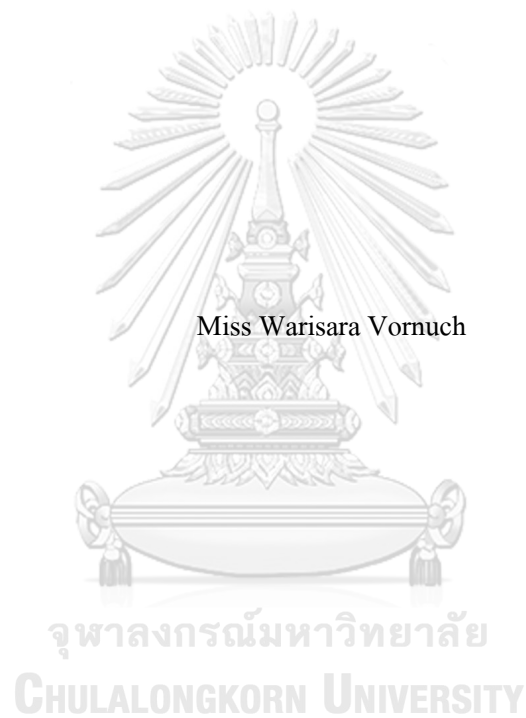


Pelletization of CaO catalyst for biodiesel production via transesterification of palm oil



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering

Department of Chemical Engineering

FACULTY OF ENGINEERING

Chulalongkorn University

Academic Year 2020

Copyright of Chulalongkorn University

การขึ้นเม็ดตัวเร่งปฏิกิริยาเคลือบออกไซด์สำหรับการผลิตไบโอดีเซลผ่านทรานส์เอสเทอริฟิเคชันของน้ำมันปาล์ม



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2563
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

Thesis Title Pelletization of CaO catalyst for biodiesel production via transesterification of palm oil
By Miss Warisara Vornuch
Field of Study Chemical Engineering
Thesis Advisor Professor SUTTICHAJ ASSABUMRUNGRAT, Ph.D.
Thesis Co Advisor Assistant Professor Kanokwan Ngaosuwan, Ph.D.

Accepted by the FACULTY OF ENGINEERING, Chulalongkorn University in Partial Fulfillment of the Requirement for the Master of Engineering

..... Dean of the FACULTY OF
ENGINEERING
(Professor SUPOT TEACHAVORASINSKUN, Ph.D.)

THESIS COMMITTEE

..... Chairman
(Akawat Sirisuk, Ph.D.)

..... Thesis Advisor
(Professor SUTTICHAJ ASSABUMRUNGRAT, Ph.D.)

..... Thesis Co-Advisor
(Assistant Professor Kanokwan Ngaosuwan, Ph.D.)

..... Examiner
(Assistant Professor Palang Bumroongsakulsawat, Ph.D.)

..... External Examiner
(Weerinda Appamana, Ph.D.)

วริศรา วรบุษ : การขึ้นเม็ดตัวเร่งปฏิกิริยาแคลเซียมออกไซด์สำหรับการผลิตไบโอดีเซลผ่านทรานส์เอสเทอร์ิฟิเคชันของน้ำมันปาล์ม. (Pelletization of CaO catalyst for biodiesel production via transesterification of palm oil) อ.ที่ปรึกษาหลัก : ศ. ดร.สุทธิชัย อัสสะบำรุงรัตน์, Ph.D, อ.ที่ปรึกษาร่วม : ผศ. ดร.กนกวรรณ ง้าวสุวรรณ

งานวิจัยนี้ศึกษาการผลิตไบโอดีเซลจากน้ำมันปาล์มโดยการทำปฏิกิริยาทรานส์เอสเทอร์ิฟิเคชันด้วยตัวเร่งปฏิกิริยา CaO ที่อัดขึ้นรูป โดยศึกษาตัวแปรที่เกี่ยวข้องกับการขึ้นเม็ดตัวเร่งปฏิกิริยา CaO ได้แก่ 1) ประเภทของสารยึดเกาะ ได้แก่ อะลูมินา ไดอะตอมไมท์และดินขาว 2) ผลของการเผาที่อุณหภูมิ 700, 800 และ 900°C 3) อัตราส่วนโดยมวลของ CaO ต่อสารยึดเกาะ เป็น 1: 1, 3: 1 และ 6: 1 นอกจากนี้ยังศึกษาเกี่ยวกับรูปร่างของตัวเร่งปฏิกิริยา CaO ที่อัดขึ้นรูป และการเพิ่มสารสร้างรูพรุน (พอลิอะคริลาไมด์) ที่มีผลต่อความว่องไวในการทำปฏิกิริยาผ่านปฏิกิริยาทรานส์เอสเทอร์ิฟิเคชัน อัตราส่วนของเมทานอลต่อน้ำมันปาล์มที่ 12 ต่อ 1 โหลดตัวเร่งปฏิกิริยา 10 wt% อุณหภูมิของปฏิกิริยาอยู่ที่ 65°C เวลาในการทำปฏิกิริยา 6 ชั่วโมงโดยใช้ความเร็วรอบในการกวน 600 รอบต่อนาที พบว่าการขึ้นรูปตัวเร่งปฏิกิริยา CaO แบบทรงกระบอกเส้นขนาดเส้นผ่านศูนย์กลาง 6 mm และ ยาว 1.5 mm จะให้ผลได้ไบโอดีเซลสูงกว่าแบบทรงกลมและทรงกระบอกยาวที่มีพื้นที่ผิวเท่ากัน นอกจากนี้ยังมีการใช้พอลิอะคริลาไมด์เป็นสารสร้างรูพรุนสามารถเพิ่มพื้นที่ผิวและปริมาตรรูพรุนในระหว่างการเผาซึ่งสามารถให้ผลผลิตไบโอดีเซลที่สูงขึ้นได้เท่ากับ 73.63%

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

สาขาวิชา วิศวกรรมเคมี

ปีการศึกษา 2563

ลายมือชื่อนิสิต

ลายมือชื่อ อ.ที่ปรึกษาหลัก

ลายมือชื่อ อ.ที่ปรึกษาร่วม

6170401221 : MAJOR CHEMICAL ENGINEERING

KEYWORD: Biodiesel; Transesterification; The extruded CaO catalyst

Warisara Vornuch : Pelletization of CaO catalyst for biodiesel production via transesterification of palm oil . Advisor: Prof. SUTTICHAJ ASSABUMRUNGRAT, Ph.D. Co-advisor: Asst. Prof. Kanokwan Ngaosuwan, Ph.D.

This thesis investigates biodiesel production from palm oil by transesterification using extruded CaO catalysts. The preparation parameters of extruded CaO catalysts were investigated including 1) binder type including activated alumina, diatomite and kaolin, 2) calcination temperature at 700, 800 and 900°C, 3) mass ratio of CaO to the binder at 1: 1, 3: 1 and 6: 1. The Effect of catalyst shape of the extruded CaO and the addition of pore forming (polyacrylamide) on the catalytic activity of extruded CaO were also studied using transesterification using methanol to palm oil. The ratio of methanol to palm oil was fixed at 12 to 1, 10 wt% catalyst loading, the reaction temperature of 65 °C, for 6 h at a stirring speed 600 rpm. The extruded CaO catalyst with a short cylindrical shape with a dimension of 6 mm in diameter and 1.5 in long offered the high biodiesel yield as compared to spherical and long cylindrical shape based on the similar surface area. In addition, using polyacrylamide as a pore forming agent can increase the surface area and pore volume during calcination which can provide the higher biodiesel yield.

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

Field of Study: Chemical Engineering

Academic Year: 2020

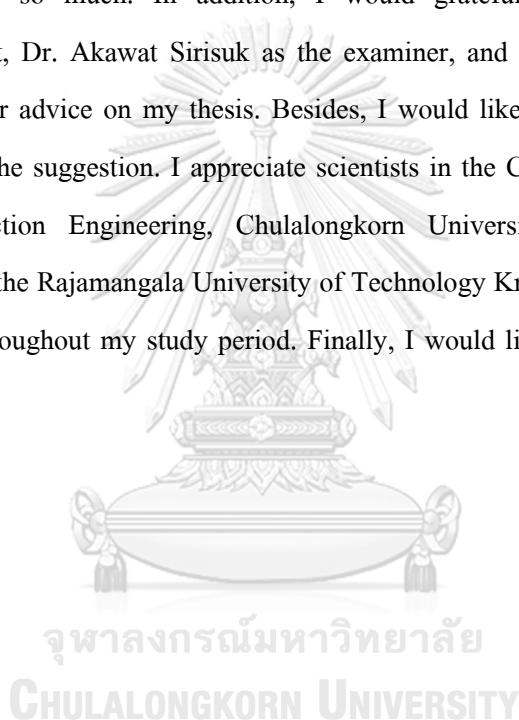
Student's Signature

Advisor's Signature

Co-advisor's Signature

ACKNOWLEDGEMENTS

Firstly, this research was supported by the "Research Chair Grant" National Science and Technology Development Agency (NSTDA). I would like to express appreciation to my advisor, Professor Dr. Suttichai Assabumrungrat, for supporting, advising, sharing a skill, and encouragement extended to me. Also, I wish to express my sincere thanks to Asst. Prof. Kanokwan Ngaosuwan, my co-advisor, for her kind suggestions on my thesis and very patiently correcting my writing. Thank you so much. In addition, I would grateful to thank Asst. Prof. Palang Bumroongsakulsawat, Dr. Akawat Sirisuk as the examiner, and Dr. Weerinda Appamana as the external examiner for advice on my thesis. Besides, I would like to thank all the teachers in the biodiesel group for the suggestion. I appreciate scientists in the Center of Excellence in Catalysis and Catalytic Reaction Engineering, Chulalongkorn University for material analysis and characterization and the Rajamangala University of Technology Krungthep very much for chemical engineering tools throughout my study period. Finally, I would like to thank my family; they are part of my success.



Warisara Vornuch

TABLE OF CONTENTS

	Page
ABSTRACT (THAI)	iii
ABSTRACT (ENGLISH).....	iv
ACKNOWLEDGEMENTS.....	v
TABLE OF CONTENTS.....	vi
LIST OF TABLES	1
LIST OF FIGURES	2
Chapter 1 Introduction	5
1.1 Background	5
1.2 Objectives.....	6
1.3 Scopes of the research.....	6
1.4 The expected benefits.....	7
1.5 Research methodology.....	8
Chapter 2.....	10
Theory and literature review.....	10
2.1 Calcium oxide (CaO)	10
2.2 Biodiesel.....	10
2.3 Biodiesel types	12
2.3.1 Direct use of vegetable oil or oil from animal fats	12
2.3.2 Hybrid biodiesel.....	12
2.3.3 Ester biodiesel.....	12
2.4 Transesterification.....	12

2.5 Catalyst for transesterification	13
2.6 Extrusion	18
2.7 Catalyst shapes	19
2.8 Mass transfer for heterogeneous catalysis.....	22
2.9 Palm oil	24
Chapter 3 Experimental	26
3.1 Chemicals.....	26
3.2 Preparation of extruded CaO catalyst	27
3.2.1 Cylindrical catalyst pellet	27
3.2.2 Spherical catalyst pellet	28
3.2.3 Addition of pore forming.....	28
3.3 Reaction procedure.....	28
3.4 Catalyst characterizations.....	29
3.4.1 Thermogravimetric analysis/differential scanning calorimeter (TGA/DSC)	29
3.4.2 X-ray diffraction (XRD).....	29
3.4.3 Fourier-transform infrared spectroscopy (FTIR).....	29
3.4.4 Scanning electron microscope and energy dispersive X-ray spectrometer (SEM/EDX)	30
3.4.5 N ₂ adsorption–desorption isotherms	30
3.4.6 Hammett indicator method	30
3.4.7 Mechanical strength.....	30
3.4.8 FAME product analysis using gas chromatography according to EN 14103 standard.....	31
Chapter 4 Results and discussion.....	33

4.1 Catalyst characterizations of the extruded CaO catalysts	33
4.1.1 Thermogravimetric analysis/differential scanning calorimeter (TGA/DSC)	33
4.1.2 X-ray diffraction (XRD)	36
4.1.3 Fourier-transform infrared spectroscopy (FTIR)	39
4.1.4 Surface morphology of the extruded CaO using scanning electron microscope and energy dispersive X-ray spectrometer (SEM/EDX)	40
4.1.5 Mechanical strength of the extruded CaO catalysts with the different shapes	41
4.1.6 N ₂ adsorption–desorption isotherms	43
4.1.7 Hammett indicator method	49
4.2 Catalytic activity of the extruded CaO catalysts via transesterification of palm oil	51
4.2.1 Effect of different binders of the extruded CaO catalysts on the catalytic activity of transesterification	51
4.2.2 Effect of calcination temperatures of the extruded CaO using Al ₂ O ₃ as a binder on the catalytic activity of transesterification	52
4.2.3 Effect of mass ratio of CaO: Al ₂ O ₃ binder on the catalytic activity of the extruded CaO via transesterification	54
4.2.4 Effect of different shapes on the catalytic activity of the extruded CaO catalysts via transesterification	55
4.2.5 Effect of pore forming agent concentration on the catalytic activity of the extruded CaO catalysts via transesterification	56
4.2.6 Reusability, regeneration and leaching test for CaO-A(800) catalyzed transesterification	58
4.2.7 Catalytic activity of the extruded CaO catalysts in a basket reactor using different stirrer speeds	61
Chapter 5 Conclusion and recommendations	64

5.1 Conclusion.....	64
5.2 Recommendations.....	65
REFERENCES	66
Appendix A.....	74
Calculation for catalyst preparation	74
Appendix B	75
Experimental setup of conventional mechanical stirred and basket reactor	75
Appendix C	77
Calculation the mass of oil, methanol and the extruded CaO catalyst.....	77
Appendix D.....	78
Determination of crystallite size of CaO CaCO ₃ and CaSiO ₃	78
Appendix E	80
Hammet indicator method.....	80
VITA	82

LIST OF TABLES

Table 2.1 ASTM standard for pure biodiesel (100%) ^a [13]	11
Table 2.2 Summary of the previous works presented in literatures.	18
Table 2.3 Different catalysts pillarization from previous researches.....	22
Table 2.4 Fatty acids content of palm oil (present as triglyceride esters).....	25
Table 3.1 Specification of chemicals used in this research.....	27
Table 3.2 Conditions for determination of free fatty acid content by gas chromatography.....	32
Table 4.1 Crystallite sizes of the extruded CaO using different binders and different temperatures.	37
Table 4.2 Mechanical strength of the extruded CaO catalyst using Al ₂ O ₃ as a binder.	42
Table 4.3 BET surface area, pore volume and pore diameter for the extruded CaO catalysts	44
Table 4.4 Basic strength and basicity of extruded CaO catalyst.....	49
Table D.1 Crystallite size of CaO CaCO ₃ , Ca(OH) ₂ and CaSiO ₃	79

LIST OF FIGURES

Figure 2.1 Transesterification of triglyceride [15].....	13
Figure 2.2 Three consecutive steps of transesterification [16]	13
Figure 2.3 Various catalyst shapes using the industrial [29]	20
Figure 2.4 Hierarchical structure of catalyst in a fixed-bed reactor [31].....	23
Figure 2.5 Effectiveness factor (η) as a function of Thiele modulus (Φ) [31]	24
Figure 4.1 Thermogravimetric analysis (TGA-DSC) of the mixture of CaCO_3 and different binders (a) CaO-A, CaO-D, CaO-K and (b) addition of pore forming agent (CaO-A-P-1, 3, 5%).....	35
Figure 4.2 X-ray diffraction patterns of the extruded CaO catalysts (a) CaO-A(700), (b) CaO-A(800) and (c) CaO-A(900).....	36
Figure 4.3 X-ray diffraction patterns of the extruded CaO catalysts (a) CaO-A(800), (b) CaO-A(900), (c) CaO-D(800) (d) CaO-D(900), (e) CaO-K(800) and (f) CaO-K(900).....	36
Figure 4.4 FTIR spectra of the extruded CaO catalysts at different calcination temperature (a) CaO-A(700), (b) CaO-A(800), (c) CaO-A(900), (d) CaO-D(800) and (e) CaO-K(800)	39
Figure 4.5 SEM/EDX images of the extruded CaO catalysts at different calcination temperatures and binders (a) CaO-A(700), (b) CaO-A(800), (c) CaO-A(900), (d) CaO-D(800) and (e) CaO K(800).....	39
Figure 4.6 Extruded CaO catalyst pellets with different shapes (a) short cylindrical (SCY), (b) long cylindrical shapes (LCY) and (c) spherical shape (SHL)	42
Figure 4.7 Adsorption/desorption isotherms of (a) CaO-A(800) 3: 1, (b) CaO-D(800) 3: 1, (c) CaO-K(800) 3: 1, (d) CaO-A(800) 3.5: 1 and (e) CaO-A(800)-P-3%.....	47
Figure 4.8 Pore size distribution curves of mesoporous CaO-A(800) 3: 1, CaO-D(800) 3: 1, CaO-K(800) 3: 1, CaO-A(800) 3.5: 1, CaO-A(800)-P-1%, CaO-A(800)-P-3% and CaO-A(800)-P-5%	47

- Figure 4.9** Catalytic activity of the CaO-A, CaO-D and CaO-K catalysts for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1, and catalyst loading 10 wt%.....51
- Figure 4.10** Catalytic activity of the CaO-A catalysts using different calcination temperatures (700, 800 and 900°C) for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt%.52
- Figure 4.11** Catalytic activity of the CaO-D catalysts using different calcination temperatures (700, 800 and 900°C) for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt%.53
- Figure 4.12** Catalytic activity of CaO-A using different mass ratio of CaO to Al₂O₃ at 1: 1, 3: 1, 3.5: 1 and 6: 1 via transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt%.54
- Figure 4.13** Catalytic activity of different shapes of the extruded CaO-A(800) for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt%.55
- Figure 4.14** Catalytic activity of the extruded CaO-A(800) catalysts using various pore forming concentration (1, 3 and 5%) for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt%.57
- Figure 4.15** Reusability test of the extruded CaO-A(800) catalyzed transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt%.....58
- Figure 4.16** Regeneration and leaching of the extruded CaO-A catalysts calcination temperatures 800°C for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 catalyst loading 10 wt%.60
- Figure 4.17** Catalytic activity of the extruded CaO catalysts for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt% in a basket reactor using different stirrer speed (500, 600 and 700 rpm).....61

Figure B.1 Setup of conventional mechanical stirred reactor	75
Figure B.2 Setup of basket reactor	76
Figure E.1 Basic strength of extruded CaO-A(800) catalyst	80



Chapter 1

Introduction

1.1 Background

Diesel is a fuel which is extensively used in transportation, industry and agriculture. However, the diesel fuel is derived from petroleum which is non-renewable and its combustion can cause the global warming [1]. Biodiesel, as a bio-fuel, is produced to replace diesel due to its similar fuel properties. It is an environmentally-friendly which is produced from renewable resources. The renewable resource is defined that it can be used repeatedly and does not run out because it is naturally replaced. Moreover, it has an endless supply such as solar energy, wind energy, and geothermal pressure as well as biomass resources which is mainly composed of carbon based as derived such as vegetable oil [2]. There are many advantages in terms of cleanliness of the exhaust gas, non-toxicity, good lubrication property and biodegradability [3]. Biodiesel, in a form of fatty acid methyl esters (FAMES), can be produced via transesterification of vegetable oil such as soybean, sun flower and palm oils with methanol. The theoretical ratio of methanol to oil is 3 to 1. In practice, it requires the excess ratio of methanol to oil more than 3 (usually 6 to 24) to achieve the complete reaction [4]. Homogeneous base catalysts such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) are conventional catalysts for the transesterification to produce biodiesel. Although the homogeneous catalyst provides a high reaction rate under mild conditions, the production process discharges a large amount of wastewater resulting in environmental impact. Heterogeneous catalyst has gained more attention to catalyze biodiesel forming reaction because this catalyst can provide the cleaner process in terms of its reusability, environmental friendliness, easy separation from the product and generation of less wastewater [5]. Nowadays, the most well-known catalyst for transesterification of vegetable oil or waste cooking oil is calcium oxide (CaO) because of its low cost and high catalytic activity compared to other metal oxide catalysts [6]. However, using this CaO as received in the powder form might not be suitable for the continuous process due to mass transfer limitation and pressure drop across flow reactor [7]. Generally, CaO catalyst can be obtained from natural source which is mainly composed of CaCO_3 . The calcination process is required for conversion of CaCO_3 to CaO catalyst which is usually used at high temperature (such as 700 to 900°C) for 5 h under static air. Based on the operating condition and maintenance for the

biodiesel in the continuous processes the extruded catalysts become more interesting such as the extruded CaO and K_2CO_3 [8]. CaO was mixed with binder and viscosity modifiers (silica sol) for extrusion in the cylindrical shape. This extruded CaO was used as a catalyst for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate reaction. It was found that this extruded CaO catalyst provided high stability with the glycerol conversion of 65.47% for the 5th cycle [9]. In addition, Jindapon et al. [10] prepared the extruded Ca, Zn and Al mixed CaO catalysts using hydroxyethylcellulose (HEC) as plasticizer in a cylindrical shape for biodiesel production in a fixed-bed reactor. The FAME yield was 96.5% when using the large methanol to oil molar ratio of 30 to 1. Euripedes et al. [11] synthesized the extruded K_2CO_3 in hollow cylindrical shape using alumina (Al_2O_3) and water as binders. This extruded K_2CO_3 provided a high oil conversion of 99.3% while high reaction temperature of 80°C was operated.

This work, therefore, synthesized the extruded CaO catalysts by varying various parameters such as binder type, calcination temperature, binder ratio and pore forming agent on their catalytic activities via transesterification of palm oil at mild reaction condition in a batch reactor.

1.2 Objectives

1.2.1 To pelletize CaO catalyst using various parameters and determine its characteristics.

1.2.2 To study the effect of various palletization parameters of the extruded CaO catalysts on their catalytic activities of transesterification of palm oil including.

- Binder type including activated alumina, diatomite and kaolin
- Calcination temperatures at 700, 800 and 900°C
- Mass ratio of CaO: binder of 1: 1, 3: 1 and 6: 1
- Shape of the extruded CaO catalyst such as short cylindrical, long cylindrical and spherical shapes.
- Addition of pore forming (polyacrylamide) with concentration of 1, 3 and 5 wt%

1.3 Scopes of the research

The synthesis of CaO/binder catalyst as cylindrical pellet forms was carried out by physical mixing of CaO catalyst and binder. Then, its paste was extruded by a syringe while the

spherical pellet forms were prepared based on the same method but the paste was extruded by a JP table-type herbal coating herbal pellet making machine with diameter of 6 mm. The extruded CaO catalysts were characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscope/energy dispersive X-ray spectrometer (SEM/EDX), N₂ adsorption-desorption, basicity and mechanical strength properties.

Transesterification of palm oil was performed in a batch reactor using methanol to palm oil molar ratio of 12 to 1, catalyst loading of 10 wt%, stirring speed of 600 rpm at atmospheric pressure and 65°C for 6 h to investigate their catalytic activities of these extruded CaO catalyst including the lists of synthesis parameter below;

- Three parameters of binder types using activated alumina, diatomite and kaolin, calcination temperature of 700, 800 and 900°C and the mass ratios of CaO to binder as 1: 1, 3: 1 and 6: 1 were investigated by using experimental design.

- Shapes of the extruded CaO catalyst are short cylindrical, long cylindrical and spherical shape using the suitable binder, calcination temperature and shape obtained from the above mentioned.

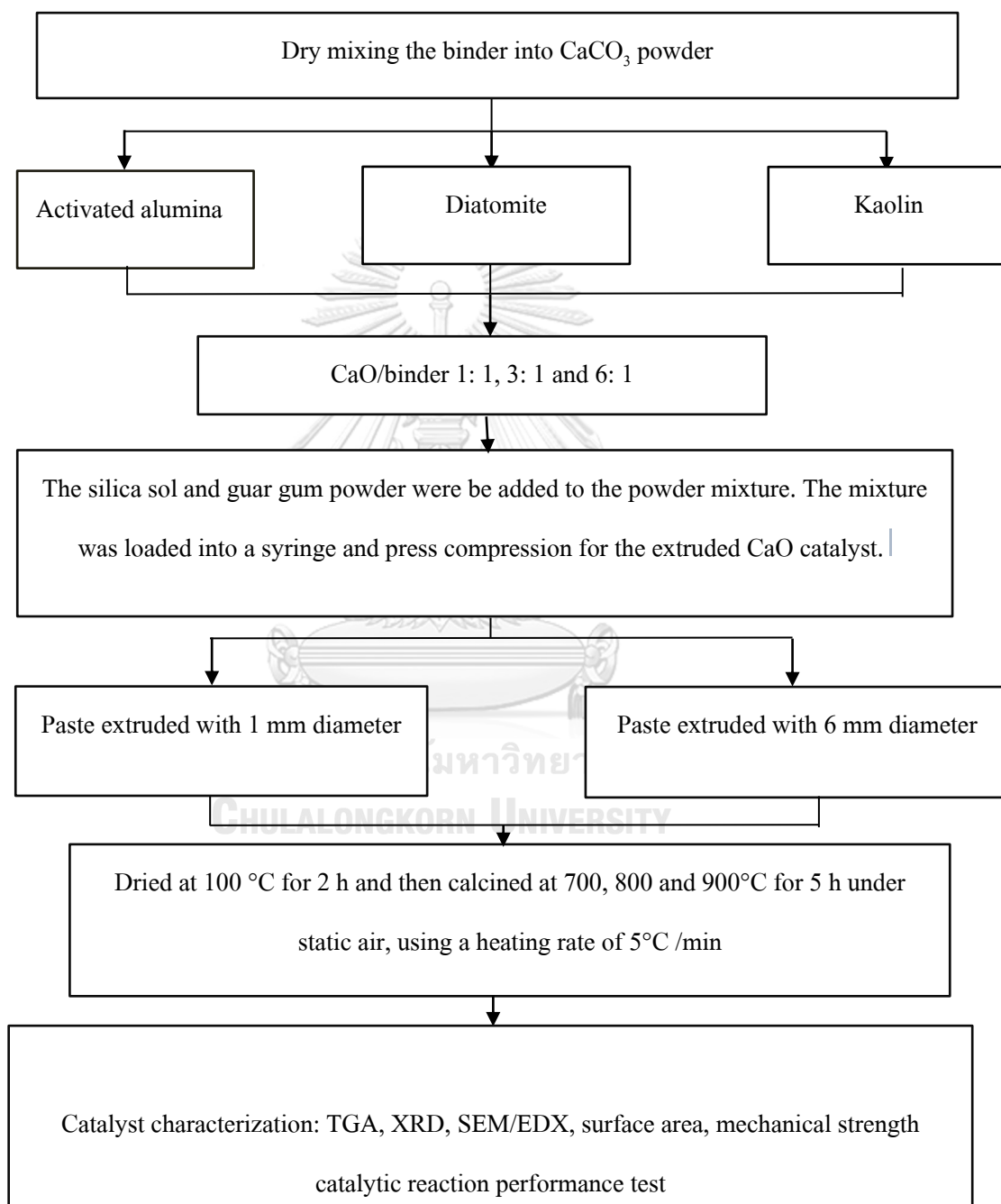
- Pore forming and its concentration using polyacrylamide with concentration of 1, 3, 5 wt% using the suitable binder, calcination temperature and shape obtained from the above mentioned.

1.4 The expected benefits

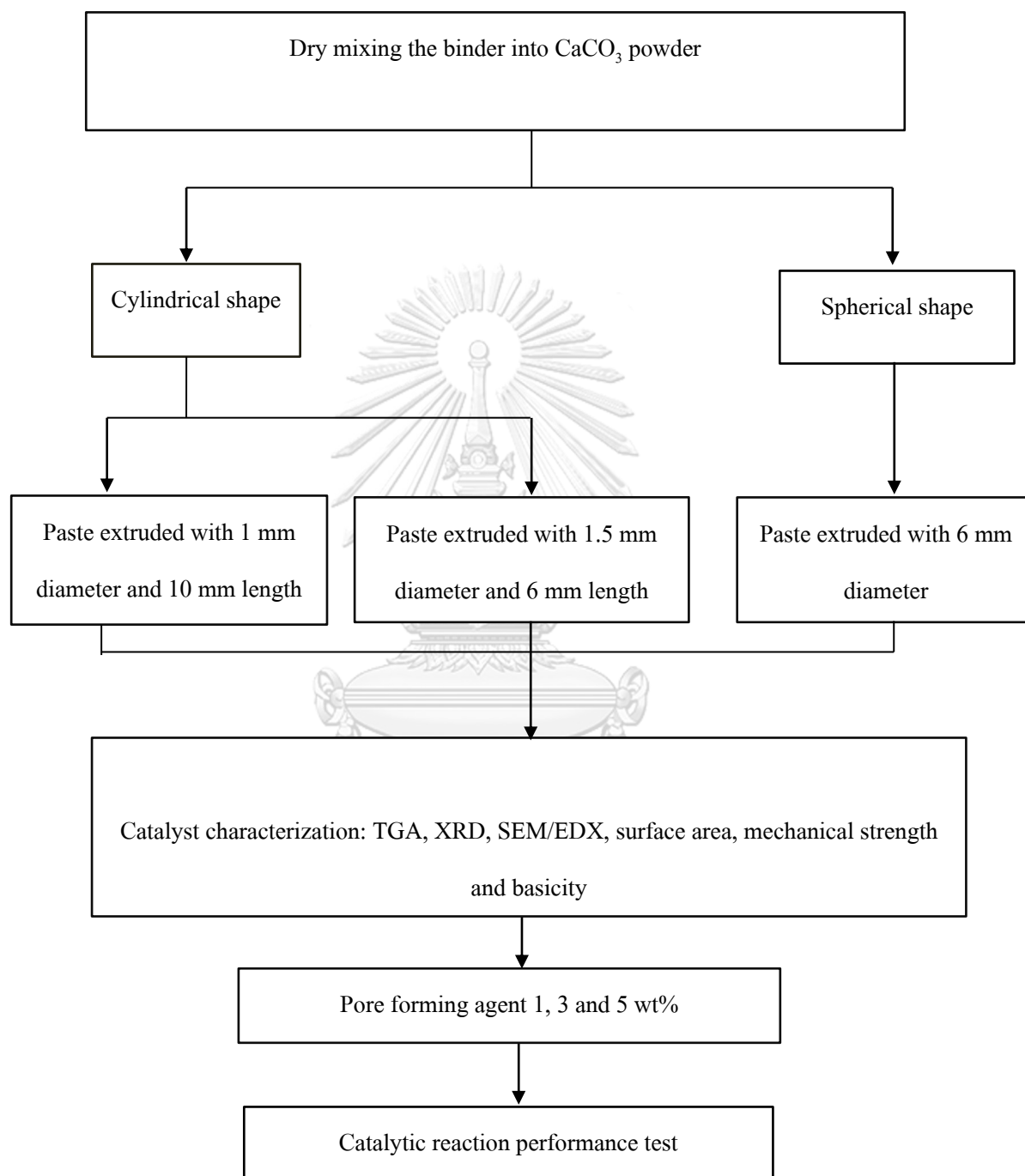
The palletized CaO catalyst could be further used in a continuous reactor to produce biodiesel

1.5 Research methodology

Part I. Effect of binder type, binder ratio and calcination temperature using experimental design.



Part II. Investigation of catalyst shapes including cylindrical and spherical shape and pore forming agent with optimal preparation method.



Chapter 2

Theory and literature review

2.1 Calcium oxide (CaO)

Calcium oxide (CaO) is a solid base catalyst being a candidate catalyst for transesterification to produce biodiesel. A major source of calcium oxide is calcium carbonate or limestone (CaCO_3) calcined in a furnace at a high temperature according to Equation (2.1). CaO has the advantages of good availability and cheap cost. Moreover, CaO can be prepared from the waste matters consisting of calcium carbonate, such as eggshells, mollusk shells and the other fishery wastes. The use of the waste matters is not only effective in enhancing the cost advantage of CaO catalysts but also related to recycling of the natural mineral resources [6].



In addition, the preparation CaO catalyst can be derived from calcium carbonate, hydroxide, acetate, nitrate and oxalate. Calcium carbonate is the major source of CaO used in a variety of industrial field while calcium hydroxide is proper for the preparation of high purity of CaO. Calcium acetate and calcium nitrate are convenient for preparing the supported CaO catalyst, due to their large solubility in water. Among these calcium salts, the calcination temperature required for maximizing the catalytic activity of the prepared CaO is in the order of using nitrate (600°C) < hydroxide (700°C) < acetate and oxalate (800°C) < carbonate (900°C) calcium precursor. However, the most active CaO catalyst is prepared from the hydroxide source having a large surface area. Among calcium carbonate, calcium acetate and calcium oxalate, there is no appreciable difference in the catalytic potentiality [12].

2.2 Biodiesel

An alternative fuel that can be used to replace diesel is biodiesel, which is produced from renewable natural resources such as vegetable oil, animal fat, and algae oil or used waste cooking oil (WCO). The advantages of biodiesel are its cleanliness of the exhaust gas, non-toxicity, good

lubrication property, biodegradability and fuel properties like petroleum diesel. Biodiesel is produced by allowing the oil to react with small molecules of alcohol (methanol or ethanol) using potassium hydroxide (KOH) or sodium hydroxide (NaOH) as a catalyst. This reaction is occurred to produce ester substance known as methyl esters or ethyl ester (depending on the type of alcohol used) and this reaction is called transesterification. When the chemical process is complete, biodiesel and glycerol are products [10].The physical and chemical properties of biodiesel following ASTM standard are included in Table 2.1.

Table 2.1 ASTM standard for pure biodiesel (100%)^a [13]

Property	ASTM method	Limits	Units
Flash point	93	100.0 min	°C
Water	1796	0.050 max	vol%
Carbon residue, 100% sample	4530 ^b	0.050 max	wt%
Sulfated ash	874	0.020 max	wt%
Kinematic viscosity, 40°C	445	1.9–6.0	mm ² /s
Sulfur	2622	0.050 max	wt%
Cetane	613	40 min	
Cloud point	2500	By customer	°C
Copper strip corrosion	130	No. 3b max	
Acid number	644	0.80 max	mg KOH/g
Free glycerol	GC ^c	0.20 max	wt%
Total glycerol	GC ^c	0.40 max	wt%

^aThis specification is the process of being evaluated by ASTM.

^bOr equivalent ASTM testing method.

^cAustrian (Christina Plank) update of USDA test method.

2.3 Biodiesel types

Biodiesel can be divided into 3 types as follows:

2.3.1 Direct use of vegetable oil or oil from animal fats

This type of biodiesel is directly used oil such as coconut oil, palm oil, peanut oil, soybean oil or oil from animal fats, such as lard, which can be used on diesel engines without having to mix or add other chemicals. This should be remarked that oil properties do not change or improve.

2.3.2 Hybrid biodiesel

This type of biodiesel is a mixture of vegetable oil or oil from animal fats and kerosene, diesel oil. Therefore, this biodiesel has some properties similar to diesel fuel.

2.3.3 Ester biodiesel

This type of biodiesel has a more complicated process. It is mostly produced through a chemical process via transesterification. Biodiesel has the same properties as diesel fuel and provides cleaner combustion. The quality of the exhaust gas is better than diesel because the oxygen in molecule helps in combustion and hence causes less carbon monoxide. In addition, biodiesel contains no sulfur as a component, resulting in reduced sulfur oxides emission problem. In addition, it has less carbon soot, which does not cause clogging of the exhaust system and can help extend engine life [14].

2.4 Transesterification

Transesterification is a reaction between triglycerides as the main component of oil or fat and low molecular alcohol (methanol or ethanol) using base or acid catalysts. In general, alcohol used for transesterification is preferred to be methanol (CH_3OH) because it is cheaper, has a shortest molecular structure which quickly reacts with oils or fats. When the transesterification completes, the desired products (biodiesel) must be separated based on the different density, allowing to obtain the glycerol as a bottom layer of the reaction mixture. The crude glycerol obtained from transesterification can be further purified to add value of the process using as raw materials for cosmetics and the pharmaceutical industry. The overall reaction is shown in Figure 2.1.

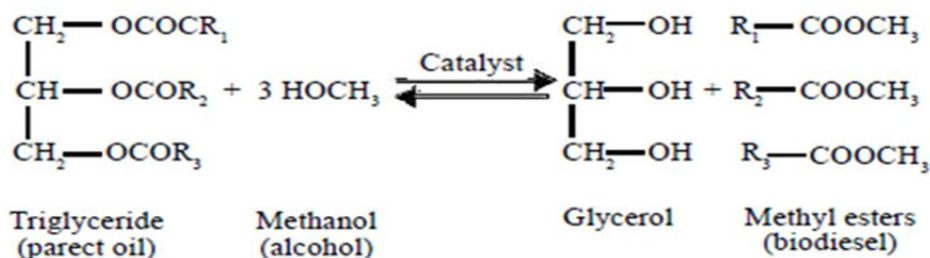


Figure 2.1 Transesterification of triglyceride [15]

Transesterification is a reversible reaction consisting of a 3 consecutive steps including conversion of triglyceride (TG) to diglyceride (DG) and biodiesel ($\text{R}'\text{COOR}_1$) and DG can be further converted to monoglyceride (MG) and biodiesel ($\text{R}'\text{COOR}_2$). Finally, MG is reacted with methanol (ROH) and converted to glycerol (GL) and biodiesel ($\text{R}'\text{COOR}_3$) as shown in Figure 2.2.

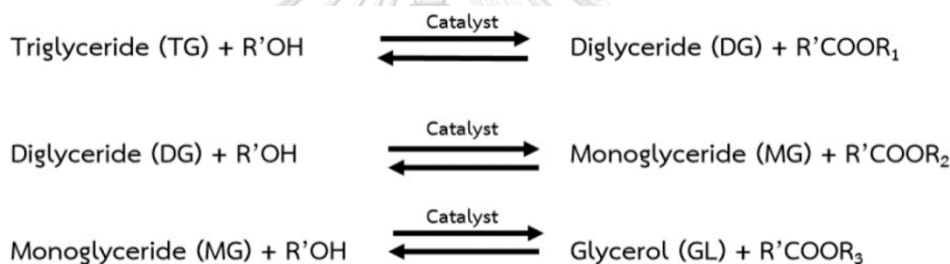


Figure 2.2 Three consecutive steps of transesterification [16]

2.5 Catalyst for transesterification

Transesterification requires a catalyst to accelerate the reaction. Various catalysts have been proposed to improve rate of reaction and conversion. In general, the biodiesel production process via transesterification using base catalysts can produce biodiesel using mild reaction condition compared to acid catalyst. As already known that using heterogeneous catalyst gains more advantages compared to homogeneous on especially CaO. Therefore, the followings summarize the previous works related to using CaO catalyst to produce biodiesel in literatures.

Kouzu et al. [17] studied the preparation of base type solid catalysts for biodiesel production. Due to the fact that it is beneficial to the environment using transesterification of soybean oil and methanol. The catalysts used in the investigation included calcium oxide (CaO), calcium hydroxide (Ca(OH)_2) and calcium carbonate (CaCO_3). After 1 h reaction, the FAME

yield of 93% was achieved when using 12 wt% of CaO catalyst. On the other hand, there was no FAME using Ca(OH)_2 catalyst as well as CaCO_3 catalysts at the same conditions. Moreover, using CaO gave the similar yield of FAME to that of using sodium hydroxide (NaOH) as a homogeneous catalyst. It can be seen that the similar amounts of FAME was also produced when using CaO catalyzed transesterification of used cooking oil (Waste cooking oil, WCO) containing free fatty acid of 5.1 mg KOH/g. The FAME yield was higher than 99% at the reaction time of 2 h. However, this condition also produced soap due to this CaO catalyst reacted with free fatty acids in WCO. It was found that the amount of calcium mixed in biodiesel increased from 187 ppm to 3,065 ppm.

Kawashima et al. [18] developed the heterogeneous catalyst used in the production of biodiesel by studying the catalytic activity of CaO through the transesterification of vegetable oil and methanol. CaO can speed up the reaction by pre-activation with methanol before reacting in this research. It was found that the suitable conditions were using 0.1 g of CaO, 3.9 g of methanol, 15 g of rapeseed oil and pretreat CaO in methanol for 1.5 h at room temperature. FAME yield was achieved 90% within 3 h at 60°C. In addition, the catalyst activation mechanism of CaO was due to the transformation into calcium methoxide, $\text{Ca(OCH}_3)_2$ which is in the form of a substrate for transesterification. Moreover, it was found that the byproduct glycerol can be combined with CaO to form a calcium-glycerol compound (calcium-glycerol complex), which can be another catalyst to assist the rate of transesterification.

Thammachai [19] studied the transesterification of palm oil and ethanol using the soaked CaO catalyst via impregnation with an aqueous solution of sodium carbonate and calcined at 800°C for 5 h in stagnant air. The results showed that the soaking with sodium carbonate solution on CaO provides higher catalytic efficiency. The impregnated CaO catalyst is able to catalyze the transesterification of palm oil with ethanol with fatty acid ethyl ester as high as 91.1% under suitable conditions (1 wt% of sodium on CaO, catalyst content of 20 wt% of oil, ethanol to palm oil molar ratio of 9: 1, temperature 75°C, time 20 h and stirring speed 300 rpm). On the other hand, no fatty acid ethyl ester was detected during the reaction using un-soaked calcium oxide as a catalyst. In addition, the catalysts prepared from calcium carbonate also provided the high catalytic activity for transesterification in absence of the soaked up with sodium carbonate solution.

Barekati-Goudarzi et al. [20] studied the extraction and transesterification of fodder seeds to produce FAME using the microwave assisted system. High level of oil extraction and oil yield efficient was obtained consequently to biodiesel yield. The process was further optimized in terms of product yields and conversion rates by using the Doehlert method from the experimental results and statistical analysis. It was found that the most suitable conditions for this process were the concentration of the catalyst of 1.74 wt%, and the solvent ratio of about 3 %v/wt (ratio by volume to the catalyst weight). The reaction time was 20 min and the temperature was 58.1°C. $^1\text{H-NMR}$ was used to determine the conversion of oil. The obtained FAME yield meets the requirements of biodiesel according to ASTM standards.

Katnanipa and Petpilin synthesized heterogeneous catalysts including of KI, CaO, and Al_2O_3 used for transesterification of palm oil and methanol. The catalysts were prepared by immersing 35 wt% of potassium iodide (KI) with 50 wt% of calcium oxide (CaO) and Al_2O_3 and then calcined at temperature of 500°C for 5 h. X-ray diffraction (XRD) technique was used to analyze the crystal structure of the catalyst. Hammett indicator method was used to determine the strength of the base. It was found that transesterification process using 5% catalyst, methanol to oil molar ratio of 9: 1 at 65°C and 1 h reaction time provided the biodiesel yield up to 98.5% [21].

Activities of single step sol-gel to prepare calcium oxide on alumina catalysts were studied as a function of CaO loading by Umdu et al. [22]. Turnover frequency (TOF) of the catalysts was calculated to better understand the relationship between the basicity/basic strength and the catalytic activity. From volcano curve, it was found that less than 50°C and methanol/oil molar ratio of 9: 1, 60% CaO/ Al_2O_3 had the highest turnover frequency, 0.028 s^{-1} whereas 85% CaO/ Al_2O_3 showed the highest FAME yield, 96.6%, but TOF obtained on it was 0.012 s^{-1} . It seemed that 60% CaO catalyst had the proper basic strength to obtain the highest TOF.

Taufiq et al. [23] prepared calcium mixed oxides catalysts (CaMgO and CaZnO) for the transesterification of jatropha curcas oil (JCO) with methanol. Both CaMgO and CaZnO catalysts were prepared by co-precipitation method of the corresponding mixed metal nitrate solution in the presence of a soluble carbonate salt about pH 8-9. The catalysts were characterized by X-ray diffraction (XRD), temperature programmed desorption of CO_2 (CO_2 -TPD), scanning electron microscopy (SEM), and N_2 adsorption (BET). The conversion of JCO using CaMgO and CaZnO were studied and compared with calcium oxide (CaO), magnesium oxide (MgO) and zinc oxide

(ZnO) catalysts. Both CaMgO and CaZnO catalysts showed high activity 83 and 81%. Under the suitable transesterification conditions at 65°C (catalyst amount 4 wt%, methanol/oil molar ratio 5: 1, reaction time 6 h), even though CaO gave the highest activity.

Biodiesel produced via transesterification of vegetable oils is a promising alternative fuel to diesel because of the limited resources of fossil fuel and environmental concerns. An environmentally benign process was developed for the production of biodiesel from jatropha curcas oil using a heterogeneous solid super base catalyst, calcium oxide as reported by Zhu et al. [24]. The results showed that the base strength of calcium oxide was higher than 26.5 after dipping in an ammonium carbonate solution followed by calcination. A study for optimizing the reaction conditions for the transesterification of jatropha curcas oil was performed. Under the optimum conditions of catalyst calcination temperature of 900°C, reaction temperature of 70°C, reaction time of 2.5 h, and methanol/oil molar ratio of 9: 1, the oil conversion was 93%.

Lee et al. [25] developed a simple method for biodiesel production from non-edible jatropha oil which contains high free fatty acid using a bifunctional acid-base catalyst. The acid-base catalyst comprising of CaO and La₂O₃ mixed metal oxides with various Ca/La atomic ratios were synthesized via co-precipitation method. The effects of Ca/La compositions on the surface area, acidity, basicity and transesterification activity were investigated. Integrated metal oxide between Ca and La enhanced the catalytic activity due to well dispersion of CaO on composite surface. This can increase the surface acidic and basic sites as compared to that of bulk CaO and La₂O₃ metal oxide. Furthermore, the transesterification tests showed that the catalytic activities of CaO-La₂O₃ series were increased with Ca/La atomic ratio to 8. However, the stability of binary system was decreased because of the highly saturated of CaO on the catalyst surface at Ca/La atomic ratio of 10. The highest FAME yield (98.76%) was achieved under transesterification condition of 160°C, 3 h, methanol/oil molar ratio of 25: 1 and 3 wt% of catalyst loading. In addition, Ca-La binary system was stable even after four cycles with negligible leaching of Ca²⁺ ion in the reaction medium.

Puna et al. [26] studied biodiesel production from semi-refined oils (SRO) and waste frying oils (WFO) from Puna using commercial CaO as heterogeneous catalyst. The methanolysis tests were carried out in mild reaction conditions (62°C and atmospheric pressure). With such conditions, soybean and rapeseed allowed to produce biodiesel containing 97–98% of fatty acid

methyl ester (FAME), whereas WFO only provided 86–87% of FAME. The lower FAME yield for WFO oil is due to the partial neutralization of the catalyst by free fatty acids. Also, soaps formation from the WFO oil could reduce the weight yield of the oil phase (containing FAME).

Ozkan et al. [27] used calcium from natural seafood wastes as a heterogeneous catalyst to produce biodiesel. Several experimental runs were conducted at varied reaction times ranging from 30 min to 8 h, at 60°C, with a mass content of 5 wt% (based on oil) and a methanol/oil molar ratio of 12: 1. After the purification process, the measured biodiesel or fatty acid methyl ester (FAME) weight content was higher than 99%, which indicated that it was high biodiesel purity.

Transesterification of palm oil with methanol was investigated over calcium oxide catalysts derived from calcination of eggshells from quail and chicken by Cho and Seo [28]. The palisade layer of quail eggshell had more closely dispersed micron-sized pores compared to chicken eggshells. The treatment with 0.005 M HCl solution for 2 h was used to remove its dense cuticle layer and subsequent calcination above 800°C for 3 h. The quail eggshell provided a large amount of strong basic sites and high catalytic activity compared to that of potassium methoxide in the transesterification. The acid-treated quail eggshell catalyst steadily maintained high conversion of over 98% during 5th cycle reusability at 65°C with a reactant composed of methanol to oil molar ratio 12: 1 and oil to catalyst of 2 g to 0.03 g.

List of CaO and its derivative catalysts for transesterification is presented in Table 2.2. This can be suggested that the methanol/oil molar ratio of 12: 1 and reaction temperature 60-65°C for CaO catalyzed transesterification could give the high conversions and yield greater than 97%.

Table 2.2 Summary of the previous works presented in literatures.

Catalysts	Condition reaction (MeOH: oil, time, stirring rate)	Temperature (°C)	Biodiesel yield (%)	Reference
CaO, Ca(OH) ₂ and CaCO ₃	1 h	-	93%, 12% and 0% FAME	[13]
CaO	9: 1, 3 h	60°C	90% FAME	[17]
Na ₂ CO ₃ /CaO	9: 1, 20 h, 300 rpm	75°C	91.1% FAME	[18]
NaOH	-	58.1°C	90% FAME	[19]
KI/CaO/Al ₂ O ₃	9: 1, 1 h	65°C	98.5 % FAME	[20]
CaO	9: 1, 4 h	50°C	96.6% FAME	[21]
CaMgO and CaZnO	15: 1, 6 h	65°C	83%,81% FAME	[22]
CaO	9: 1, 2.5 h	70°C	93% FAME	[23]
CaO/La ₂ O ₃	24: 1, 6 h	65°C	86.5% FAME	[24]
CaO	12: 1, 3.5 h	62°C	97-98% FAME	[25]
CaO	12: 1, 8 h	60°C	99% FAME	[26]
CaO	12: 1, 3 h	65°C	98% FAME	[27]

2.6 Extrusion

Extrusion process is the lowest cost and basic shaping technique used for preparation of catalysts and their supports in the pellet form. This process requires a wet paste with additives to achieve a moldability. There are various additives used in the formulation of the paste. For example, organic compounds can improve the rheological behavior such as clays or starch while a binder such as alumina or clays can enhance the powder contact and the mechanical strength of the shaped particles obtained after calcination [10]. Pore forming agents as a combustible material

is used to increase the porosity such as polyacrylamide and polyethylene glycol [8]. The plasticizers (hydroxyethylcellulose (HEC), methylcellulose and MgO) are used to adjust the viscosity and lubricity of the catalyst paste to facilitate processing [10]. Various factors have an influence on the extrusion process including additive content, mixing time, and solution viscosity. The high viscosity mixture increases the extrusion force. In addition, mixing and homogenization are very important, in the extrusion process.

The extruded catalysts preparation is divided in two methods including 1) physical mixing technique - a catalyst, binder, or pore forming agent are adequately mixed. The plasticizer is added subsequently to the powder mixture giving the paste form. The paste is mixed using a spatula and loaded into the extruder. This method is easy, but the catalyst spreads unevenly on the support [8]. 2) incipient wetness impregnation technique - a binder, or pore-forming agent is adequately mixed with solvent. The forming of support is similar to the physical mixing. After that, the powder of active species or catalyst precursor is dissolved in water and impregnation onto the support. This method has the advantage that if done appropriately, almost all active species or catalyst precursor containing in the solution for the coating are able to get into the pores of the support. There is very small residue on the surface of the container used for coating after heat treatment such as calcination at high temperature. However, this method might be limited, if the pore volume of the supports is low resulting in the low solvent volume and the use of less solvent to active species or catalyst precursor ratio [11].

2.7 Catalyst shapes

Industrial catalysts are ordinarily shaped a variety of forms, for instance, monolith, rings, spheres, pellets, granulate, and cylinders as shown in Figure 2.3. The shaping process is one of key steps in the preparation of catalysts. Selection of appropriate shapes and sizes of catalyst should be based on their catalytic performance, mass transfer resistance and the strength of crushing. The literature review followings of the previous works will be presented as conclude below:



Figure 2.3 Various catalyst shapes using the industrial [29]

Wang et al. [9] prepared CaO mixed with binder and viscosity modifiers (silica sol) for extrusion in the cylindrical vessel in the size 4 mm diameter and 15 mm long/pieces. This extruded CaO was used as a catalyst for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate reaction. It was found that this extruded CaO catalyst provided high stability with the glycerol conversion of 65.47% for the 5th cycle at reaction temperature of 80°C derived from the CaO/binder mass ratio of 3: 1, and calcination temperature of 800°C. In addition, add pore-forming agents can be increased catalytic activity from 65.47 to 95.39%. This should be due to the increase of the pore volume during calcination.

Jindapon et al. [10] prepared the extruded Ca, Zn and Al mixed catalysts in a cylinder in the size to 2 and 3.5 mm using hydroxyethylcellulose (HEC) as plasticizer for biodiesel production in a fixed-bed reactor. FAME yield was 96.5% using the large methanol to oil molar ratio of 30: 1. Calcium oxides are hard but brittle materials. This formulation requires the addition of binders and plasticizers. Inorganic binders (magnesium oxide, alumina, aluminum phosphates, clay and boehmite) enhance mechanical strength of the shaped particles obtained after calcination. Plasticizers (HEC, methylcellulose, and magnesium oxide) are used to adjust the viscosity and lubricity of the catalyst paste to facilitate processing.

Silveira et al. [11] synthesized the extruded K_2CO_3 in hollow cylindrical shape with outside diameter of 5 mm and inside diameter of 2 mm using alumina and water as binders. The commercial boehmite powder was used as received and calcined at 500°C for 4 h. The boehmite

was in hollow cylindrical shape and solid cylinder using the same calcination temperature at 500°C for 4 h impregnated on γ -Al₂O₃. This extruded K₂CO₃ provided a high oil conversion of 99.3% using high reaction temperature of 80°C.

Aminul et al. [30] reported that the using spherical gamma-alumina (γ -Al₂O₃) as a catalyst support for the production of biodiesel from palm oil. The catalyst support produced using oil drop granulation method and KI species was then loaded on the support using impregnation method. The highest biodiesel yield of 98% was obtained when the reaction carried out under the conditions of catalyst of 0.6 g, reaction time of 4 h, reaction temperature of 60°C and methanol to palm oil molar ratios of 14: 1. KI/ γ -Al₂O₃ expressed a long life time and maintained sustained activity even after being used for 11th cycles. Biodiesel yields after the 11th cycle obtained in this work were 79%.

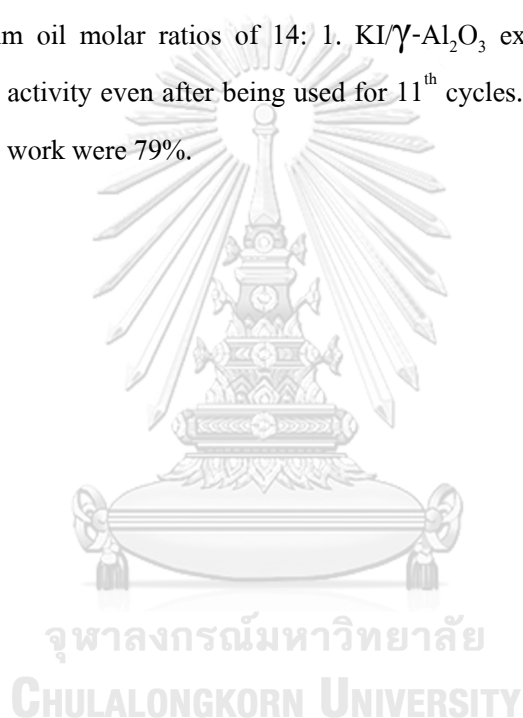


Table 2.3 Different catalysts pillarization from previous researches

Catalyst	Catalyst Shapes	Size	Binder Type	Reaction	Catalytic activity	Reference
CaO	Cylindrical	D = 4 mm, L = 15 mm	Alumina	Glycerol carbonate production	65.47% FAME	[8]
Ca, Zn, and Al	Cylindrical	D = 2 mm D = 3.5 mm	Alumina	Transesterification	96.5% FAME (methanol: oil molar ratio of 30:1)	[9]
K ₂ CO ₃	Hollow cylindrical	Outside diameter 5 mm and inside diameter 2 mm	Alumina and water	Transesterification	99.3% FAME	[10]
KI	Spherical		Alumina		96.4% FAME	[30]

2.8 Mass transfer for heterogeneous catalysis

The crucial step for the heterogeneous catalysis system is mass transfer. The hierarchical structure of solid catalysts is illustrated in Figure 2.4. Usually, mass transfer phenomena comprise of the diffusion in gas or liquid phase, the diffusion in interparticle space of catalyst pellets the diffusion in gas or liquid phase, the diffusion in interparticle space of catalyst pellets, and the diffusion in micro - to macropores in primary or secondary particles (intraparticle space). If the diffusion of reactant molecules is slow in comparison with the rate of catalytic reaction, the

reactant molecules is consumed before they reach near the center of catalyst pellet or particle. In this case, the reaction can occur only near the surface of pellets or particles and active sites only near the surface can function. The ratio of effective active sites to that of entire active sites in the catalyst is called effectiveness factor of catalyst, which is expressed using the dimensionless group, namely, Thiele modulus (ϕ) as showed in Equation (2.2).

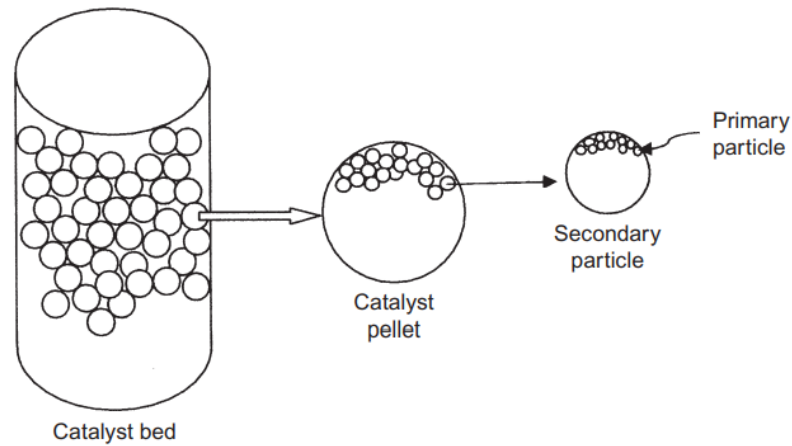


Figure 2.4 Hierarchical structure of catalyst in a fixed-bed reactor [31]

$$\phi = \frac{R}{3} \sqrt{\frac{k}{D_e}} \quad (2.2)$$

Where k is rate constant and D_e effective diffusion constant, as in Equation (2.3). This equation is illustrated as a function of ϕ in Figure 2.5. As the diffusion rate becomes slower relatively to the reaction rate, the effective portion of catalyst decreases greatly in a certain range as shown below:

$$\eta = \frac{1}{\phi} \left\{ \frac{1}{\tan 3\phi} - \frac{1}{3\phi} \right\} \quad (2.3)$$

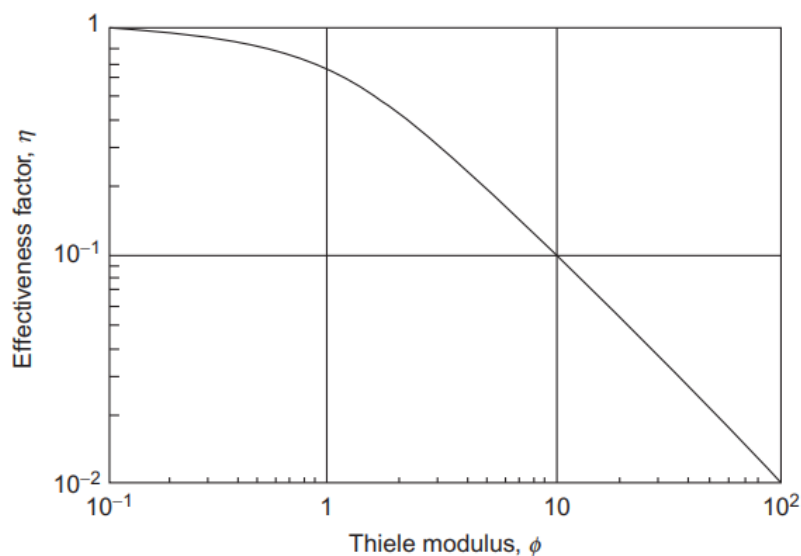


Figure 2.5 Effectiveness factor (η) as a function of Thiele modulus (ϕ) [31]

2.9 Palm oil

Palm oil is a vegetable oil, which is obtained from the fruit of the palm whose compositions of fatty acids are shown in Table 2.4. However, several vegetable oils are used as feedstock for biodiesel production such as palm oil, rapeseed and soybean oil. When, compared with other vegetable oil, palm oil has a far better advantage and potential as a feedstock for biodiesel production especially in Thailand. Palm oil is a perennial crop, unlike soybean and rapeseed [32]. Thailand, in the southern part, has a suitable climate condition for palm cultivation. Oil palm plantations have been continuously expanding since the first commercial plantations were introduced in 1969. Plantation areas cover 22 provinces (mainly in the southern part of Thailand) with a total production capacity of about 9.03 million tons of fresh fruit bunch (FFB). Moreover, oil palm is now increasingly attracting attention as an energy crop since the Thai government has introduced policy to promote the production of palm oil-based biodiesel as a renewable source of energy for the transport sector. According to the 15 years renewable energy development plan (2008-2022), the targets of biodiesel production in Thailand by the years 2011, 2016 and 2022 are set at 3, 3.64 and 4.5 million liters/day [33].

Table 2.4 Fatty acids content of palm oil (present as triglyceride esters)

Type of fatty acid	Percent (%)
Myristic acid (C14: 0)	1.0
Palmitic acid (C16: 0)	43.5
Stearic acid (C18: 0)	4.3
Oleic acid (C18: 1)	36.6
Linoleic acid (C18: 2)	9.1
Other	5.5



Chapter 3

Experimental

This chapter provides the chemicals and experimental methods for the synthesis of extruded calcium oxide catalysts including the effect of binder type and their ratio, the calcination temperature, pore forming agent and shape of the extruded catalyst on their catalytic activities of transesterification of palm oil as presented below.

3.1 Chemicals

A powder activated alumina (Al_2O_3 , MW 101.96 g/mol, melting point of 2,040°C, pore size 58 Å), guar gum powder and silica sol were obtained from Sigma-Aldrich Chemical Co., Ltd. Calcium carbonate was obtained from Kemaus (Australia) Co., Ltd. Polyacrylamide was obtained from Organics Thermo Fisher Scientific (New Jersey, USA) Co., Ltd. All these chemicals were used without further purification. Morakot palm oil was obtained from Morakot industries public company limited, Thailand. Chemicals specification were presented in Table 3.1.

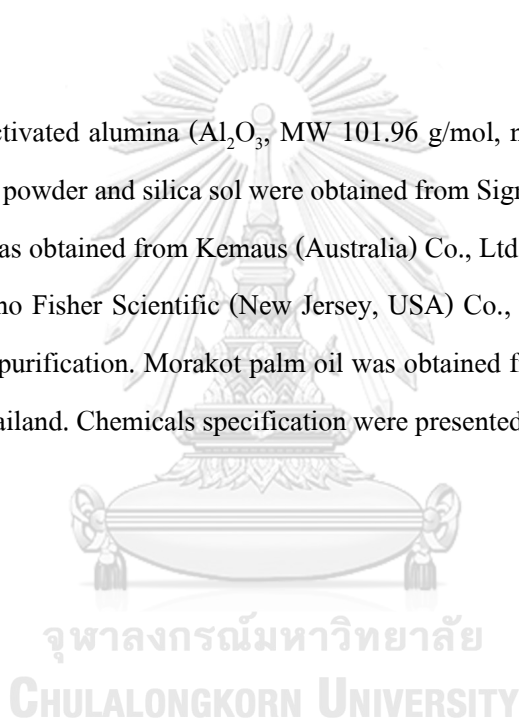


Table 3.1 Specification of chemicals used in this research

Chemicals	Formula	Molecular weight	Company
Calcium carbonate	CaCO_3	100.5 g/mol	Kemaus (Australia) Co., Ltd.
Activated alumina	Al_2O_3	101.96 g/mol	Sigma-Aldrich Chemical Co. Ltd.
Diatomite	SiO_2	60 g/mol	Kemaus (Australia) Co., Ltd.
Kaolin	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	210 g/mol	Kemaus (Australia) Co., Ltd.
Guar gum powder	$\text{C}_{10}\text{H}_{14}\text{N}_5\text{Na}_2\text{O}_{12}\text{P}_3$	535 g/mol	Sigma-Aldrich Chemical Co., Ltd.
Silica sol of 24% concentration	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$	$60 + n(18)$ g/mol	Sigma-Aldrich Chemical Co., Ltd.
Polyacrylamide	$(\text{C}_3\text{H}_5\text{NO})_n$	$n(71)$ g/mol	Organics Thermo Fisher Scientific (New Jersey, USA) Co., Ltd.

3.2 Preparation of extruded CaO catalyst

3.2.1 Cylindrical catalyst pellet

The extrusion process in this work was done by preparation of CaO catalyst in a homogeneous paste comprised of (1) binder (activated alumina, diatomite and kaolin) was used to form the CaO powder to improve the mechanical strength of the shaped particles obtained after calcination; (2) calcium carbonate was used as precursor of CaO as active species; (3) guar gum powder and (4) silica sol as plasticizers lubricity [7] were used to adjust the viscosity and lubricity [8]. The extruded CaO catalyst was prepared step by step; the binder in powder form was dried at 100°C for 12 h to remove water. After that, the desired amount of calcium carbonate, binder, guar gum powder, were mixed adequately. Then, the silica sol was added to the powder mixture. The mixture was loaded into a syringe and press compression for the extruded CaO catalyst. A piston

of 6 mm diameter and 1.5 mm length as a size of short cylindrical (SCY) and 1 mm diameter and 10 mm length as size of long cylindrical (LCY) was used to make a cylindrical shape. Then, the resulting sample was dried at 100°C for 2 h. The calcination at temperature of 700, 800 and 900°C were used for 5 h under static air using a heating rate of 5°C/min. Finally, the obtained extruded CaO catalysts were used to catalyze transesterification of palm oil under similar condition.

3.2.2 Spherical catalyst pellet

The resulting paste was first shaped in the cylindrical catalyst as preparation of extruded CaO catalyst in section 3.2.1. After a piston of 6 mm diameter was used to make spherical pellet forms (SHL) by spherical pellet forms by physical mixture method and extruded by JP table-type herbal coating herbal pellet making machine with diameter of 6 mm. Then, the resulting sample was dried at 100°C for 2 h. The selected calcination at temperature was carried out for 5 h under static air using a heating rate of 5°C/min. Finally, the obtained extruded CaO catalysts were used to catalyze transesterification of palm oil under similar condition.

3.2.3 Addition of pore forming

Addition of the pore-forming process in this work was done by preparation of CaO catalyst in a homogeneous paste comprising of (1) binder; (2) calcium carbonate; and (5) polyacrylamide as a pore-forming reagent. The extruded CaO catalyst was prepared to step by step as similar to section 3.2.1. The extruded CaO using Al₂O₃ binder, calcination temperature of 800°C and polyacrylamide as a pore forming agent with various concentration of 1, 3 and 5 % (3) guar gum powder (4) silica sol were named as CaO-A(800)-P-1%, CaO-A(800)-P-3% and CaO-A(800)-P-5%, respectively.

3.3 Reaction procedure

Catalytic activity of the extruded CaO catalyst test was carried out in a 150 mL round bottom 3-neck glass flask fitted with a magnetic stirrer, a reflux condenser and a thermometer. The reaction temperature was controlled using a silicon oil bath and a hot plate stirrer. In each experimental run, the extruded CaO catalyst and methanol were firstly mixed in the flask at room

temperature. Then, preheated palm oil was added to the mixture at the reaction temperature to start the reaction. The ratio of methanol to palm oil was fixed at 12: 1, 10 wt% of extruded CaO catalyst loading, at the temperature of 65°C, for 6 h using a stirring speed of 600 rpm [34]. On the reaction period, the liquid reaction mixture was taken out from the glass flask and sampled to analyze biodiesel yield. The selected extruded CaO catalyst was also tested the catalytic activity in stainless steel basket reactor with the dimension length of 200 mm and an inner diameter of 45 mm, connected with a reflux condenser and a thermocouple.

3.4 Catalyst characterizations

3.4.1 Thermogravimetric analysis/differential scanning calorimeter (TGA/DSC)

Thermal stability of uncalcined extruded CaO catalyst was analyzed by thermogravimetric analysis with differential scanning calorimeter (TGA/DSC, SDT Q600 Diamond Thermogravimetric and Differential Analyzer, TA Instruments). The analysis was operated from room temperature to 1000°C at a heating rate of 10°C/min using 100 mL/min of air zero.

3.4.2 X-ray diffraction (XRD)

Crystallinity and phase of the prepared catalysts were characterized by XRD (Bruker D8 Advance, Cu K α at 0.154056 nm) between 10° and 80° with a step size of 0.04° and a scan rate of 0.5 s per step.

3.4.3 Fourier-transform infrared spectroscopy (FTIR)

FTIR-ATR spectra was recorded using the Perkin-Elmer® Spectrum TM 400 FT-IR/NIR spectrometer (Perkin Elmer Inc., Tres Cantos, Madrid) in mid-IR mode, equipped with a universal attenuated total reflectance (ATR) sampling device containing diamond/Zn-Se crystal. The spectra was scanned at room temperature in absorbance mode over the wavenumber range of 4000–650 cm⁻¹, with a scan speed of 0.20 cm/s, and 30 accumulations a resolution of 4 cm⁻¹.

3.4.4 Scanning electron microscope and energy dispersive X-ray spectrometer (SEM/EDX)

Surface morphology of the extruded CaO and elemental composition were analyzed with scanning electron microscope equipped (SEM) by JEOL JSM-35 the SEM model S3400N and Link Isis Series 300 program Apollo model x is performed for EDX.

3.4.5 N₂ adsorption–desorption isotherms

Surface area, pore volume and average pore size were analyzed by N₂ adsorption-desorption with micrometrics ASAP 2020. All samples were crushed and degassed before the test under vacuum at 200°C for 12 h. The surface area was calculated with Brunauer-Emmett-Teller (BET) model, while the pore volume and pore size were calculated by Barrett-Joyner-Halenda (BJH) model.

3.4.6 Hammett indicator method

Hammett indicator method was used to determine the basicity and basic strength using four indicators including of bromothymol blue ($H_{-}=7.2$), phenolphthalein ($H_{-}=9.8$), 2, 4-dinitroaniline ($H_{-}=15.0$) and 4-nitroaniline ($H_{-}=18.4$). Extruded CaO catalyst 0.3 g was added into methanol 10 mL and left for 2 h to reach equilibrium. The clear solution was obtained from filtration. The selected indicator was dropped in the clear solution to test the basic strength. After that, for the clear solution was titrated with HCl 0.1 M to determine the basicity concentration.

3.4.7 Mechanical strength

Mechanical strength of the extruded catalyst pellets was evaluated by a mechanical testing machine (UTM (1 Tons) - H10 KM). During a test, the individual extruded catalyst particle was set on the test bench by placing the extruded catalyst pellets vertically where the force load surface of a cylindrical catalyst is a circular cross-sectional surface. Two sizes of cylindrical catalyst pellets are 1) pellet with 1.5 mm diameter and 6 mm length, and 2) pellet of 1 mm diameter and 10 mm length. For spherical catalyst pellet, the force load surface of a spherical is at the little surface area of the sphere in contact with the mechanical testing machine. The desired force was applied to the extruded catalyst particle until it was fractured. The force-time curve was drawn automatically by the tester. Thus, the maximum force of the particle sample can

support was obtained. At least three tests were performed for each extruded catalyst to obtain an average strength value.

3.4.8 FAME product analysis using gas chromatography according to EN 14103 standard

1) Standard solution of methyl heptadecanoate was weighed to 0.05 ± 0.0005 g in a 5 mL brown bottle.

2) Reaction mixture samples were weighed to 0.0250 ± 0.0015 g, 5 mL heptane using pipette. Close the lid immediately and shake to allow the solution to be mixed. Then, the sample solution was injected in the amount of 1 μ L. Biodiesel (FAME) content obtained from transesterification of palm oil was then analyzed using gas chromatography column DB-WAX 30 m x 0.320 mm 0.25 micron 20 to 250/260°C as presented in Table 3.3 according to EN14103.

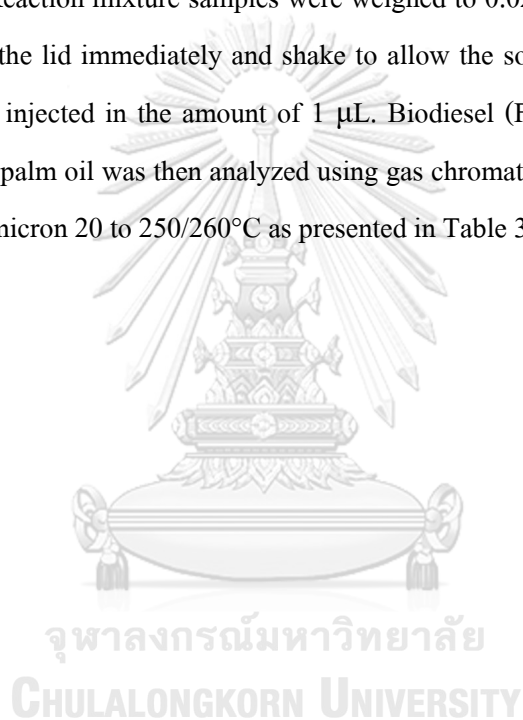


Table 3.2 Conditions for determination of free fatty acid content by gas chromatography

Parameter	Condition
Injection port	
Injection mode	Split
Carrier gas	He
Temperature	250°C
Pressure	99kPa
Injection volume	1 μ L
Column oven	
Initial temperature	150°C
Total program time	22 min
Ramp rate	10°C/min
Zone 1	150°C hold 5 min
Zone 2	190°C hold 5 min
Zone 3	220°C hold 5 min
Column final temperature	220°C

Chapter 4

Results and discussion

This chapter is a section of experimental results and discussion providing the characterization of extruded CaO catalysts, their catalytic activities of transesterification of palm oil and their reusability. For production of biodiesel through the transesterification of palm oil, the operating condition in a batch reactor was fixed at 10 wt% CaO catalysts, reaction temperature of 65°C, a methanol to oil of 12: 1 and a stirring speed of 600 rpm.

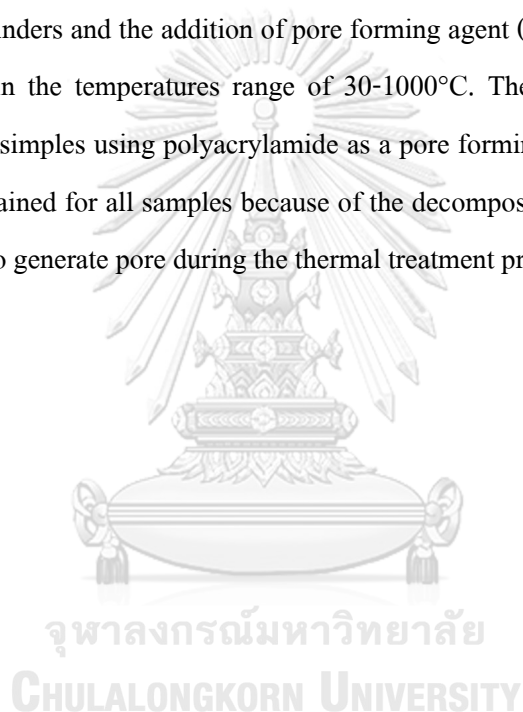
4.1 Catalyst characterizations of the extruded CaO catalysts

4.1.1 Thermogravimetric analysis/differential scanning calorimeter (TGA/DSC)

Figure 4.1 (a) shows the results of thermogravimetric analysis (TGA-DSC) of the mixture of calcium carbonate (CaCO_3) as a Ca source and different binders (Al_2O_3 , diatomite and kaolin) before calcination process in a temperature range of 30-1000°C. There were the major three stages of weight loss profiles obtained from the mixture of CaCO_3 with binders. Weight loss at temperature below 200°C was derived from the dehydration of moisture in the solid mixture. While weight loss in the temperature range of 200-450°C could be due to decomposition of organic matter such as guar gum powder as an ingredient of the extruded CaO catalyst [35]. The last stage of weight loss exhibited the formation of CaO via calcination of CaCO_3 . This can be seen the order to complete calcination temperature to generate CaO species were 750, 790 and 950°C as derived from Al_2O_3 , kaolin and diatomite binders, respectively. DTA results also indicated the endothermic reaction of the CaCO_3 decomposition to generate CaO. It was also noted that, the weight loss of the extruded CaO-D was significantly dropped more than 25% from its original as well as CaO-A. CaO-K, on the other hand, the total weight loss was only 8%. This means that the potential calcination temperature to obtain CaO phase for the extruded CaO using Al_2O_3 and diatomite should be greater than 800°C while that of the extruded CaO using kaolin should be greater than 950°C. Moreover, this can be described that the extruded CaO using diatomite was less thermal resistant than the others. DTA curve of CaO-A and CaO-K indicated

the endothermic heat of reaction at the temperature about 400°C due to the decomposition of organic matter during thermal treatment process. In addition, DTA curve of CaO-A, CaO-D and CaO-K also indicated the endothermic heat of reaction at the temperature greater than 700°C due to the transformation of CaCO_3 to CaO following the weight loss observed from the TGA results [36]. Moreover, the broad exothermic peak of DTA was also observed at the temperature greater than 850°C which could be attributed to generation of the composite material of calcium aluminates as CaAl_2O_4 formula [37].

Figure 4.1 (b) shows the results of thermogravimetric analysis (TGA-DSC) of the mixture of CaCO_3 , binders and the addition of pore forming agent (CaO-A-P-1, 3 and 5%) before calcination process in the temperatures range of 30-1000°C. The similar temperature profiles were observed in all samples using polyacrylamide as a pore forming. However, more significant weight loss were obtained for all samples because of the decomposition of pore forming agent as a template polymer to generate pore during the thermal treatment process [38].



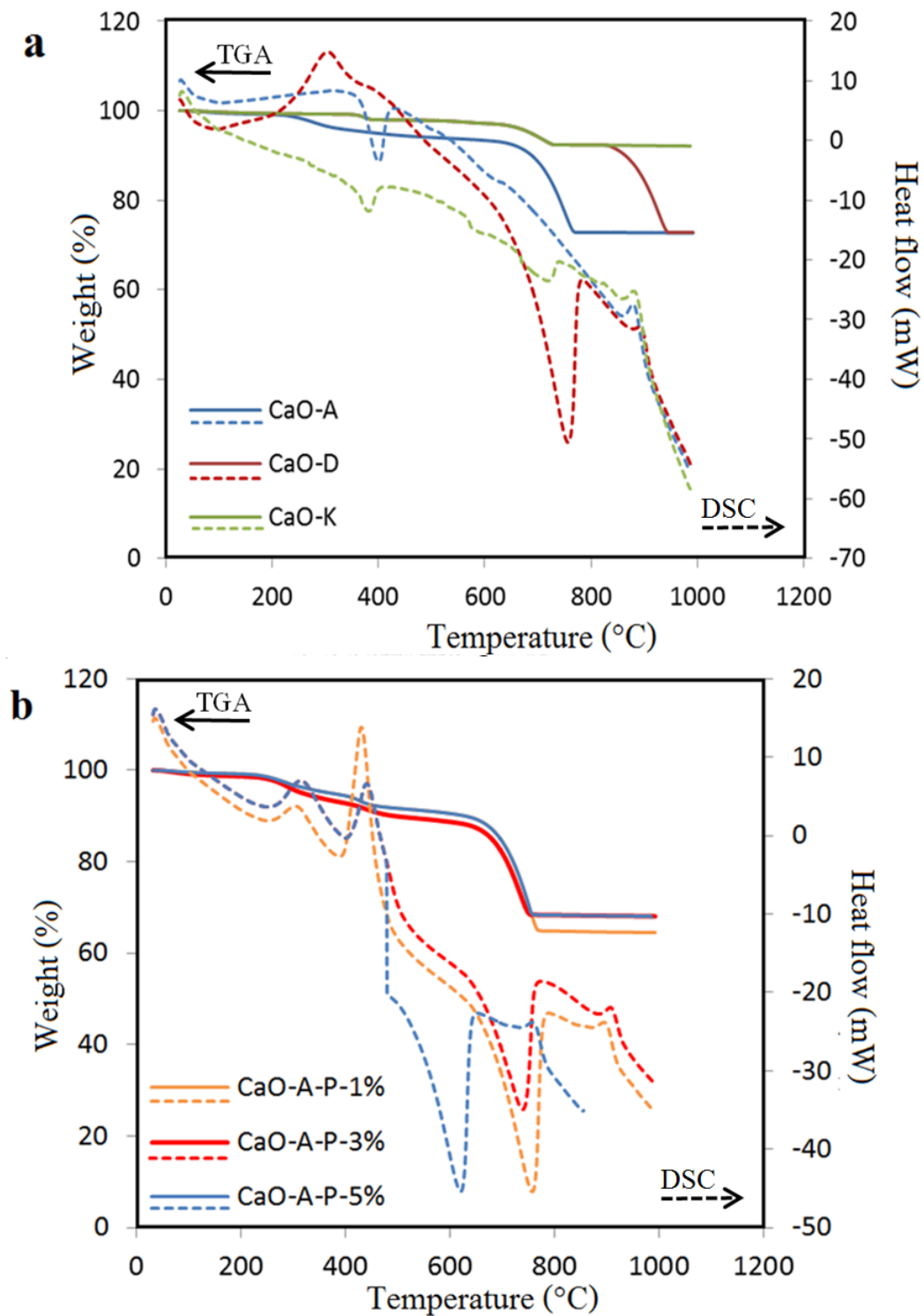


Figure 4.1 Thermogravimetric analysis (TGA-DSC) of the mixture of CaCO₃ and different binders (a) CaO-A, CaO-D, CaO-K and (b) addition of pore forming agent (CaO-A-P-1, 3, 5%).

4.1.2 X-ray diffraction (XRD)

Crystalline structures of catalyst pellets prepared by different binders (Al_2O_3 , diatomite and kaolin) at different calcination temperatures were examined by X-ray diffractometer as shown in Figures 4.2 - 4.3.

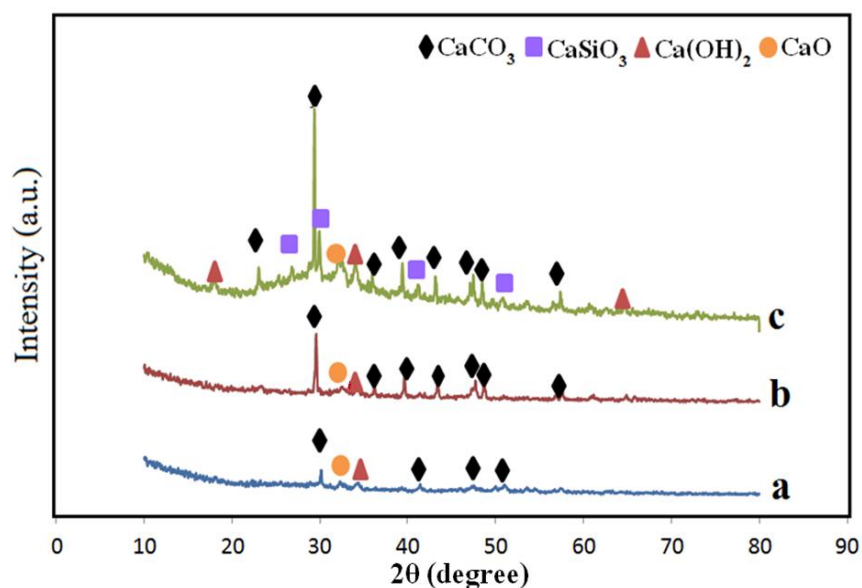


Figure 4.2 X-ray diffraction patterns of the extruded CaO catalysts (a) CaO-A(700), (b) CaO-A(800) and (c) CaO-A(900)

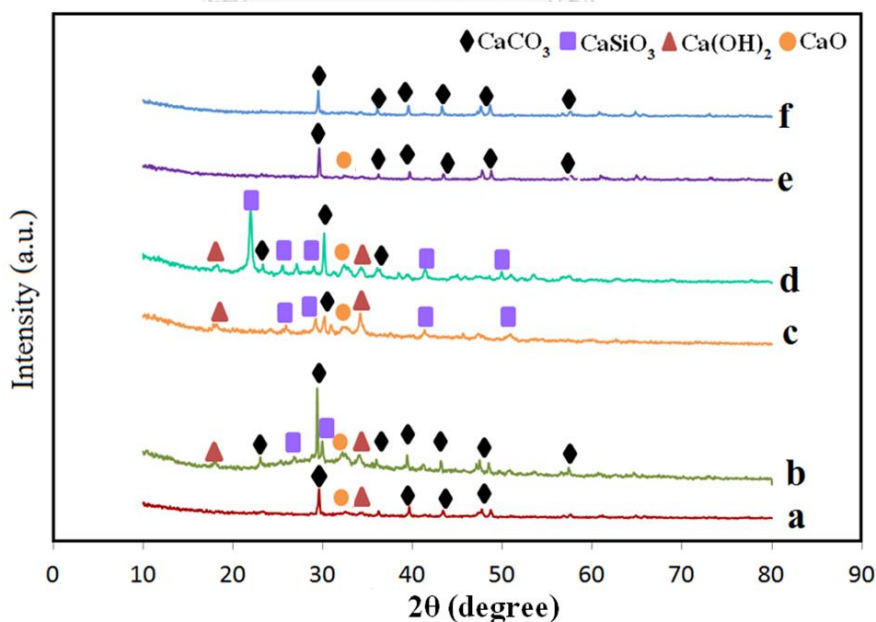


Figure 4.3 X-ray diffraction patterns of the extruded CaO catalysts (a) CaO-A(800), (b) CaO-A(900), (c) CaO-D(800) (d) CaO-D(900), (e) CaO-K(800) and (f) CaO-K(900)

Figure 4.2 shows extruded CaO catalyst using Al₂O₃ binder at different calcination temperatures. This illustrated that the increased calcination temperature can increase the crystallinity of CaO which was observed at 2θ equal to 32.04° as a characteristic peak of CaO [8]. While the intensity of CaCO₃ phase at 2θ equal to 22.77°, 29.03°, 35.54°, 39.20°, 43.23°, 46.8°, 47.8° and 56.10° obtained for all CaO-A(700), CaO-A(800) and CaO-A(900) samples were stronger than the other phases [39]. Moreover, the characteristic peaks of Ca(OH)₂ phase at 2θ equal to 17.97° and 33.88° were also found which could be due to the hydration and carbonation of CaO species with adsorbed air [8]. The XRD results were not corresponding to TGA results that the calcination temperature of 800°C could provide the complete calcination process of the extruded CaO-A and CaO-K. This could be attributed that the preparation of the extruded CaO catalysts and carbonation of CaO during the storage [40].

Table 4.1 Crystallite sizes of the extruded CaO using different binders and different temperatures.

Extruded CaO catalyst	Crystallite size (nm)	
	CaO	CaCO ₃
CaO-A(700)	31.04	45.82
CaO-A(800)	41.73	99.99
CaO-D(800)	27.61	62.32
CaO-K(800)	-	61.25
CaO-A(900)	47.01	132.17
CaO-D(900)	22.84	83.91
CaO-K(900)	-	81.24

Crystallite sizes of CaO and CaCO₃ were determined by Debye Scherer formula as can be seen in Table 4.1. It was found that the crystallite size of CaO was calculated as 31.04, 41.73 and 47.01 nm for CaO-A(700), CaO-A(800) and CaO-A(900), respectively. The crystallite sizes of CaO and CaCO₃ phase were increased when increasing the calcination temperature. The similar trend of the crystallite size of CaCO₃ and CaO for all extruded CaO catalysts were

increased with increasing the calcination temperature because the sintering of material was found at high temperature [41].

Figure 4.3 exhibits the diffractogram of the extruded CaO catalyst using different binders. The similar XRD patterns of CaCO_3 phase were observed for all binders using calcination temperatures of 800 and 900°C which were not in agreement to TGA results. It is worth to mention that no diffraction peak of CaO was observed when using kaolin as a binder CaO-K(900). While the small broad characteristic peak of CaO was found in CaO-K(800). This might be due to the CaO species was in an amorphous phase which could not be detected by XRD technique [42]. Using diatomite as a binder tended to increase the crystallinity phase of CaSiO_3 because diatomite contains high amount of SiO_2 than the other binders. Tangboriboon et al. [43] reported that the incorporation of Si in the composite material resulted in reducing the crystallite size at high calcination temperature. In addition, the crystallite size of CaO was calculated as 27.61 and 22.84 nm for CaO-D (800) and CaO-D (900), respectively. While the crystallite sizes of CaCO_3 phase were in the range of 62.32 to 83.91 nm which increased with the calcination temperature and larger than that of CaO for all extruded CaO catalysts.

The presence of CaCO_3 phase for all XRD patterns of extruded CaO catalyst was not in agreement to the other works which used the similar composite material and calcination temperature. The hypothesis of this obtained result was more likely due to the calcination process might not be complete to obtain the uniform carbonation of CaCO_3 to CaO of the cylindrical shape of the extruded CaO catalyst. While the mixture paste used as a sample for TGA characterization can provide the uniform calcination temperature.

4.1.3 Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra of the extruded CaO catalysts using different binders and calcination temperatures were illustrated in Figure 4.4.

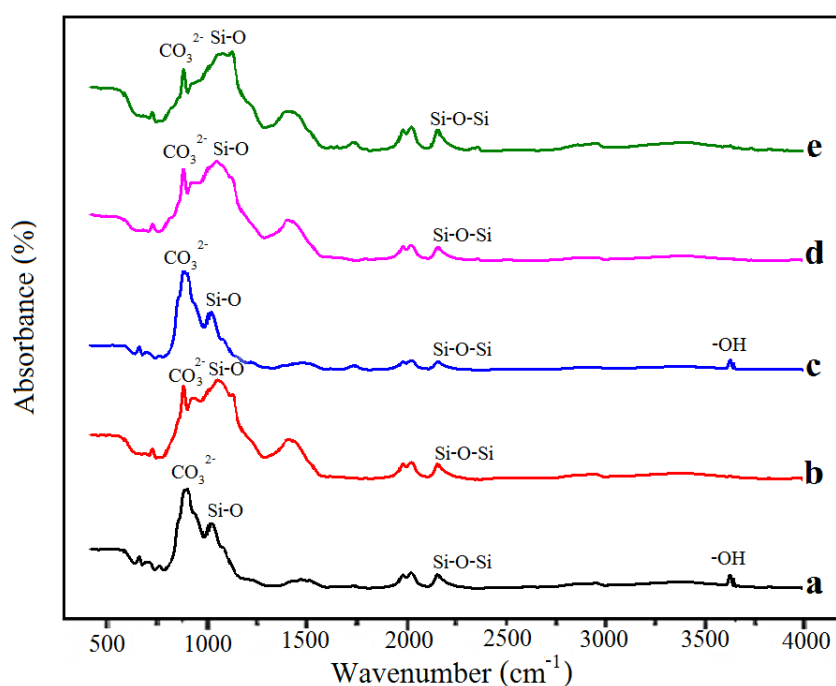


Figure 4.4 FTIR spectra of the extruded CaO catalysts at different calcination temperature (a) CaO-A(700), (b) CaO-A(800), (c) CaO-A(900), (d) CaO-D(800) and (e) CaO-K(800)

The spectra of all extruded CaO catalysts showed the similar adsorption peaks. The peaks appearing at 1400-1500 cm^{-1} and 800-900 cm^{-1} suggested that the presence of carbonate species. The wide band at 3640 cm^{-1} was attributed to the -OH stretching vibration for $\text{Ca}(\text{OH})_2$. The intense band at wave number below 600 cm^{-1} was ascribed to the vibration modes of metal oxide (CaO) [4]. The peaks at 1050 and 2350 cm^{-1} were corresponding to the Si-O stretching and Si-O-Si vibrations, respectively [8]. The FTIR spectra were also similar to with the previous reports [4, 8]. The FTIR spectra of $\gamma\text{-Al}_2\text{O}_3$ was not found in this research, which is in contrast to the report of Dalibor et al. [44]. This previous research found the broad intense peaks of amorphous $\gamma\text{-Al}_2\text{O}_3$ in the range of 1000-500 cm^{-1} .

4.1.4 Surface morphology of the extruded CaO using scanning electron microscope and energy dispersive X-ray spectrometer (SEM/EDX)

All extruded CaO samples presented the aggregation of CaO as observed by their morphology and size shown in Figure 4.5.

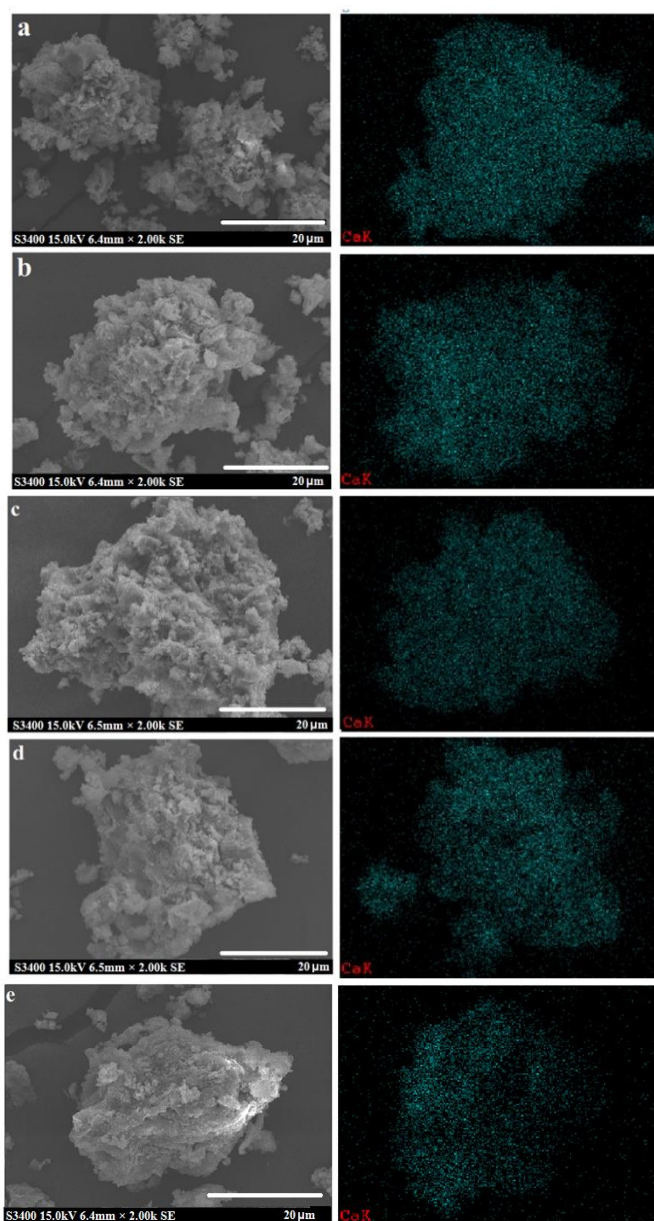


Figure 4.5 SEM/EDX images of the extruded CaO catalysts at different calcination temperatures and binders (a) CaO-A(700), (b) CaO-A(800), (c) CaO-A(900), (d) CaO-D(800) and (e) CaO-K(800)

The morphologies of CaO-A using calcination of 700, 800 and 900°C showed differences in size and morphology. The particles size for the extruded CaO-A (900) was 25.35 μm which was obviously larger than that of CaO-A (800) of 23.59 μm and CaO-A (700) 20.73 μm , respectively [45]. When the calcination temperature was increased, the agglomeration of the particles of catalyst was also increased due to the sintering process at high temperature. However, using diatomite and kaolin as a binder tended to obtain the smaller particle sizes of CaO-D and CaO-K (16.61 and 19.80 μm , respectively) as compared to that of CaO-A. Since silica was contained in the both substances which could resist the sintering process at the high calcination temperature [46]. This finding result was also corresponding the crystallite size of CaO and CaCO_3 derived from XRD pattern of CaO-D(800) and CaO-D(900) because it contains more amount of SiO_2 which could resist the sintering process at high temperature [47]. The morphology of the extruded CaO catalyst using calcination temperature was also similar to the previous work [4]. Figure 4.5 also shows the Ca distribution of the extruded CaO catalysts pellet using different binders. It indicated that all extruded catalysts exhibit the high Ca distribution, especially of CaO-A(800). This could be due to the strong interaction between Ca species and Al_2O_3 binders. It should be noted that the calcination temperature of 800°C could be an appropriate condition to prepare the extruded CaO using Al_2O_3 binder.

4.1.5 Mechanical strength of the extruded CaO catalysts with the different shapes

The extruded catalyst requires an appropriate shape to obtain high mechanical property as well as high catalytic activity. Therefore, this section will investigate the effect of different shapes of the extruded CaO using Al_2O_3 as a binder on their mechanical properties based on their similar surface area. Mechanical strength of prepared catalyst pellets by different shapes is presented in Table 4.2 and the extruded catalyst shapes as presented in Figure 4.6.

Table 4.2 Mechanical strength of the extruded CaO catalyst using Al₂O₃ as a binder.

Sample	Size and shapes	Mechanical strength (N/mm ²)	Solid density g/cm ³
CaO-A(800)-LCY	D= 1.006 mm L= 10 mm	31.11	0.42
CaO-A(800)-SCY	D= 5.476 mm L= 1.5 mm	30.45	0.30
CaO-A(800)-SHL	D = 5.200 mm	105.9	0.34

**Figure 4.6** Extruded CaO catalyst pellets with different shapes (a) short cylindrical (SCY), (b) long cylindrical shapes (LCY) and (c) spherical shape (SHL)

It was found that the mechanical strength of the extruded CaO with LCY shape was 31.11 N/mm² as well as the extruded CaO with SCY shape (30.45 N/mm²) while the extruded CaO with SHL shape was significantly as high as 105.9 N/mm². The extruded CaO catalyst with spherical shape (SHL) gave a higher mechanical strength than that of long cylindrical (LCY) and short cylindrical (SCY) because the interfacial surface area of the SHL shape was smallest as compared to the other SCY and LCY shapes as presented in Figure 4.6. When the similar compressible force was applied on the interfacial surface area of SHL resulting in a higher mechanical strength. This is because the SHL has a lower catalyst volume than the LHY and SCY [48]. Density of the extruded CaO with different shape was also shown in Table 4.2. They have different bulk density based on the similar surface area because the differences in mass and volume of each shape. Kim et al. [49] produced the extrusion panel using the similar binder of the

Ca, Si and Al mixture. The similar mechanical strengths were 30-45 N/mm² as well as their extruded CaO catalysts in this research. The bulk density of dry extrusion panel was also similar to that of the extruded CaO due to the similar composition and preparation process.

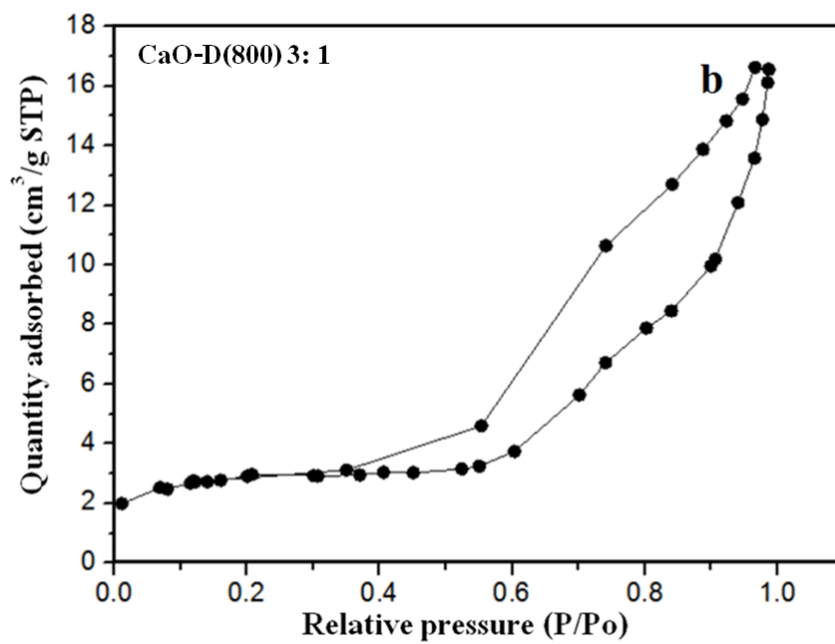
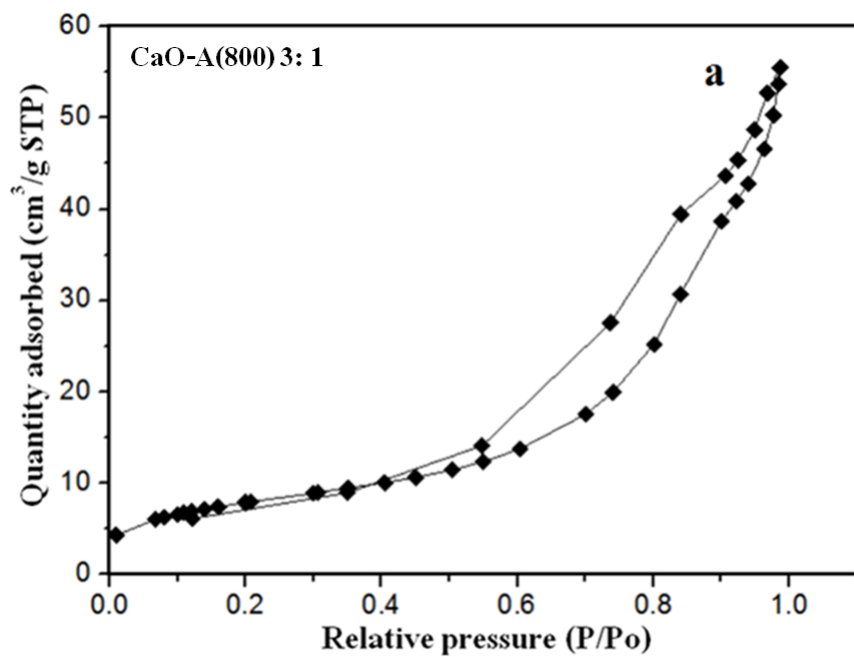
4.1.6 N₂ adsorption–desorption isotherms

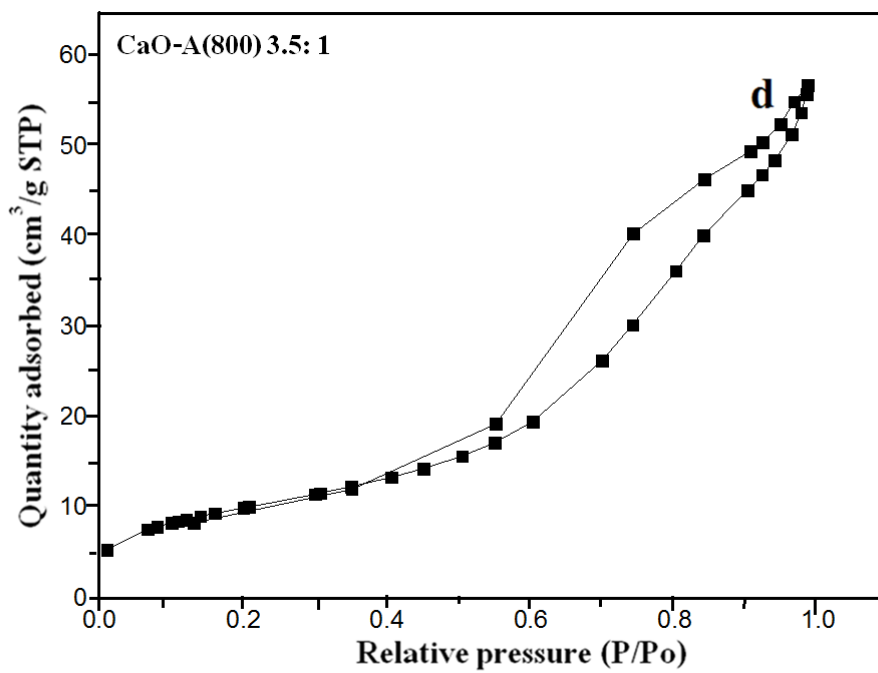
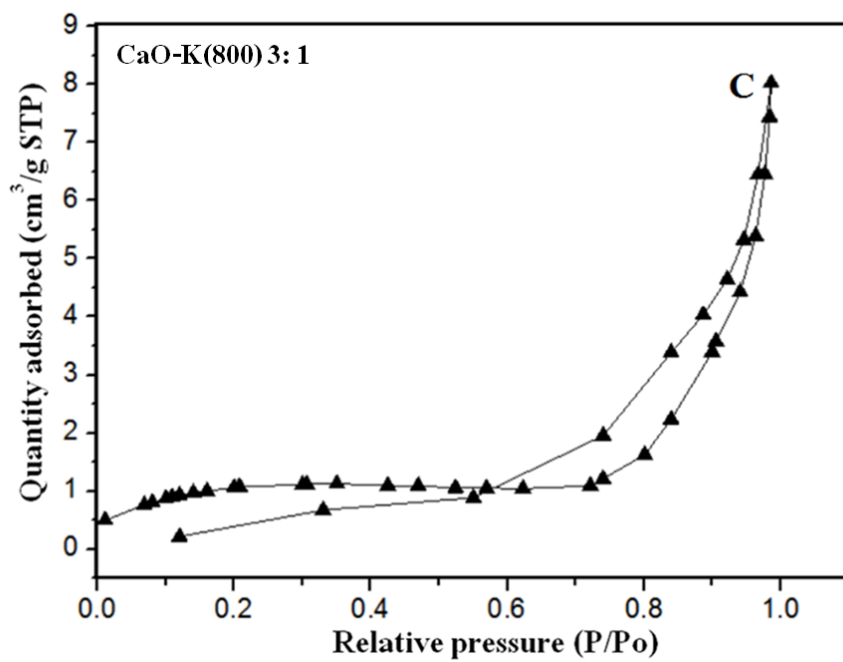
Table 4.3 exhibits surface areas, pore-volume and average pore size of the extruded CaO catalyst prepared from different binders and concentrations of pore forming. It was found that the incorporation of CaO with all binders tended to increase surface areas, pore-volume and average pore size as compared to CaO powder. However, there was remarkably difference in the surface area of binders such as Al₂O₃, diatomite and kaolin before calcined as 129.86, 21.01 and 13.11 m²/g which could result in the surface area of the extruded CaO due to pore blockage and sintering at high temperature [50]. There was difference in the surface area of the extruded CaO catalyst as following: CaO-A(800), CaO-D(800) and CaO-K(800) using CaO: binder (3: 1) were 15.21, 10.15 and 4.06 m²/g, respectively while the surface area of the extruded CaO-A(800) catalyst of different CaO: binder ratios of 1: 1, 3: 1, 3.5: 1 and 6: 1 were 12.82, 15.21, 36.78 and 18.57 m²/g, respectively. This was due to the effect of binder on the surface area that was in accordance to their original surface area of binders. In addition, it was found of CaO: binder to 3.5: 1, the surface area of CaO-A(800) was the highest value (Table 4.3). To further examine the effect of pore forming on the surface area, pore volume and average pore size, polyacrylamide was used a pore forming agent as shown in Table 4.3. The surface area of CaO-A(800)-P-1%, CaO-A(800)-P-3% and CaO-A(800)-P-5% was larger than that of CaO-A(800). The addition of pore forming agent should increase the porosity and surface area [51]. This is because of the addition of polyacrylamide as a polymer template was decomposed at high calcination temperature resulting to increase a surface area, pore volume and average pore size of the extruded CaO catalyst [52]. The order of surface area for CaO-A(800)-P-1%, CaO-A(800)-P-3% and CaO-A(800)-P-5% were 25.74, 22.49 and 18.87 m²/g, respectively. Increasing the pore forming concentration resulted in decreased surface area of the extruded CaO catalyst. This was probably due to the non-homogeneity of calcination process of extruded CaO leading to the pore forming agent residue. Wang et al. [8] reported that the BET surface area of different binder was in the similar trend. CaO-A(800) was the higher surface area than that of CaO-D(800) and CaO-

K(800). However, the BET surface areas of all extruded CaO catalysts with and without pore forming in this research were lower than that from the previous reported. The hypothesis could be due to the non-uniform heat treatment of the extruded CaO catalysts during the calcination process resulting to incomplete decomposition of pore forming reagent. N₂ adsorption-desorption isotherm and pore size distribution curves are shown in Figures 4.7 and 4.8, respectively.

Table 4.3 BET surface area, pore volume and pore diameter for the extruded CaO catalysts

Catalyst and binder	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
CaO(800)	4.88	0.013	11.11
Al ₂ O ₃	129.86	0.23	7.15
Diatomite	21.01	0.06	9.41
Kaolin	13.11	0.02	6.67
CaO-A(800) 3: 1	15.21	0.02	7.01
CaO-D(800) 3: 1	10.15	0.02	9.81
CaO-K(800) 3: 1	4.06	0.01	11.30
CaO-A(800) 1: 1	12.82	0.03	10.23
CaO-A(800) 3.5: 1	36.78	0.08	9.38
CaO-A(800) 6: 1	18.75	0.04	9.18
CaO-A(800)-P-1%	25.74	0.08	10.06
CaO-A(800)-P-3%	22.49	0.06	10.60
CaO-A(800)-P-5%	18.87	0.03	7.70





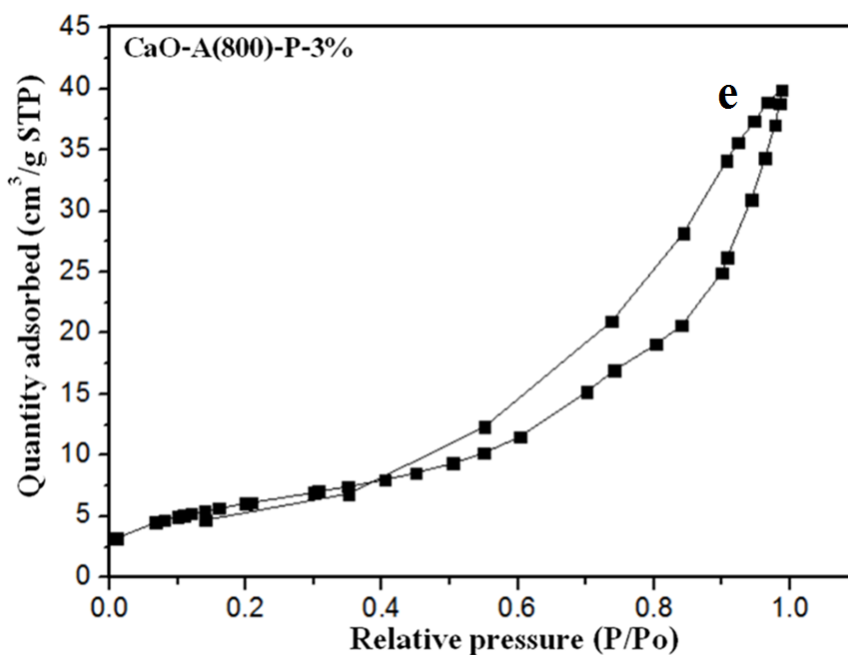


Figure 4.7 Adsorption/desorption isotherms of (a) CaO-A(800) 3: 1, (b) CaO-D(800) 3: 1, (c) CaO-K(800) 3: 1, (d) CaO-A(800) 3.5: 1 and (e) CaO-A(800)-P-3%

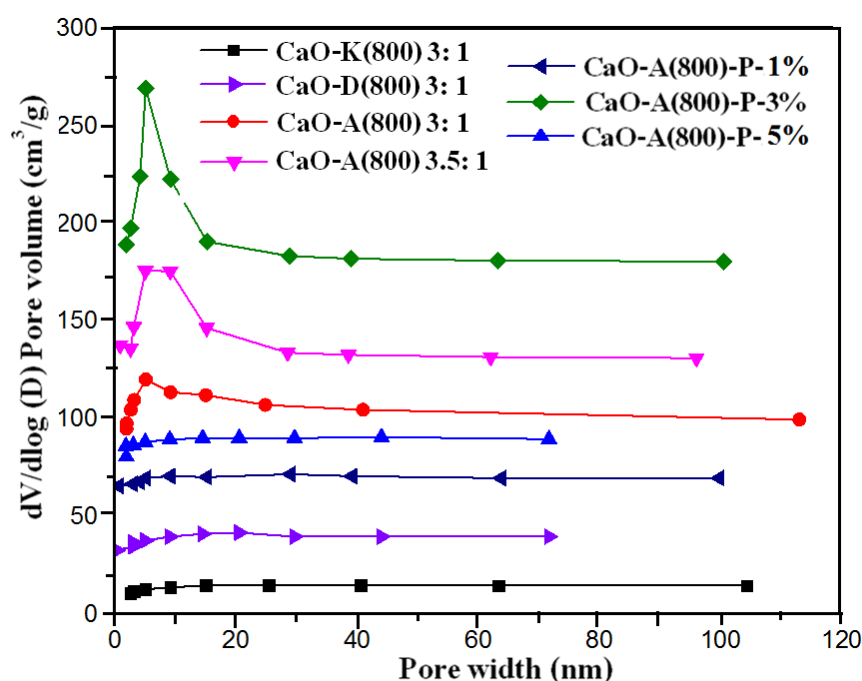


Figure 4.8 Pore size distribution curves of mesoporous CaO-A(800) 3: 1, CaO-D(800) 3: 1, CaO-K(800) 3: 1, CaO-A(800) 3.5: 1, CaO-A(800)-P-1%, CaO-A(800)-P-3% and CaO-A(800)-P-5%

N_2 adsorption-desorption isotherm and pore size distribution curves are shown in Figures 4.7 and 4.8. All extruded CaO catalysts showed the similar adsorption-desorption isotherm as type IV according to IUPAC classification indicating mesoporous structure [53]. It can be observed that when the relative pressure was greater than 0.4, the amount of N_2 adsorption was significantly increased, which is characterized by the presence of a large number of mesoporous. A steep slope at high relative pressure is associated with capillary condensation in the pores and a narrow pore size distribution [54]. This also indicated the advantage of using binder to prepare the extruded CaO which provided the higher surface with controlling of the mesoporous structure. Figure 4.8 shows the pore size distribution profiles of the extruded CaO using different binders and different amounts of pore forming agent. A very narrow peak of pore size distribution was only found for CaO-A(800)-P-3%. The mesoporous CaO-A(800)-P-3% was well-defined uniform pore dimensions as compared to the other extruded CaO catalysts.

4.1.7 Hammett indicator method

Basic strength and basicity of extruded CaO catalyst prepared under different calcination temperatures of 700, 800 and 900°C (using Al₂O₃ binder), and different binders of Al₂O₃, diatomite and kaolin (at calcination temperatures of 800 and 900°C), and addition of polyacrylamide (CaO-A(800)-P-1, 3 and 5%) obtained from the Hammett indicator method were shown in Table 4.4.

Table 4.4 Basic strength and basicity of extruded CaO catalyst

Catalyst	Basic Strength (H ₋)	Basicity (mmol/g _{cat})			
		(H ₋ =7.2)	(H ₋ =9.8)	Total	S.D.
CaO(800)	7.2<H ₋ <9.8	0.053	6.67x10 ⁻³	0.0553	0.0014
CaO-A(700) 3: 1	7.2<H ₋ <9.8	0.003	0.00455	0.0036	0.0020
CaO-A(800) 3: 1	7.2<H ₋ <9.8	0.0453	0.0461	0.0457	0.0085
CaO-A(900) 3: 1	7.2<H ₋ <9.8	0.0128	0.0167	0.0147	0.0028
CaO-A(800) 1: 1	7.2<H ₋ <9.8	0.0345	0.0375	0.0360	0.0017
CaO-A(800) 3.5: 1	7.2<H ₋ <9.8	0.1475	0.155	0.1512	0.0348
CaO-A(800) 6:1	7.2<H ₋ <9.8	0.0325	0.035	0.0337	0.0028
CaO-D(800) 3: 1	7.2<H ₋ <9.8	0.015	0.01	0.0125	0.0050
CaO-D(900) 3: 1	7.2<H ₋ <9.8	0.0270	0.0159	0.0215	0.0069
CaO-K(800) 3: 1	7.2<H ₋ <9.8	0.025	0.01	0.0175	0.0095
CaO-A(800)-P-1%	7.2<H ₋ <9.8	0.0285	0.01	0.0290	0.0014
CaO-A(800)-P-3%	7.2<H ₋ <9.8	0.059	0.0505	0.0545	0.0069
CaO-A(800)-P-5%	7.2<H ₋ <9.8	0.0775	0.0775	0.0775	0.0021

It was found that all of the extruded CaO catalysts exhibited the basic strength in the range of 7.2 to 9.8. There was no change of the color indicator in the higher indicator range ($H_{>9.8}$) for all extruded CaO samples. The total basicity of the extruded CaO-A catalysts using different calcination temperatures of 700, 800 and 900°C were 0.0036, 0.0457 and 0.0147 mmol/g.cat while total basicity of the extruded CaO-A catalysts using different CaO: binder ratios of 1: 1, 3: 1, 3.5: 1 and 6: 1 were 0.036, 0.0457, 0.1512 and 0.0337 mmol/g.cat, respectively. The total basicity using different binder for CaO-A(800), CaO-D(800) and CaO-K(800) were 0.0457, 0.0125 and 0.0175 mmol/g.cat, respectively. The total basicity of CaO-A(800) was higher compared to the CaO-A(700) and CaO-A(900) with similar CaO: binder ratio of 3: 1. This could be due to the high concentration of CaO phase as active species as corresponding to TGA results. In addition, it was found that at a CaO: binder of 3.5: 1, the total basicity of CaO-A(800) was the highest value (Table 4.4). In contrast to, the total basicity of CaO-D(900) catalysts was 0.0215 mmol/g.cat which was greater than that of CaO-D(800) with similar CaO: binder ratio of 3: 1. This can be described by the TGA result of uncalcined CaO-D sample. The constant weight loss was observed at the temperature greater than 900°C resulting from more CaO species for CaO-D(900) sample. In addition, using polyacrylamide as a pore forming agent was found the order of total basicity for CaO-A(800)-P-1%, CaO-A(800)-P-3% and CaO-A(800)-P-5% were 0.029, 0.0545 and 0.0515 mmol/g.cat, respectively. The total basicity of CaO-A(800)-P-3% and CaO-A(800)-P-5% were greater than the bare CaO-A(800) which was probably due to their higher surface area, pore volume and average pore size. The basicity, surface area, pore volume and average pore size values obtained from the previous result showed similar trend [55]. The calcination temperature can affect the total basicity of the extruded CaO catalyst due to the formation of the distribution CaO from CaCO₃ as shown in Table 4.4.

4.2 Catalytic activity of the extruded CaO catalysts via transesterification of palm oil

4.2.1 Effect of different binders of the extruded CaO catalysts on the catalytic activity of transesterification

Figure 4.9 exhibits the catalytic performance of the extruded CaO catalysts using different binders via transesterification of palm oil using similar operating condition.

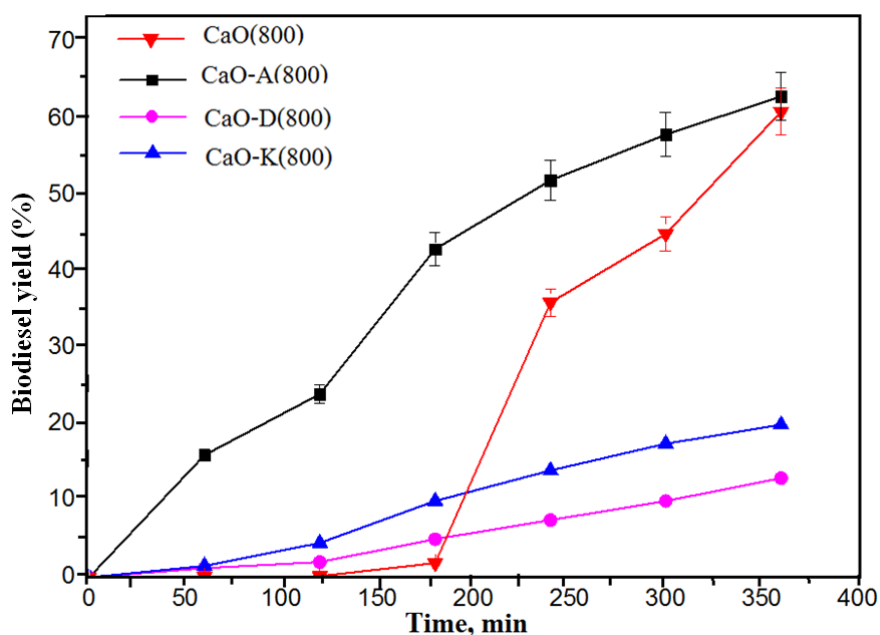


Figure 4.9 Catalytic activity of the CaO-A, CaO-D and CaO-K catalysts for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1, and catalyst loading 10 wt%.

The catalytic activity of CaO powder was also investigated for the comparison. It was not surprising that using the extruded CaO with all binders can reduce the induction period as found in the initial stage of transesterification as can be seen in the transesterification profile obtained from CaO powder. The reason should be due to the CaO-A catalyst have the larger surface area with mesoporous structure to overcome the internal diffusion limitation as observed when using CaO powder catalyst [56]. Moreover, CaO-A also provided the similar biodiesel yield (63.12%) as well as using CaO powder at reaction time of 360 min. While using CaO-D and CaO-K catalyzed transesterification gave the lower biodiesel yield at the reaction time of 360 min

as compared to using CaO powder as a catalyst. This could be described by the total basicity of CaO-D and CaO-K catalysts which were 4 times lower than that of CaO powder.

4.2.2 Effect of calcination temperatures of the extruded CaO using Al_2O_3 as a binder on the catalytic activity of transesterification

Figure 4.10 exhibits the catalytic performance of the extruded CaO catalysts with different calcination temperature via transesterification of palm oil using similar operating condition.

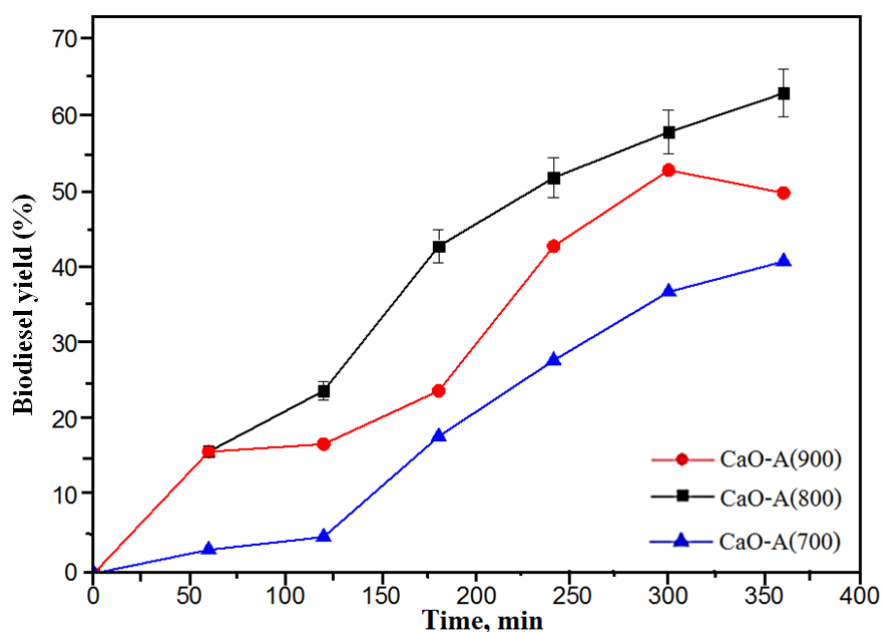


Figure 4.10 Catalytic activity of the CaO-A catalysts using different calcination temperatures (700, 800 and 900°C) for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt%.

According to Figure 4.10, this indicated that the extruded CaO at calcination temperature of CaO-A(800) provided the highest biodiesel (63.12%) than CaO-A(900) and CaO-A(700). At calcination temperature of 800°C, the highest biodiesel yield was achieved because this CaO-A(800) showed the highest total basicity, surface area, pore volume and average pore size to facilitate the triglyceride to react with methanol. The calcination temperature has remarkable effect on the catalytic activity of the extruded CaO catalyst. For CaO-A, the biodiesel yield was increased when increasing the calcination temperature from 700 to 800°C. However,

biodiesel yield was decreased when the calcination temperature further increased to 900°C. It could be due to the sintering of particles was more dominated resulting in lowered biodiesel yield even through this extrudes CaO catalyst composed of CaO as an active species. Umdu and Seker [10] also reported that the CaO catalyst with the highest total basicity with a comparable basic strength gave the highest biodiesel yield. The effect of calcination temperature on the catalytic activity of CaO-D was also investigated as presented in Figure 4.11.

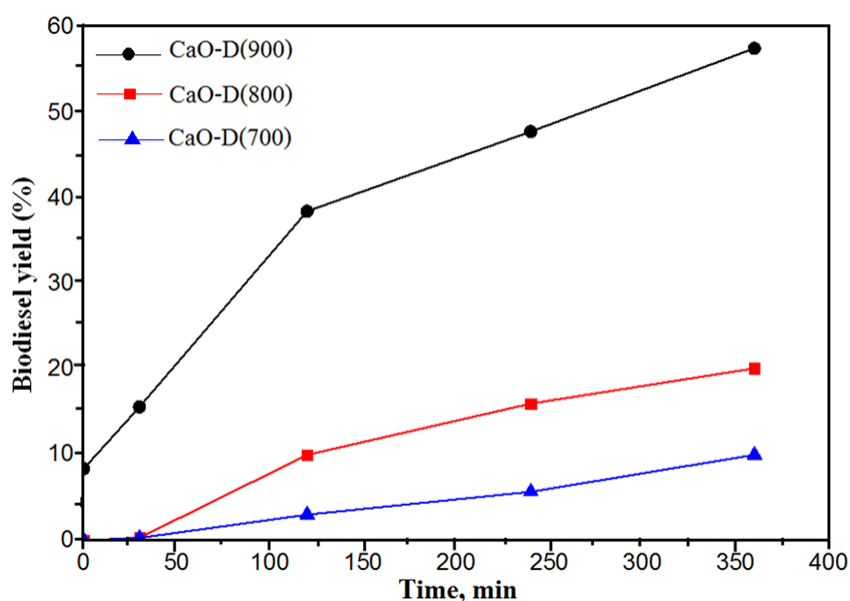


Figure 4.11 Catalytic activity of the CaO-D catalysts using different calcination temperatures (700, 800 and 900°C) for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt%.

Based on the TGA results that the optimum calcination temperature of CaO-D should be greater than 900°C. Therefore, the effect of calcination temperature on the catalytic activity of CaO-D was also investigated as presented in Figure 4.11. Biodiesel yield using CaO-D catalyst was increased with an increase in the calcination temperature. The evidence was corresponding to TGA results that the higher calcination temperature of the extruded CaO using diatomite binder can obtain the complete calcination process to generate CaO as an active species resulting in higher total basicity and biodiesel yield. Furthermore, the biodiesel yield of CaO-K(800) catalyst was lowest compared to the other binder which was strongly related to the total basicity. The extruded CaO-D required the higher calcination temperature from 900°C to generate the CaO phase (Figure 4.1) providing the higher basicity. Therefore, CaO-D(800) was lowest total basicity

(Table 4.4). This can be concluded that for the calcination temperature in the range of 700-900°C, the activated alumina was a suitable binder to prepare the extruded CaO catalyst.

4.2.3 Effect of mass ratio of CaO: Al₂O₃ binder on the catalytic activity of the extruded CaO via transesterification

The previous results confirmed that the presence of high concentration CaO species can increase the basicity resulting in increasing biodiesel yield. Therefore, the effect of mass ratio of CaO: Al₂O₃ was further investigated as illustrated in Figure 4.12.

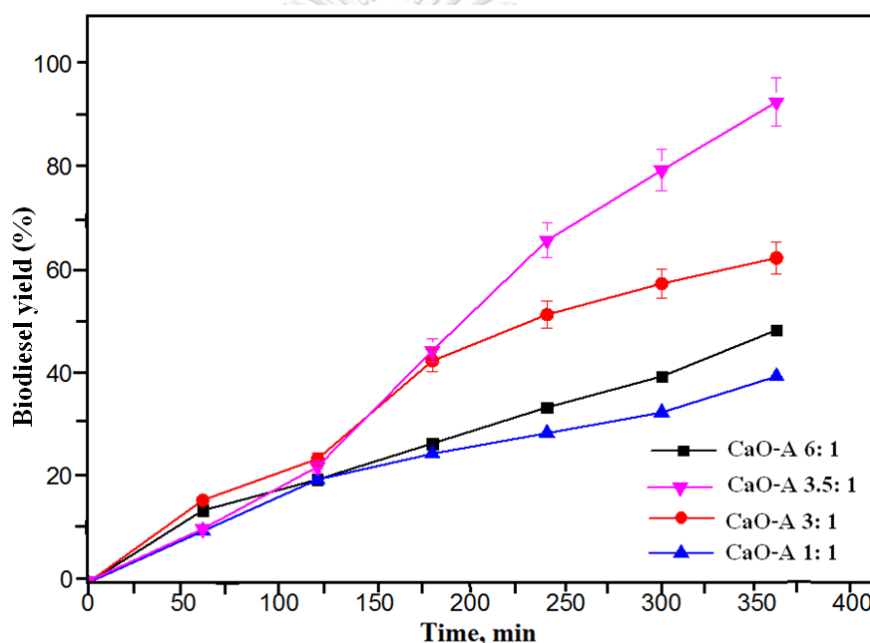


Figure 4.12 Catalytic activity of CaO-A using different mass ratio of CaO to Al₂O₃ at 1: 1, 3: 1, 3.5: 1 and 6: 1 via transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt%.

It was found that biodiesel yield was increased from 40.73 to 93.15% with the increase of CaO: Al₂O₃ binder mass ratio increases from 1: 1 to 3.5: 1. On the other hand, when the CaO to Al₂O₃ mass ratio was further increased to 6: 1, biodiesel yield was decreased to 49.00%. This finding could be attributed to the increase in CaO mass ratio to 6: 1 resulting to generate more agglomeration of CaO species. The available CaO active species was more likely to decrease

leading to decrease in biodiesel yield [57]. This can be noted that the optimum mass ratio of CaO to Al_2O_3 to prepare the extruded CaO catalyst was 3.5: 1.

4.2.4 Effect of different shapes on the catalytic activity of the extruded CaO catalysts via transesterification

Figure 4.13 exhibits the catalytic performance with different shapes of the extruded CaO-A(800) via transesterification of palm oil using similar operating condition.

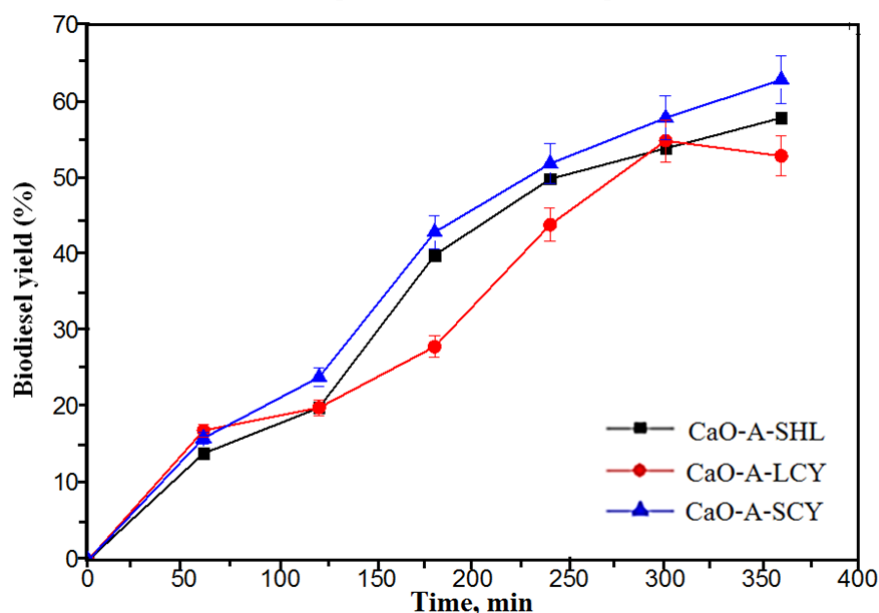


Figure 4.13 Catalytic activity of different shapes of the extruded CaO-A(800) for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt%.

Transesterification was carried out at 65°C under atmospheric pressure, oil: methanol equal to 1: 3 molar ratio using different shape of CaO-A(800) including of short cylindrical shape (SCY), long cylindrical shape (LCY) and spherical shape (SHL). It can be observed that there was no induction period on the biodiesel profile for all catalyst shapes. From this result, it can be explained that the extruded CaO catalyst can overcome the mass transfer limitation in term of the internal diffusion of CaO powder. Biodiesel yield of CaO-A(SCY) was highest compared to that of CaO-A(LCY) and CaO-A(SHL). The order of biodiesel yield at the reaction time of 360 min was 63.12, 53 and 58% for CaO-A(SCY), CaO-A(LCY) and CaO-A(SHL), respectively. This indicated that catalyst shapes might not significantly have effect on the catalyst activity but it

could affect the stability for long run or reusability. Cao et al. [58] investigated the effect of size and shape on the catalytic performances of oxidation and reduction reactions using nano-catalysts for various reactions. The oxidation of benzylic alcohol using Au nanoparticles catalyst was found that the size of the catalyst was strongly effect on the catalytic activity than that of the catalyst's shape. In addition, Lee et al. [59] reported that the catalytic activity of a catalyst is depended on the particle size. The smaller catalyst particles are supposed to demonstrate a higher reaction rate owing to an increase in the external surface area available. On the other hand, the bigger the particle size of a solid, the smaller the surface area available for the reaction to take place, and the reduction in the number of collisions between the molecules (solid-liquid phase) during the transesterification. Therefore, the size of catalyst is more dominate preparation parameter than that of catalyst shape in term of catalytic activity.

4.2.5 Effect of pore forming agent concentration on the catalytic activity of the extruded CaO catalysts via transesterification

Using pore forming agent can increase the pore volume during calcination, the pore forming agent was decomposed or burned to generate some gases and vaporize to the atmosphere. Then, the catalyst matrix expanded resulting to increase the pore of the extruded catalyst. The catalytic performance of the CaO-A(800) catalyst with different pore forming concentration are shown in Figure 4.14.

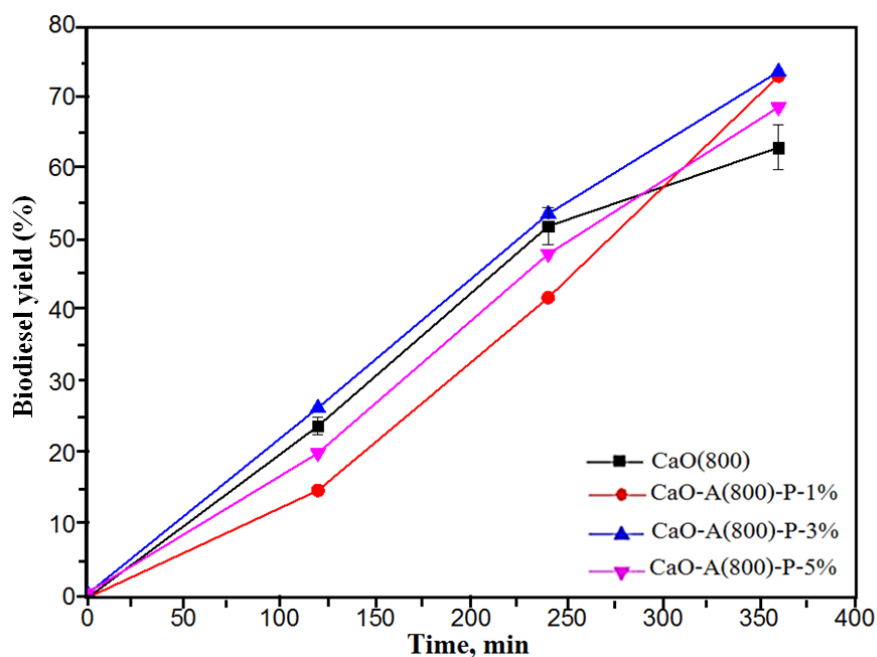


Figure 4.14 Catalytic activity of the extruded CaO-A(800) catalysts using various pore forming concentration (1, 3 and 5%) for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt%.

Biodiesel yield at the reaction time of 360 min for all the CaO-A(800)-P-1%, CaO-A(800)-P-3% and CaO-A(800)-P-5% were higher than that of CaO-A(800) catalyst. It indicates that the using polyacrylamide as a pore-forming agent can increase the catalytic activity of the extruded CaO-A catalyst via transesterification. Owing to the mechanism of pore forming agent with the expansion of pore size resulted to increase the distribution of CaO as an active species leading to increase biodiesel yield as compared to CaO-A(800) [60]. This explanation was also corresponding to the total basicity of CaO-A (800)-P-3% which was the highest total basicity. Increase the concentration of polyacrylamide from 1 to 3%, biodiesel yield was significantly increased especially during the reaction time less than 240 min. However, the obtained biodiesel yield at 360 min was no significant different for CaO-A(800)-P-1%, CaO-A(800)-P-3% and CaO-A(800)-P-5% catalysts with 73.00, 73.63, and 68.65%, respectively. The textural properties of the extruded CaO catalysts with addition of polyacrylamide from the BET model analysis were summarized in Table 4.3. The results indicated that the average pore size of CaO-A(800)-P-1, 3

and 5% were higher than that of the CaO-A(800). Especially, CaO-A(800)-P-3% was the highest uniform average pore size compared to the other extruded CaO catalysts (Figure 4.8). This can be concluded that using polyacrylamide as pore-forming agent can help increase the porosity to facilitate the adsorption of reactant to reach an active site and desorption of product based on the heterogeneous catalyzed transesterification [4, 61] The values of powder, CaO-A(800) and CaO-A(800)-P-1, 3, 5% catalysts determined by Hammett indicator method were also supported this evidence as increase in the total basicity.

4.2.6 Reusability, regeneration and leaching test for CaO-A(800) catalyzed transesterification

Reusability test of CaO-A(800) catalyst was performed by washing the CaO-A catalyst with methanol 3 times. The used CaO-A(800) was separated from the reaction mixture and place in the close vessel. Then methanol was added and stirred for 20 min. This stage was repeated for three times to obtain the clear solution. After that, the catalyst was dried at 100°C for 2 h to remove the methanol and water. The pretreatment CaO-A(800) was further used for the next run. Reusability experiments were also carried out to investigate the stabilities of the CaO-A(800) as shown in Figure 4.15.

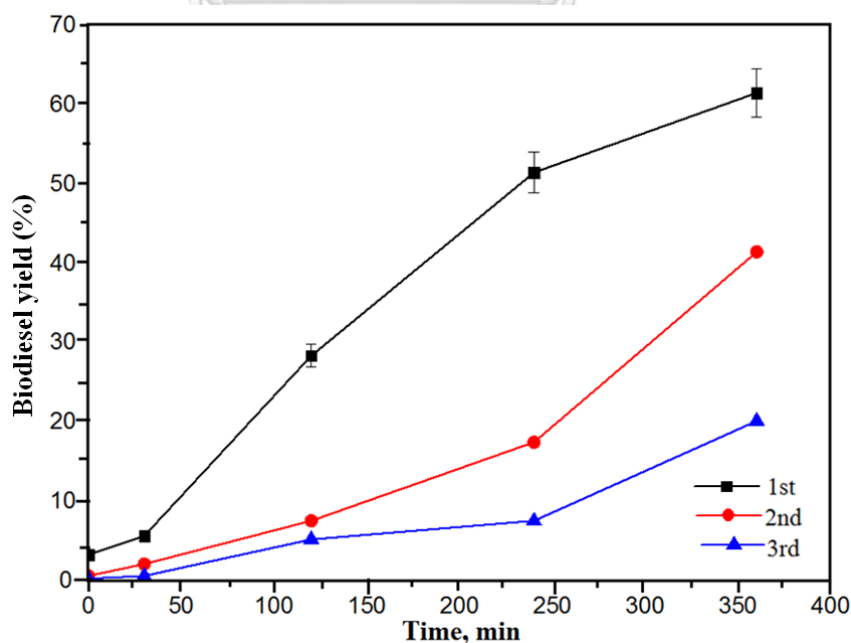


Figure 4.15 Reusability test of the extruded CaO-A(800) catalyzed transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt%.

Biodiesel yield of CaO-A(800) catalyst was decreased from 63.12 to 41.50% after the second run. At the 3rd run, the biodiesel yield was remarkably decreased to 20.11%. This could be due to the deactivation of the extruded CaO catalyst by reaction mixture blocking of the active sites and/or leaching of active species as usually found during CaO catalyzed transesterification [62]. To determine the deactivation cause of this CaO-A(800) catalyst, the regeneration and leaching test for the catalytic activity of the extruded CaO catalyst was performed as presented in Figure 4.16 The catalyst regeneration was obtained by washing the used CaO-A(800) with methanol for three times and the resulting catalyst was calcined at 800°C for 5 h. While the leaching test was performed by stirring the fresh CaO-A(800) with the desired amount of methanol used for transesterification. Then, the catalyst was separated from the methanol solution. The resulting solution was mixed with palm oil to carry out transesterification at the reaction temperature of 65°C. This was found that biodiesel yield using the regenerated CaO-A(800) was higher than that for the 2nd run but it was still lower as compared to the 1st run. These results indicated that the regeneration process can remove some adsorption species from the CaO-A(800). However, there was any adsorption species accumulated in the pore of CaO-A(800) catalyst resulting to lower biodiesel yield than that of fresh CaO-A(800). In addition, the weight of the regenerated catalyst was greater than that of fresh catalyst indicated that the accumulation of the reaction mixture on the CaO-A(800) catalyst. Leaching test of CaO-A(800) catalyzed transesterification was confirmed that the deactivation cause of this extruded CaO-A(800) was not due to the leaching of Ca as an active species. Biodiesel yield less than 5% was obtained from the transesterification of resulting methanol with palm oil in absence of CaO-A(800) catalyst. Udaykumar et al. [63] also confirmed that the leaching of Ca species was negligible. Only 3.13 mg of the CaO catalyst was loss during the reusability process. This can be concluded that the deactivation of the extruded CaO catalyst using Al₂O₃ binder was more likely due to the adsorption of the reaction mixture on the active site as well as pore blocking. This finding was corresponding to Argyle et al. work to prepare zeolite extrudes catalyzed transesterification of vegetable oil [64, 65].

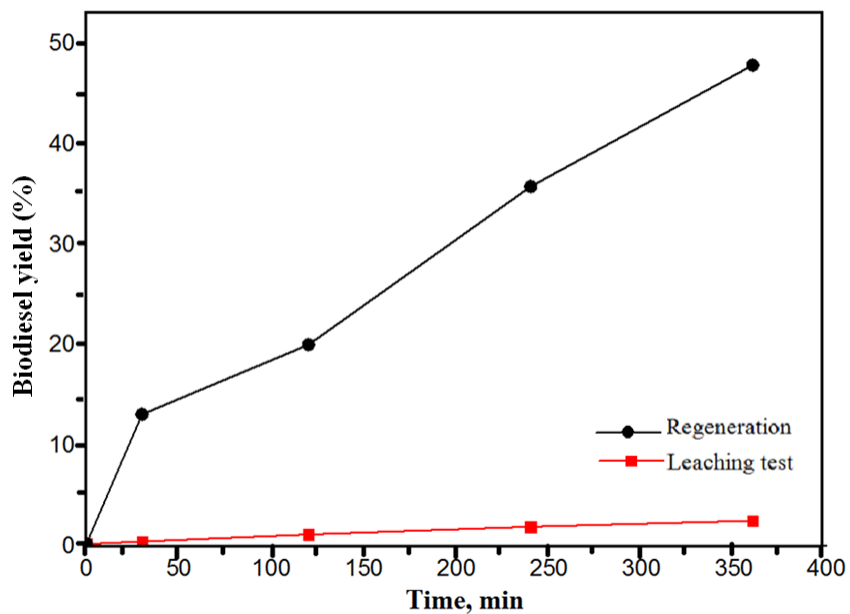


Figure 4.16 Regeneration and leaching of the extruded CaO-A catalysts calcination temperatures 800°C for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 catalyst loading 10 wt%.

4.2.7 Catalytic activity of the extruded CaO catalysts in a basket reactor using different stirrer speeds

Catalytic activity of the extruded CaO catalyst in a basket reactor was investigated to decrease the catalyst broken from mechanical force as obtained using magnetic stirrer.

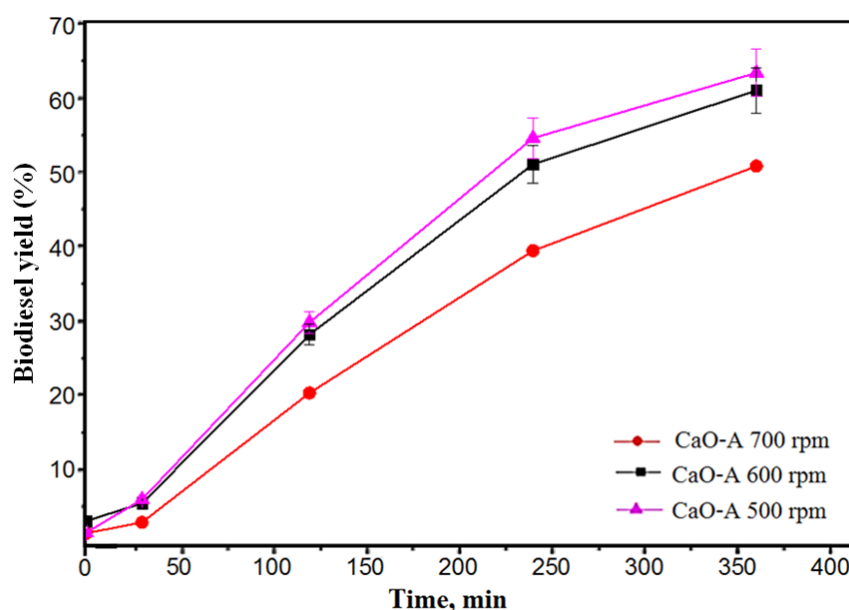


Figure 4.17 Catalytic activity of the extruded CaO catalysts for transesterification using reaction temperature of 65°C, methanol to oil molar ratio of 12: 1 and catalyst loading 10 wt% in a basket reactor using different stirrer speed (500, 600 and 700 rpm).

Catalytic activities of CaO-A(800) catalyzed transesterification in a basket reactor using different stirrer speed are illustrated in Figure 4.17. Biodiesel yield was 61.56% using stirrer speed of 600 rpm. When the stirrer speed was reduced, biodiesel yield was slightly increased from 61.56 to 63.95% for the stirrer speed of 600 and 500 rpm, respectively. This observation was different from biodiesel production in a batch reactor experiment. However, the increase of stirrer speed to 700 rpm, biodiesel yield was reduced to 51.32%. This should be due to the higher stirrer speed resulted to increase the shear force leading to increase the local temperature and the cyclone shape of fluid [66]. The higher local temperature gave the higher vaporization of methanol which was lower methanol to oil molar ratio in the liquid phase. While cyclone shapes of fluid rotation could reduce the residence time of reactant which gave the negative effect in the biodiesel yield. Roy et al. [67] also mentioned that the increase of excessive

speed, the production of biodiesel was declining and fluctuation. This is due to the fact that increasing stirrer speed enhances the volatility of alcohol which acts as a reactant as well as medium for the transesterification. Vaporization of methanol from the reaction system not only decreases the amount of one of the reactants but also hampers the proper ratio of alcohol to triglyceride in the reaction mixture. It has also been observed from this finding that at the stirrer speed of 600 rpm, the yield of biodiesel was optimum stirrer speed for biodiesel production in a basket reactor.



Chapter 5

Conclusion and recommendations

5.1 Conclusion

This work investigated the preparation parameters for synthesizing the extruded CaO catalyst. The binder, guar gum and silica sol were used as an ingredient to produce the extruded CaO catalysts. The effect of calcination at temperature of 700, 800, and 900°C, the effects of different binders (activated alumina, diatomite and kaolin), the effects of shape of the extruded CaO catalyst of SCY, LCY and SHL and addition of pore forming (polyacrylamide) with concentration of 1, 3 and 5 wt% were studied for the catalytic activities of extruded CaO catalyst via transesterification. The reaction was performed in a batch reactor using stirring speed 600 rpm which was fixed at a ratio of methanol to palm oil of 12 to 1 using 10 wt% catalyst loading, the reaction temperature of 65°C, for 6 h. Moreover, the characterization results of TGA, XRD, FT-IR, SEM/EDX basic strength, and total basicity of the extruded CaO catalyst were also studied. In addition, reusability, regeneration, leaching test and the catalytic activity in a basket reactor using different stirrer speed for the extruded CaO catalyst were also investigated.

The extruded CaO-A(800) using CaO: binder (3.5: 1) and calcination temperature at 800°C provided the highest biodiesel of 93.15%. While the extruded CaO using diatomite and kaolin as binder to catalyze transesterification gave the lower biodiesel yield as compared to using extruded CaO-A catalyst. Because the total basicity, the surface area and pore volume of CaO-D and CaO-K catalysts were lower than that of CaO-A catalyst. In addition, the calcination temperature has a remarkable effect on the catalytic activity of the extruded CaO catalyst for all binder types. For CaO-A catalyst, the biodiesel yield was decreased when the calcination temperature further increased to 900°C. It could be because the sintering of particles had more dominated effect resulting in lowered biodiesel yield. While CaO-D(900) catalyst, provided the higher biodiesel (57%) than that of CaO-D(700) and CaO-D(800) catalysts because of the total basicity for CaO-D(800) catalyst resulting in lowered biodiesel yield. Al₂O₃ was a most suitable binder to prepare the extruded CaO catalyst. For the effect of the mass ratio of CaO to binder on the catalytic activity, the biodiesel yield was increased with the increase CaO: binder mass ratio increases from 1: 1 to 3.5: 1. On the other hand, when the CaO: mass ratio was further increased to 6: 1, biodiesel

yield was decreased for all binders. This finding could be attributed to the increase in CaO mass ratio to 6: 1 resulting in generation of more agglomeration of CaO species. The available CaO active species was more likely to be lower leading to a decrease in biodiesel yield. This can be noted that the optimum mass ratio of CaO to binder to prepare the extruded CaO catalyst was 3.5: 1. The above results were consistent with the predicted response, showing good agreement with the experimental results.

Using polyacrylamide as a pore forming agent can increase the surface area and pore volume during calcination which can provide the higher biodiesel yield due to the uniform CaO distribution. The short cylindrical shape of the extruded CaO catalyst gave the highest biodiesel (63.12%).

In addition, the biodiesel yield of CaO-A(800) catalyst was decreased from 63.12 to 41.50% after the second run. In the third run, the biodiesel yield was remarkably decreased to 20.11%. Owing to the deactivation of the extruded CaO catalyst was more likely due to the adsorption of the reaction mixture on the active site as well as pore blocking.

5.2 Recommendations

From the experimental results, the following recommendations are suggested:

5.2.1 The cylindrical catalyst shaping process should be performed by controlling the force for extruding catalyst paste into the extruder to obtain the uniform shape and size.

5.2.2 The extruded CaO should be further investigated the catalytic activity in the pack bed reactor for commercial process.

5.2.3 Biodiesel yield obtained from the extruded CaO catalyzed transesterification did not conform to EN 14103 standard. Therefore, the enhancement of the catalytic activity of the extruded CaO with addition of co-metal (Cu, Co, Fe, Ni) should be further studied.

REFERENCES



จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

- [1] Hong J., Uncertainty propagation in life cycle assessment of biodiesel versus diesel: global warming and non-renewable energy. *Bioresource Technology* 2012; 113: 3-7.
- [2] Masjuki H., Abul K., An overview of biofuel as a renewable energy source: development and challenges. *Procedia Engineering* 2013; 56: 39-53.
- [3] Huang D., Zhou H., Lin L., Biodiesel: an alternative to conventional fuel. *Energy Procedia* 2012; 16: 1874-1885.
- [4] Mardhiah H., Ong C., Masjuki H., Lim S., Lee V., A review on latest developments and future prospects of heterogeneous catalyst in biodiesel production from non-edible oils. *Renewable and Sustainable Energy Reviews* 2017; 67: 1225-1236.
- [5] Vasić K., Podrepšek G.H., Knez Ž., Leitgeb M., Biodiesel production using solid acid catalysts based on metal oxides. *Catalyst* 2020; 10(237): 1-20.
- [6] Kouzu M., Hidaka J., Transesterification of vegetable oil into biodiesel catalyzed by CaO: A review. *Fuel* 2012; 93: 1-12.
- [7] Walter S., Malmberg S., Schmidt B., Liauw M., Mass transfer limitations in microchannel reactors. *Catalysis Today* 2005; 110: 15-25.
- [8] Wang S., Shan R., Wang Y., Lu L., Yuan H., Synthesis of calcium materials in biochar matrix as a highly stable catalyst for biodiesel production. *Renewable Energy* 2019; 130: 41-49.
- [9] Lu P., Wang H., Hu K., Synthesis of glycerol carbonate from glycerol and dimethyl carbonate over the extruded CaO-based catalyst. *Chemical Engineering Journal* 2013; 228: 147-154.
- [10] Jindapon W., Kuchonthara P., Ngamcharussrivichai C, Biodiesel production over Ca, Zn, and Al mixed compounds in fixed-bed reactor: effects of premixing catalyst extrudates with methanol, oil and fatty acid methyl esters. *Fuel Processing Technology* 2016; 148: 67-75.
- [11] Silveira E., Haber J., Perez-Inés R., Serrano-L.A., Rodriguez O., Biodiesel production from heterogeneous catalysts based K_2CO_3 supported on extruded $\gamma-Al_2O_3$. *Fuel* 2019; 241: 311-318.

- [12] Ivana L., Zeljka K., Miodrag Z., Ljiljana M., Dejan S., Calcium oxide based catalysts for biodiesel production: A review *Chemical Industry and Chemical Engineering Quarterly* 2016; 10: 391-408.
- [13] Balat M., Production of Biodiesel from vegetable oils: A survey. *energy sources, part A: recovery, utilization, and environmental effects* 2007; 29(10): 895-913.
- [14] Meemuk B., Production of biodiesel from palm fatty acid distillate using chitosan membrane reactor. Master of Science Thesis, Chulalongkorn University 2011.
- [15] Chokchai M., Ruamporn N., Feasibility study of biodiesel production from waste coffee grounds oil. Master of Science Thesis, Thaksin University 2017.
- [16] Sittikan R., Biodiesel production using polymer-supported phase transfer catalyst Master of Materials Science and Engineering Thesis, Silpakorn University 2011.
- [17] Kouzu M., Kasuno T., Tajika M., Sugimoto Y., Yamanaka S., Hidaka J., Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. *Fuel* 2008; 87(12): 2798-2806.
- [18] Kawashima A., Matsubara K., Honda K., Acceleration of catalytic activity of calcium oxide for biodiesel production, *Bioresource Technology* 2009; 100(2): 696-700.
- [19] Thammachai P., Transesterification reaction of palm oil under ethanol using impregnated calcium oxide as solid base catalyst. Master of Engineering Thesis, Chemical Engineering, Chulalongkorn University 2011.
- [20] Barekati-Goudarzi M., Boldor D., Nde B., In-situ transesterification of seeds of invasive Chinese tallow trees (*Triadica sebifera* L.) in a microwave batch system (GREEN⁽³⁾) using hexane as co-solvent: Biodiesel production and process optimization. *Bioresource Technology* 2016; 201: 97-104.
- [21] Katnanipa W., Petpilin P., Synthesized heterogeneous catalysts including of KI, CaO, and Al₂O₃ used for transesterification of palm oil and methanol. *Science and Technology* 2015; 41: 176-182.
- [22] Umdu S., Seker E., Transesterification of sunflower oil on single step sol-gel made Al₂O₃ supported CaO catalysts: effect of basic strength and basicity on turnover frequency. *Bioresource Technology* 2012; 106: 178-181.

- [23] Taufiq-Yap H., Lee V., Hussein Z., Yunus R., Calcium-based mixed oxide catalysts for methanolysis of *Jatropha curcas* oil to biodiesel. *Biomass and Bioenergy* 2011; 35(2): 827-834.
- [24] Zhu H., Wu Z., Chen Y., Zhang P., Duan S., Liu X., I. Preparation of biodiesel catalyzed by solid Super base of calcium oxide and its refining process. *Chinese Journal of Catalysis* 2006; 27(5): 391-396.
- [25] Lee V., Juan C., Taufiq H., Preparation and application of binary acid–base CaO–La₂O₃ catalyst for biodiesel production. *Renewable Energy* 2015; 74: 124-132.
- [26] Puna F., Correia N., Dias S., Gomes J., Bordado J., Biodiesel production from waste frying oils over lime catalysts. *Reaction Kinetics, Mechanisms and Catalysis* 2013; 109(2): 405-415.
- [27] Ozkan S., Puna F., Gomes F., Cabrita T., Palmeira V., Santos T., Preliminary study on the use of biodiesel obtained from waste vegetable oils for blending with hydrotreated kerosene fossil fuel using calcium oxide (CaO) from natural waste materials as heterogeneous catalyst. *energies* 2019; 12(22): 1-22.
- [28] Cho B., Seo G., High activity of acid-treated quail eggshell catalysts in the transesterification of palm oil with methanol. *Bioresource Technology* 2010; 101(22): 8515-8519.
- [29] Saengsawang J., Pelletization of nickel catalyst for hydrogen production from glycerol steam reforming. Master of Engineering Thesis, Chemical Engineering, Chulalongkorn University 2019.
- [30] Islam A., Taufiq H., Ravindra P., Teo H., Sivasangar S., Chan S. Biodiesel synthesis over millimetric γ -Al₂O₃/KI catalyst. *Energy* 2015; 89: 965-973.
- [31] Misono M., Basis of heterogeneous catalysis. in: heterogeneous catalysis of mixed oxides - perovskite and heteropoly Catalysts; 2013; 12(9)1-23.
- [32] Mekhilef S., Siga S., Saidur R., A review on palm oil biodiesel as a source of renewable fuel. *Renewable and Sustainable Energy Reviews* 2011; 15(4): 1937-1949.
- [33] Silalertruksa T., Bonnet S., Gheewala H., Life cycle costing and externalities of palm oil biodiesel in Thailand. *Journal of Cleaner Production* 2012; 28: 225-232.

- [34] Jakkrapong L., Napaphat S., Biodiesel production from canola oil and methanol using Ba impregnated calcium oxide with microwave irradiation-assistance. *Chiang Mai Journal. Science* 2019; 46(5): 987-1000.
- [35] Makwaya M., Synthesis and characterization of polysaccharide/TiO₂/Fe₃O₄ nanocomposite materials for photocatalytic antimicrobial application *Science in chemistry the university of dodoma* 2018; 17: 36-38, 98-105.
- [36] Sharifah M., Zulkifly J., study of calcination condition on decomposition of calcium carbonate in waste cockle shel to calcium oxide using thermal gravimetric analysis. *ARPN Journal of engineering and applied sciences* 2016; 11(16): 9927-9921.
- [37] Rivas Mercury M., De H., Pena P., Synthesis of CaAl₂O₄ from powders: Particle size effect. *Journal of the European Ceramic Society* 2005; 25(14): 3269-3279.
- [38] Joseph M., Bruce R., *Thermal analysis of polymers*. a john wiley & sons, INC, publication 2009; 57: 1-208.
- [39] Chu H., Vinoba M., Bhagiy M., Hyun B., Nam C., Yoon Y., CO₂ mineralization into different polymorphs of CaCO₃ using an aqueous-CO₂ system. *RSC Advances* 2013; 3(44): 44-57.
- [40] Biasin A., Segre U., Strumendo M., CaCO₃ crystallite evolution during CaO carbonation: critical crystallite size and rate constant measurement by in-situ synchrotron radiation x-ray powder diffraction. *Crystal growth & design* 2015; 15(11): 5188-5201.
- [41] Berent K., Komarek S., Lach R., Pyda W., The Effect of calcination temperature on the structure and performance of nanocrystalline mayenite powders. *Materials (Basel)* 2019; 12(21): 35-39.
- [42] Balwant C., Peter V., Robert G., Detection of amorphous alumino-silicate by X-ray diffraction and chemical analysis to detect firing in archaeological sediments author. *Archaeology in Oceania*, 1991; 26(1): 17-20.
- [43] Tangboriboon N., Khongnakhon T., Kittikul S., Kunanuruksapong R., Sirivat A. An innovative CaSiO₃ dielectric material from eggshells by sol-gel process. *Journal of Sol-Gel Science and Technology* 2010; 58(1): 33-41.

- [44] Dalibor M., Milorad C., The synthesis of CaO loaded onto Al₂O₃ from calcium acetate and its application in transesterification of the sunflower oil, *Advanced Technologies* 2015; 4: 26-32.
- [45] Mines P., *Industrial Minerals-HandBook*. 2007; 271: 57-131.
- [46] Rashid R., Shamsudin R., Abdul A., Jalar A., Low temperature production of wollastonite from limestone and silica sand through solid-state reaction. *Journal of Asian Ceramic Societies* 2018; 5(4): 77-81.
- [47] Lee C., Lin W., Lu H., Chen J., Lee H., Influence of SiO₂ addition on the dielectric properties and microstructure of (Ba_{0.96}Ca_{0.04})(Ti_{0.85}Zr_{0.15})O₃ Ceramics. *International Journal of Applied Ceramic Technology* 2009; 6(6): 692-701.
- [48] Wu D., Song L., Zhang B., Li Y., Effect of the mechanical failure of catalyst pellets on the pressure drop of a reactor. *Chemical Engineering Science* 2003; 58(17): 3995-4004.
- [49] Kim H., Park S., Lee S., Characteristics of an extrusion panel made by applying a modified curing method. *materials (Basel)* 2016; 9(5): 55-67.
- [50] Dave E., High temperature sintering a cost effective way to future high performance materials. *Montréal, Canada* 2005; 5(4): 1-5
- [51] Wisniewska M., Chibowski S., Urban T., Sternik D., Terpilowski K., Impact of anionic polyacrylamide on stability and surface properties of the Al₂O₃-polymer solution system at different temperatures. *Colloid Polymer Science*. 2016; 294: 1511-1517.
- [52] Nitin J., Chang K., Umapada P., Jinheung K., Young K., Concentration and temperature effect on controlling pore size and surface Area of mesoporous titania by using template of F-68 and F-127 co-polymer in the sol-gel process. *Journal of Nanoscience and Nanotechnology* 2012; 12: 5638-5643.
- [53] Muttakin M., Mitra S., Thu K., Ito K., Saha B., Theoretical framework to evaluate minimum desorption temperature for IUPAC classified adsorption isotherms. *International Journal of Heat and Mass Transfer*. 2018; 122: 795-805.
- [54] Jörg P., Frank G., Robert S., Christian H. Pore structure and surface area of silica SBA-15: Influence of washing and scale-up. *Nanotechnol* 2011; 2, 110-118.

- [55] Charoenchaipet J., Piumsomboon P., Chalermssinsuwan B., Development of CO₂ capture capacity by using impregnation method in base condition for K₂CO₃/Al₂O₃. *Energy Reports* 2020; 6: 25-31.
- [56] Chawalit M., Anawat K., Kunn B., Preparation of heterogeneous catalysts from limestone for transesterification of vegetable oils—Effects of binder addition. *Journal of industrial and engineering chemistry* 2011; 17: 587-595.
- [57] Hangun-Balkir Y., Green biodiesel synthesis using waste shells as sustainable catalysts with camelina sativa oil. *Journal of Chemistry* 2016; 51-10.
- [58] Cao S, Tao F., Tang Y., Li Y., Yu J., Size- and shape-dependent catalytic performances of oxidation and reduction reactions on nanocatalysts. *Chem Soc Rev* 2016; 45(17): 4747-4765.
- [59] Lee V., Juan C., Binti F., Nizah R., Taufiq H., Heterogeneous base catalysts for edible palm and non-edible *Jatropha*-based biodiesel production. *Chemistry Central Journal* 2014; 8: 30.
- [60] Ismail S., Ahmed S., Anr R., Hamdan S., Biodiesel production from castor oil by using calcium oxide derived from mud clam shell. *Journal of Renewable Energy* 2016; 50(45): 1-8.
- [61] Naomi B., Klinghoffer C., Ange N., Towler F., Catalyst properties and catalytic performance of char from biomass gasification. *Chemical Society*, 2012; 51(40): 13113-13122.
- [62] Al-Muhtaseb H., Jamil F., Al-Haj .L, Myint T., Mahmoud E., Ahmad M., Biodiesel production over a catalyst prepared from biomass-derived waste date pits. *Biotechnology (Amst)* 2018; 51(40): 245-284.
- [63] Udaykumar A., Lakshaman J., Pinjari V., Pandit B. Efficacy of newly developed nano-crystalline calcium oxide catalyst for biodiesel production. *Chemical Engineering and Processing -Process Intensification* 2018; 133: 312-319.
- [64] Argyle M., Bartholomew C., Heterogeneous catalyst deactivation and regeneration: a review. *Catalysts* 2015; 5(1): 145-269.
- [65] Bingre R., Louis B, Nguyen P., An overview on zeolite shaping technology and solutions to overcome diffusion limitations. *Catalysts* 2018; 8(4): 35-46

- [66] Elijah A., Adesoji O., Musiliu S., Michael O., Design, construction and performance evaluation of a mini-scale batch reactor for biodiesel production: A case study of shea butter. *Science Technology* 2018; 40(5): 1066-1075.
- [67] Roy K., Datta S., Nandi S., Al Basir F., Effect of mass transfer kinetics for maximum production of biodiesel from *Jatropha Curcas* oil: A mathematical approach. *Fuel* 2014; 134: 39-44.



Appendix A

Calculation for catalyst preparation

The extrusion process in this work was done by preparation of CaO catalyst in a homogeneous paste comprised:

Step 1 physical mixing technique - a catalyst, binder, or pore forming agent are adequately mixed. The plasticizer is added subsequently to the powder mixture giving the paste form.

- 1) The binder 2.5 g was dried at 100°C for 12 h
- 2) Calcium carbonate was used as precursor of CaO as active species

$$\begin{aligned}
 & 1 \text{ mole CaO} = 1 \text{ mole CaCO}_3 \\
 \text{when } & \text{Mw CaO} = 56 \text{ g/mol, Mw CaCO}_3 = 100 \text{ g/mol} \\
 & \text{CaO } 7.5 \text{ g} / 56 \text{ g/mol} = 0.1339 \text{ mol} \\
 & 0.1339 \text{ mole CaO} = 0.1339 \text{ mole CaCO}_3 \\
 & \text{CaCO}_3 0.1339 \text{ mol} \times 100 \text{ g/mol} = 13.39 \text{ g}
 \end{aligned}$$

- 3) Guar gum powder 1 g
- 4) Silica sol as plasticizers lubricity 16 g
- 5) The addition of the pore-forming 1, 3 and 5%

Step 2 the mixture was loaded into a syringe and press compression for the extruded CaO catalyst. A piston of 6 mm diameter and 1.5 mm length as a size of short cylindrical (SCY) and 1 mm diameter and 10 mm length as size of long cylindrical (LCY). Spherical shape use a piston of 6 mm diameter was used to make spherical pellet forms (SHL) by spherical pellet forms by physical mixture method and extruded by JP table-type herbal coating herbal pellet making machine with diameter of 6 mm.

Step 3 The resulting sample was dried at 100°C for 2 h. The calcination at temperature of 700, 800 and 900°C were used for 5 h under static air using a heating rate of 5°C/min.

Appendix B

Experimental setup of conventional mechanical stirred and basket reactor

The method being described here is for transesterification of palm oil. The first step is to mix the methanol for reaction with the catalyst, typically a strong base such as CaO or ZnO. The methanol/catalyst is then reacted so that calcium methoxide compound ($\text{Ca}(\text{OCH}_3)_2$) is an active species accelerating transesterification. After oil was added in the reaction mixture at the temperature of 65°C , then a reaction was start at 0 min.

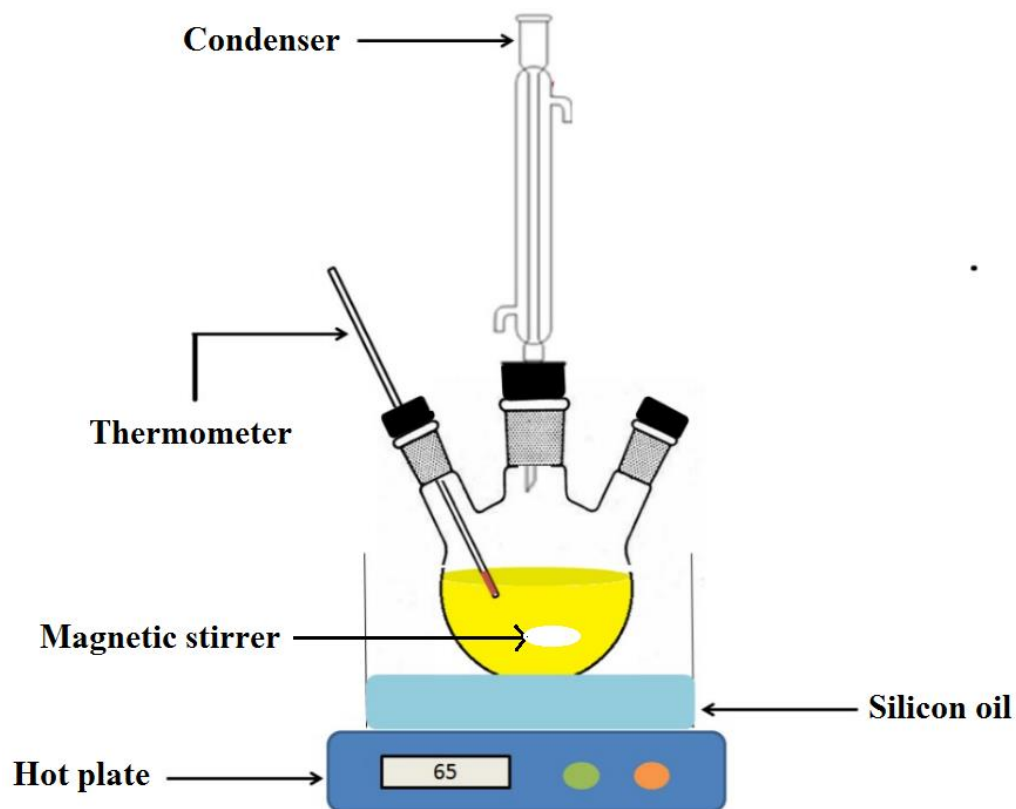


Figure B.1 Setup of conventional mechanical stirred reactor

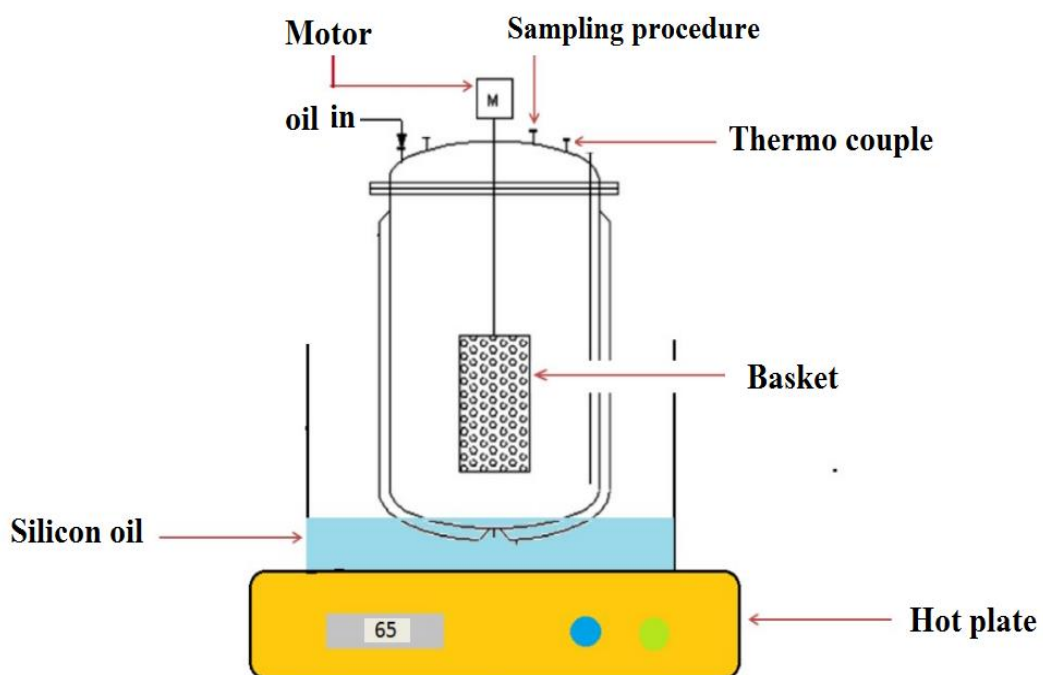


Figure B.2 Setup of basket reactor



Appendix C

Calculation the mass of oil, methanol and the extruded CaO catalyst

$$\text{From } \rho = \frac{M}{V}, M = \rho \times v \text{ and } n = \frac{M}{Mw}$$

V of round bottom 3-neck glass flask = 150 mL ($V_{\text{total}} = \frac{3}{4}$ in 3-neck glass flask) so that $V_{\text{oil}} = 50$ mL

Where M of oil (ρ of oil = 0.89 g/mL, $V_{\text{oil}} = 50$ mL)

$$M_{\text{oil}} = \rho \times V_{\text{oil}}$$

$$M_{\text{oil}} = (0.89 \text{ g/mL})(50 \text{ mL})$$

$$M_{\text{oil}} = 44.5 \text{ g}$$

Where n of oil (Mw of oil = 847 g/mol)

$$n_{\text{oil}} = \frac{M}{Mw}$$

$$n_{\text{oil}} = \frac{44.5}{847} = 0.0525 \text{ mol}$$

When the ratio of methanol to palm oil is 12 to 1, $n_{\text{MeOH}} = n_{\text{oil}} \times 12$

$$n_{\text{MeOH}} = n_{\text{oil}} \times 12$$

$$n_{\text{MeOH}} = (0.0525 \text{ mol})(12) = 0.63 \text{ mol}$$

Where $M_{\text{of methanol}}$ (Mw of methanol = 32.04 g/mol)

$$M_{\text{MeOH}} = n_{\text{MeOH}} \times Mw$$

$$M_{\text{MeOH}} = (0.63 \text{ mol})(32.04 \text{ g/mol}) = 20.19 \text{ g}$$

Where V_{MeOH} (ρ of methanol 0.792 g/mL)

$$\text{From } \rho = \frac{M}{V}, V_{\text{MeOH}} = \rho \times M$$

$$V_{\text{MeOH}} = \rho \times M$$

$$V_{\text{MeOH}} = (0.792 \text{ g/mL})(20.19 \text{ g}) = 15.99 \text{ mL}$$

Example of calculating the weight of catalyst of the reaction oil using 10% wt of catalyst content.

$$\text{When } M \text{ of oil } 44.5 \text{ g; catalyst weight} = (44.5 \text{ g})\left(\frac{10}{100}\right) = 4.45 \text{ g}$$

$$\text{Where } V_{\text{Tatol}} = V_{\text{oil}} + V_{\text{MeOH}}; V_{\text{Tatol}} = 50 \text{ mL} + 16 \text{ mL} = 66 \text{ mL}$$

Appendix D

Determination of crystallite size of CaO CaCO₃ and CaSiO₃

The crystallite size of CaO CaCO₃ and CaSiO₃ were determined by Debye Scherer formula is show in this below:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

D is the mean size of the ordered (crystalline) domains.

K is a dimensionless shape factor, with a value close to unity. The shape factor has a

typical value of about 0.9, but varies with the actual shape of the crystallite.

λ is the X-ray wavelength. (in the case of CuK α is 0.15405 nm)

β is the line broadening at half maximum intensity (FWHM),after subtracting the instrumental line ,in radians.

θ is the Bragg angle.

For example; The crystallite size of CaO-A(800)

When

$$K = 0.9$$

$$\lambda = 0.15405 \text{ nm}$$

$$\beta(\text{FWHM}) = 0.01983 \quad \beta \text{ in radian} = 3.46 \times 10^{-4}$$

$$2\theta = 32.6220 \quad 2\theta/2 = 16.31101$$

$$\theta \text{ in radian} = 0.2846$$

From

$$D = \frac{K\lambda}{\beta \cos \theta}$$

$$D = \frac{(0.9)(0.15405 \text{ nm})}{(0.000346 \text{ rad})(\cos 0.2846)} = 417.3576 \text{ \AA}$$

$$D = 41.73576 \text{ nm}$$

Table D.1 Crystallite size of CaO CaCO₃, Ca(OH)₂ and CaSiO₃

		rad					FWHM	FWHM rad	d in rad	ρ (Å)	D (nm)		
CaO-A(700)	CaO	32.3723	16.18615	0.282502	0.9	0.15405	32.07719	32.3723	32.9398	0.026646701	0.000465	310.4194	310.4194
	Ca(OH) ₂	34.2451	17.12255	0.298845	0.9	0.15405	33.9728	34.2451	34.71056	0.021543409	0.000376	385.8346	38.58346
	CaSiO ₃	30.1362	15.0681	0.262988	0.9	0.15405	30.0681	30.1362	30.23836	0.005649684	9.86E-05	1456.121	145.6121
CaO-A(800)	CaCO ₃	47.7337	23.86683	0.416555	0.9	0.15405	47.28126	47.73365	48.18605	0.018954951	0.000331	458.2748	45.82748
	CaO	32.6220	16.31101	0.284681	0.9	0.15405	32.33825	32.62202	32.9852	0.019831694	0.000346	417.3576	41.73576
	Ca(OH) ₂	34.2225	17.11125	0.298648	0.9	0.15405	33.9387	34.2225	34.5062	0.016582658	0.000289	501.2277	50.12277
CaO-A(900)	CaCO ₃	29.5619	14.78093	0.257976	0.9	0.15405	29.4552	29.56186	29.6981	0.008216668	0.000143	999.8751	99.98751
	CaO	32.4999	16.24995	0.283615	0.9	0.15405	32.2838	32.4999	32.8558	0.017600054	0.000307	470.1311	47.01311
	Ca(OH) ₂	34.0250	17.01249	0.296924	0.9	0.15405	33.7798	34.02497	34.2565	0.014010299	0.000245	592.9418	59.29418
CaO-D(800)	CaSiO ₃	29.9387	14.96935	0.261264	0.9	0.15405	29.8706	29.9387	30.0749	0.006823944	0.000119	1204.996	120.4996
	CaCO ₃	29.9262	14.9631	0.261155	0.9	0.15405	29.849	29.9262	30.03518	0.006221304	0.000109	1321.681	132.1681
	CaSiO ₃	29.1487	14.57435	0.25437	0.9	0.15405	28.9262	29.1487	29.3871	0.015812026	0.000276	519.0914	51.90914
CaO-D(900)	CaCO ₃	30.1022	15.0511	0.262691	0.9	0.15405	29.9432	30.1022	30.3405	0.013198371	0.00023	623.2563	62.32563
	CaSiO ₃	21.9342	10.9671	0.191412	0.9	0.15405	21.71169	21.9342	22.1566	0.020283849	0.000354	398.916	39.8916
	CaO	32.4699	16.23495	0.283353	0.9	0.15405	31.9773	32.4699	33.1532	0.036215079	0.000632	228.4601	22.84601
CaO-K(800)	CaCO ₃	29.6095	14.80475	0.258392	0.9	0.15405	29.3712	29.6095	29.7684	0.013414614	0.000234	612.507	61.2507
CaO-K(900)	Ca(OH) ₂	63.3780	31.689	0.553077	0.9	0.15405	62.9807	63.378	63.6004	0.009777841	0.000171	954.771	95.4771

Appendix E

Hammet indicator method

Basic strength and basicity of extruded CaO catalyst using Hammet indicator method was performed as shown below.

Step 1 extruded CaO catalyst 0.3 g was added into methanol 10 mL and left for 2 h to reach equilibrium.

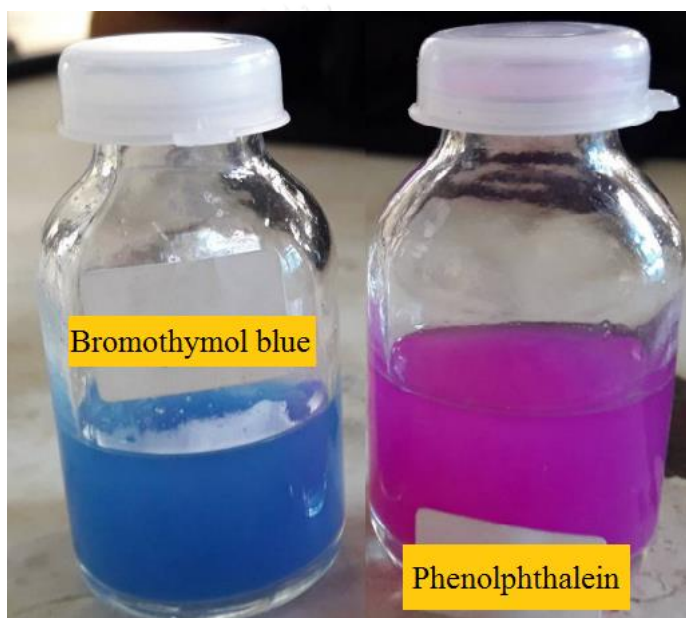


Figure E.1 Basic strength of extruded CaO-A(800) catalyst

Step 2 the clear solution was obtained from filtration. The selected indicator was dropped in the clear solution to test the basic strength (Figure F.1). The basic strength in the range of 7.2 to 9.8. After that, for the clear solution was titrated with HCl 0.1 M.

Step 3 determines the basicity concentration.

For example; The basicity of CaO-A(800)

Form HCl 0.1 M and solution of CaO-A(800) 10 mL

$$(C_{\text{HCl}})(V_{\text{HCl}}) = (C_{\text{CaO}})(V_{\text{CaO}})$$

Bromothymol blue

$$(1\text{M})(3.5 \text{ mL}) = (C_{\text{CaO}})(10 \text{ mL})$$

$$C_{\text{CaO}} = \frac{(1 \text{ M})(0.11 \text{ mL})}{(10 \text{ mL})} = 0.0367 \text{ M}$$

$$\left(0.013 \frac{\text{mol}}{1000} \times \frac{10^{-3}}{10^{-3}}\right) / 0.3 \text{ g} = 0.0367 \text{ mmol/g}$$

Phenolphthalein

$$(1\text{M})(4.5 \text{ mL}) = (C_{\text{CaO}})(10 \text{ mL})$$

$$C_{\text{CaO}} = \frac{(1 \text{ M})(0.13 \text{ mL})}{(10 \text{ mL})} = 0.013 \text{ M}$$

$$\left(0.013 \frac{\text{mol}}{1000} \times \frac{10^{-3}}{10^{-3}}\right) / 0.3 \text{ g} = 0.043 \text{ mmol/g}$$

$$(0.0367 + 0.043) / 2 = 0.03983 \text{ mmol/g}$$

VITA

NAME Warisara Vornuch

DATE OF BIRTH 24 May 1995

PLACE OF BIRTH Bangkok

INSTITUTIONS ATTENDED Finished high school from Triamudomsuksanomklaosamutprakan school in 2014.

Graduated in bachelor's degree from Faculty of Engineering, Rajamangala university of technology krungthep in 2018.

HOME ADDRESS 24/66 M.12 Bang Hua Suea, Phra Pradaeng District, Samut Prakan 10130.