catalysts with various calcination temperatures	48
4.8	FTIR spectra of the spent Ca ₁ Zn ₃ catalysts after durability testing: a) CP and b) IWI techniques	55

FIGURE	PAGE
4.9 Effect of reaction time on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 1:3 atomic ratio of Ca:Zn, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed	57
4.10 Effect of calcination temperature on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 8 h of reaction time, 1:3 atomic ratio of Ca:Zn, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed	59
4.11 Effect of Ca:Zn atomic ratio on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 8 h of reaction time, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed	60
4.12 Durability of the CaO–ZnO catalysts on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 8 h of reaction time, 1:3 atomic ratio of Ca:Zn, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed	61
A.1 Methyl ester content of biodiesel from CaO–ZnO (1:3;CP:calcined 600 °C) catalyst	68
A.2 Methyl ester content of biodiesel from CaO–ZnO (1:3;CP:calcined 800 °C:8h) catalyst	69
A.3 Methyl ester content of biodiesel from CaO–ZnO (1:3;CP:calcined 900 °C) catalyst	70
A.4 Methyl ester content of biodiesel from CaO–ZnO (1:3;CP:calcined 800 °C:2h) catalyst	71
A.5 Methyl ester content of biodiesel from CaO–ZnO (1:3;CP:calcined 800 °C:4h) catalyst	72

FIGURE	PAGE
A.6 Methyl ester content of biodiesel from CaO–ZnO (1:3:CP:calcined 800 °C:12h) catalyst	73
A.7 Methyl ester content of biodiesel from CaO–ZnO (1:5:CP:calcined 800 °C) catalyst	74
A.8 Methyl ester content of biodiesel from CaO–ZnO (1:1;CP:calcined 800 °C) catalyst	75
A.9 Methyl ester content of biodiesel from CaO–ZnO (1:3;IWI:calcined 600 °C) catalyst	76
A.10 Methyl ester content of biodiesel from CaO–ZnO (1:3:IWI:calcined 800 °C:8h) catalyst	77
A.11 Methyl ester content of biodiesel from CaO–ZnO (1:3;IWI:calcined 900 °C) catalyst	78
A.12 Methyl ester content of biodiesel from CaO–ZnO (1:3:IWI:calcined 800 °C:2h) catalyst	79
A.13 Methyl ester content of biodiesel from CaO–ZnO (1:3:IWI:calcined 800 °C:4h) catalyst	80
A.14 Methyl ester content of biodiesel from CaO–ZnO (1:3:IWI:calcined 800 °C:12h) catalyst	81
A.15 Methyl ester content of biodiesel from CaO–ZnO (1:5:IWI:calcined 800 °C) catalyst	82
A.16 Methyl ester content of biodiesel from CaO–ZnO (1:1:IWI:calcined 800 °C) catalyst	83
A.17 Methyl ester content of biodiesel from CaO–ZnO (3:1:IWI:calcined 800 °C) catalyst	84
A.18 Methyl ester content of biodiesel from CaO–ZnO (1:3;CP:spent 1) catalyst	85
A.19 Methyl ester content of biodiesel from CaO–ZnO (1:3;CP:spent 2) catalyst	86

FIGURE	PAGE
A.20 Methyl ester content of biodiesel from CaO–ZnO (1:3;IWI:spent 1) catalyst	87
A.21 Methyl ester content of biodiesel from CaO–ZnO (1:3;IWI:spent 2) catalyst	88
A.22 The chromatogram of CaO–ZnO (1:3, CP) catalyst from High Performance Liquid Chromatography (HPLC)	89
A.23 The chromatogram of CaO–ZnO (1:3, IWI) from High Performance Liquid Chromatography (HPLC)	91