# DEOXYGENATION OF BEEF FAT FOR THE PRODUCTION OF HYDROGENATED BIODIESEL OVER Pd AND NiMo CATALYSTS: EFFECT OF CATALYST SUPPORT



Rutkorn Chinsutthi

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science

The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with

The University of Michigan, The University of Oklahoma,
Case Western Reserve University, and Institut Français du Pétrole

2011

Thesis Title:

Deoxygenation of Beef Fat for the Production of

Hydrogenated Biodiesel over Pd and NiMo Catalysts: Effect

of Catalyst Support

By:

Rutkorn Chinsutthi

Program:

Petrochemical Technology Program

**Thesis Advisors:** 

Asst. Prof. Siriporn Jongpatiwut

Asst. Prof. Thammanoon Sreethawong

Dr. Suchada Butnark

Prof. Somchai Osuwan

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

(Asst. Prof. Pomthong Malakul)

Thy T. S. My

**Thesis Committee:** 

(Asst. Prof. Siriporn Jongpatiwut)

(Asst. Prof. Thammanoon Sreethawong)

(Dr. Suchada Butnark)

(Prof. Somchai Osuwan)

Supak Trakannroek

(Asst. Prof. Boonyarach Kitiyanan)

(Dr. Supak Trakarnroek)

#### **ABSTRACT**

5271030063: Petrochemical Technology Program

Rutkorn Chinsutthi: Deoxygenation of Beef Fat for the Production of

Hydrogenated Biodiesel over Pd and NiMo Catalysts: Effect of

Catalyst Support

Thesis Advisors: Asst. Prof. Siriporn Jongpatiwut, Asst. Prof.

Thammanoon Sreethawong, Dr. Suchada Butnark, and Prof.

Somchai Osuwan 73 pp.

Keywords: Deoxygenation/ Pd/Al<sub>2</sub>O<sub>3</sub>/ SiO<sub>2</sub>/ TiO<sub>2</sub>/ C/ KL/ Triglyceride/

Hydrogenated biodiesel/ Beef fat/ Pd catalysts/ NiMo catalysts

Hydrogenated biodiesel is one of the biofuels not containing oxygen in its molecules. The absence of oxygen leads to many advantages such as high cetane number, high heating value, and high miscibility with fossil fuels. In this research, the effect of catalyst supports on the production of hydrogenated biodiesel using beef fat as feedstock has been investigated. Pd-based catalysts (Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/F-Al<sub>2</sub>O<sub>3</sub>, Pd/SiO<sub>2</sub>, Pd/TiO<sub>2</sub>, Pd/C, and Pd/KL) and NiMo-based catalysts (i.e. NiMo/Al<sub>2</sub>O<sub>3</sub>, NiMo/F-Al<sub>2</sub>O<sub>3</sub>, NiMo/SiO<sub>2</sub>, NiMo/TiO<sub>2</sub>, NiMo/C, and NiMo/CeO<sub>2</sub>-ZrO<sub>2</sub>) were prepared by incipient wetness impregnation. The fresh and spent catalysts were characterized by XRD, TPR, BET, and TPO. The prepared catalysts were tested in a continuous flow packed-bed reactor at 500 psig, 325 °C, H<sub>2</sub>/feed molar ratio of 30, and LHSV 1 h<sup>-1</sup>. The products obtained from all catalysts were hydrocarbons in diesel specification range. The results showed that by varying catalyst supports the corresponding catalyst had different properties in term of surface area and metal particle size. The triglyceride conversion increased with decreasing Pd crystallite size. However, hydrocarbon selectivity was not significantly changed with catalyst supports. The main products from Pd catalysts were heptadecane and pentadecane, resulting from hydrodecarbonylation. Among Pd catalysts, Pd/TiO<sub>2</sub> exhibited the highest hydrocarbon yield. For NiMo catalysts, octadecane and hexadecane were the main hydrocarbon products, resulting from hydrodeoxygenation.

## บทคัดย่อ

รัตน์กรณิ์ ชินสุทธิ์ : การกำจัดออกซิเจนออกจากไขมันวัวในเครื่องปฏิกรณ์แบบต่อเนื่อง เพื่อผลิตไฮโดรจีเนตเตทไบโอคีเซล : (Deoxygenation of Beef Fat for the Production of Hydrogenated Biodiesel over Pd and NiMo Catalysts: Effect of Catalyst Support) อ. ที่ปรึกษา: ผศ. คร. สิริพร จงผาติวุฒิ ผศ. คร. ธรรมนูญ สรีทะวงศ์ คร.สุชาคา บุตรนาค และ ศ. คร.สมชาย โอสุวรรณ 73 หน้า

ไฮโครจีเนตเตทไบโอคีเซลเป็นน้ำมันชีวมวลที่ไม่มีออกซิเจนอยู่ในโครงสร้างโมเลกุล ทำให้มีคณสมบัติที่คีกว่าใบโอคีเซลทั่วไป เช่น ค่าซีเทนสูง ค่าพลังงานความร้อนสูงและมี ความสามารถในการผสมรวมกับน้ำมันดีเซลที่ได้จากปีโตรเถียมดี งานวิจัยนี้ศึกษาตัวรองรับใน ตัวเร่งปฏิกิริยาที่มีผลต่อการผลิตไฮโครจึเนตเตทไบโอคีเซลจากไขมันวัวผ่านกระบวนการคืออกซิ จีเนชัน ตัวเร่งปฏิกิริยาที่มีโลหะพัลลาเคียมบนตัวรองรับหลายชนิค (Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/F-Al<sub>2</sub>O<sub>3</sub>, Pd/SiO2, Pd/TiO2, Pd/C, และ Pd/KL) และตัวเร่งปฏิกิริยาที่มีโลหะนิเกิลกับโมลิบดินัมบนตัว รองรับหลายชนิด (NiMo/Al<sub>2</sub>O<sub>3</sub>, NiMo/F-Al<sub>2</sub>O<sub>3</sub>, NiMo/SiO<sub>2</sub>, NiMo/TiO<sub>2</sub>, NiMo/C, และ NiMo/CeO<sub>2</sub>-ZrO<sub>2</sub>) เตรียมโดยวิธีการฝั่งแบบชื้น ตัวเร่งปฏิกิริยาก่อนและหลังทำปฏิกิริยาจะถูก วิเคราะห์โดยใช้เทคนิค XRD, TPR, BET, และ TPO และถูกทคสอบความว่องไวในการทำ ปฏิกิริยาโคยใช้เครื่องปฏิกรณ์แบบไหลต่อเนื่องชนิคเบคนิ่งที่สภาวะความคัน 500 ปอนค์ต่อ ตารางนิ้ว อุณหภูมิ 325 องศาเซลเซียส อัตราส่วนโดยโมลระหว่างไฮโครเจนกับสารที่ป้อนเท่ากับ 30 และอัตราการใหลของสารป้อนต่อปริมาตรตัวเร่งปฏิกิริยาเท่ากับ 1 ต่อชั่วโมง ผลิตภัณฑ์ ของเหลวที่ได้จากตัวเร่งปฏิกิริยาทุกตัวเป็นไฮโครคาร์บอนอยู่ในช่วงน้ำมันคีเซล จากผลการ ทคลองพบว่าตัวรองรับมีผลทำให้ตัวเร่งปฏิกิริยามีคุณสมบัติแตกต่างกันในค้านพื้นที่ผิวและขนาด ของผลึกของตัวเร่งปฏิกิริยา การเปลี่ยนไตรกลีเซอไรค์ไปเป็นผลิตภัณฑ์เพิ่มขึ้นเมื่อขนาคผลึกของ โลหะพัลลาเคียมลคลง อย่างไรก็ตามการเลือกเกิดไฮโครคาร์บอนไม่ขึ้นกับตัวรองรับ ตัวเร่ง ปฏิกิริยาที่มีโลหะพัลลาเคียมมีเฮปตะเคคเคนและเพนตะเคคเคนเป็นผลิตภัณฑ์หลักเป็นผลมาจาก การเกิดปฏิกิริยาไฮโครคีคาร์บอนิลเลชัน เมื่อเทียบในกลุ่มตัวเร่งปฏิกิริยาที่มีโลหะพัลลาเคียม พบว่า Pd/TiO<sub>2</sub> ให้สัดส่วนผลิตภัณฑ์ที่เป็นไฮโดรการ์บอนสูงสุด สำหรับตัวเร่งปฏิกิริยาที่มีโลหะ นิกเกิลกับโมลิบคินัมได้ออกตะเดคเคนและเฮกซะเดคเคนเป็นผลิตภัณฑ์หลักเนื่องจากเกิดปฏิกิริยา ไฮโดรดีออกซีจีเนชัน

#### **ACKNOWLEDGEMENTS**

This work would not have been possible without the assistance of the following individuals.

First and foremost, my utmost gratitude to Asst. Prof. Siriporn Jongpatiwut, Asst. Prof. Thammanoon Sreethawong, Dr. Suchada Butnark, and Prof. Somchai Osuwan, my thesis advisors, for encouragement, invaluable recommendations, and kindly support.

I am grateful to thank Asst. Prof. Boonyarach Kitiyanan and Dr. Supak Trakarnroek for their kind advice and for being my thesis committee.

This thesis work is funded by S&T Postgraduate Education and Research Development Office, the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand, and the Petroleum and Petrochemical College.

I would like to thank staff of the Petroleum and Petrochemical College for their kind help with the analytical instruments.

I am heartly thankful to my friends at PPC for their friendly support, assistance, encouragement, and cheerfulness.

I offer my regards and blessings to all of those who supported me to complete this work.

Last but not least, I would like to thank my parent and my family for their love, understanding, and unconditionally support, thank you so much.

## TABLE OF CONTENTS

|    |       |  | PAGE |
|----|-------|--|------|
|    | Title | Page   | i    |
|    | Abst  | ract (in English)                                | iii  |
|    | Abst  | ract (in Thai)                                   | iv   |
|    | Ackr  | nowledgements                                    | v    |
|    | Table | e of Contents                                    | vi   |
|    | List  | of Tables  | ix   |
|    | List  | of Figures                                       | x    |
|    |       |  |      |
| CH | APTE  | R  |      |
|    | I     | INTRODUCTION                                     | 1    |
|    |       |  |      |
|    | II    | LITERATURE REVIEW                                | 3    |
|    |       | 2.1 Bio-based Diesel                             | 3    |
|    |       | 2.1.1 Biodiesel                                  | 4    |
|    |       | 2.1.2 Hydrogenated Biodiesel or Renewable Diesel | 5    |
|    |       | 2.2 Feedstock                                    | 5    |
|    |       | 2.2.1 Animal Fat                                 | 8    |
|    |       | 2.3 Biodiesel Production                         | 9    |
|    |       | 2.3.1 Transesterification Process                | 9    |
|    |       | 2.3.2 Hydrodeoxygenation Process                 | 11   |
|    |       | 2.3.3 Influence of Condition                     | 14   |
|    |       | 2.4 Catalyst                                     | 16   |
|    |       | 2.4.1 Heterogeneous Catalyst                     | 16   |
|    |       | 2.4.1.1 Kinetics Model of Heterogeneous          |      |
|    |       | Catalytic Reaction                               | 16   |
|    |       | 2.4.1.2 Catalyst Deactivation                    | 17   |
|    |       | 2.4.1.3 Preparation of Supported Metal Catalysts | 19   |
|    |       | 2.4.1.3.1 Impregnation                           | 19   |

| CHAPTER |     |  | PAGE |
|---------|-----|--|------|
|         |     | 2.4.1.3.2 Co-precipitation                     | 20   |
|         |     | 2.4.2 Catalyst for Deoxygenation               | 20   |
|         |     | 2.4.3 Influence of Catalyst Support            | 24   |
| III     | EX  | PERIMENTAL                                     |      |
|         | 3.1 | Equipment                                      | 28   |
|         | 3.2 | Catalyst supports                              | 28   |
|         | 3.3 | Chemicals                                      | 29   |
|         | 3.4 | Gases  | 29   |
| , i     | 3.5 | Experimental Procedures                        | 29   |
|         |     | 3.5.1 Catalyst Preparation                     | 29   |
|         |     | 3.5.1.1 Incipient Wetness Impregnation         | 30   |
|         |     | 3.5.1.2 Co-precipitation                       | 30   |
|         |     | 3.5.2 Catalyst Pretreatment                    | 31   |
| 3       |     | 3.5.3 Catalyst Characterizations               | 31   |
|         |     | 3.5.3.1 Temperature-programmed Reduction (TPR) | 31   |
|         |     | 3.5.3.2 Thermogravimetry and Differential      |      |
|         |     | Thermal Analysis (TG-DTA)                      | 31   |
|         |     | 3.5.3.3 Brunauer Emmett Telller(BET) Method    | 31   |
|         |     | 3.5.3.4 X-ray diffraction (XRD)                | 32   |
|         |     | 3.5.3.5 Hydrogen Chemisorption                 | 33   |
|         |     | 3.5.3.6 Temperature-programmed Oxidation (TPO) | 33   |
|         |     | 3.5.4 Hydrodeoxygenation Experiments           | 33   |
|         |     | 3.5.5 Feed and Product Analysis                | 35   |
|         |     | 3.5.5.1 Feed Analysis                          | 35   |
|         |     | 3.5.5.2 Product Analysis                       | 35   |

| CHAPTER |  | PAGE |
|---------|--|------|
| IV      | RESULTS AND DISCUSSION                           | 6    |
|         | 4.1 Catalyst Characterization                    | 38   |
|         | 4.1.1 Thermogravimetric and Differential Thermal |      |
|         | Analysis (TG-DTA)                                | 38   |
|         | 4.1.2 Temperature-programmed Reduction (TPR)     | 39   |
|         | 4.1.3 X-ray Diffraction (XRD)                    | 42   |
|         | 4.1.4 Brunauer Emmett Telller (BET) Method       | 43   |
|         | 4.1.5 Hydrogen Chemisorption                     | 45   |
|         | 4.1.6 Temperature-programmed Oxidation (TPO)     | 45   |
|         | 4.2 Hydrodeoxygenation of Beef Fat               | 47   |
|         | 4.2.1 GC Analysis of Standard Chemical, Feed,    |      |
|         | and Product                                      | 47   |
|         | 4.2.2 Effect of Catalyst Supports on the         |      |
|         | Hydrodeoxygenation of Beef Fat over              |      |
|         | Pd-Supported Catalysts                           | 54   |
|         | 4.2.3 Effect of Catalyst Supports on the         |      |
|         | Hydrodeoxygenation of Beef Fat over              |      |
|         | NiMo-Supported Catalysts                         | 60   |
| v       | CONCLUSIONS AND RECOMMENDATIONS                  | 65   |
|         | REFERENCES                                       | 67   |
|         | APPENDIX   | 72   |
|         | CURRICULUM VITAE                                 | 73   |

## LIST OF TABLES

| TABL | E   | P            | AGE |
|------|---|--------------|-----|
| 2.1  | Classification of renewable biofuel based on their          |              |     |
|      | production technologies                                     |              | 1   |
| 2.2  | Fatty acid composition of some common edible fat and oil    |              | 8   |
| 2.3  | Steps in a catalytic reaction                               |              | 17  |
| 2.4  | Mechanisms of catalyst deactivation                         |              | 17  |
| 3.1  | List of investigated catalysts                              |              | 30  |
| 3.2  | Description of flow diagram                                 |              | 34  |
| 3.3  | The reaction conditions for producing the hydrogenated bid  | odiesel      | 35  |
| 3.4  | The chromatographic temperature program for liquid produced | uct          |     |
|      | analysis  |              | 36  |
| 4.1  | The suitable calcination temperatures for NiMo-supported    |              |     |
|      | catalysts   |              | 39  |
| 4.2  | The suitable reduction temperatures for NiMo-supported of   | atalysts     | 41  |
| 4.3  | The Pd crystallite size and metal dispersion over Pd-suppo  | rt catalysts | 43  |
| 4.4  | BET results of the studied catalysts                        |              | 44  |
| 4.5  | The amount of hydrogen uptake and percent metal             |              |     |
|      | dispersion of Pd- supported catalysts                       |              | 45  |
| 4.6  | Amount of carbon deposit on studied catalyst after reaction | 1            | 47  |
| 4.7  | Retention times and response factors of standard chemical   | S            | 48  |
| 4.8  | Fatty acid composition of beef fat                          |              | 53  |
| 4.9  | Conversion and product distribution obtained over differen  | nt           |     |
|      | Pd-supported catalysts                                      |              | 59  |
| 4.10 | Conversion and product distribution obtained over           |              |     |
|      | different NiMo-supported catalysts                          |              | 64  |
| A.1  | The amount of hydrogen uptake and percent metal dispersi    | ion          |     |
|      | of NiMo catalysts   |              | 72  |

### LIST OF FIGURES

| FIGUF | GURE   |     |
|-------|--|-----|
| 2.1   | A chemical structure of triglyceride   | 6   |
| 2.2   | The production of biodiesel via transesterification of triglyceride                  | 10  |
| 2.3   | The transesterification reactions of triglyceride with alcohol                       |     |
|       | to ester and glycerol  | 10  |
| 2.4   | The transesterification reactions of triglyceride with methanol                      | 11  |
| 2.5   | Flow chart for transformation of lipid materials (biodiesel                          | * . |
|       | and renewable diesel by hydrodeoxygenation) to products                              |     |
|       | of engine combustion   | 12  |
| 2.6   | The possible liquid-phase reaction pathways for production                           |     |
|       | of straight- chain hydrocarbons from fatty acids                                     | 13  |
| 2.7   | Gas phase reactions of CO or CO <sub>2</sub> with H <sub>2</sub> or H <sub>2</sub> O | 14  |
| 2.8   | Mechanisms of catalyst deactivation ( $M = metal$ )                                  | 19  |
| 2.9   | The reaction pathways for conversion of triglycerides to                             |     |
|       | renewable diesel   | 22  |
| 2.10  | The framework structure of LTL-type compounds in the                                 |     |
|       | highest possible topological symmetry P 6/mmm.                                       |     |
|       | View parallel [001] rotated by 5 about [100] and [120]                               | 24  |
| 2.11  | The hydrodeoxygenation reaction scheme of aliphatic                                  |     |
|       | methyl esters (n=6) for methyl heptanoate and n=5 for                                |     |
|       | methyl hexanoate)  | 26  |
| 3.1   | A schematic flow diagram of high pressure experimental setup                         | 34  |
| 4.1   | TG-DTA profiles of Pd-supported catalysts: a) Pd/Al <sub>2</sub> O <sub>3</sub> ,    |     |
|       | and b) Pd/KL   | 38  |
| 4.2   | TPR profiles of the prepared Pd-supported catalysts                                  | 40  |
| 4.3   | TPR profiles of NiMo-supported catalysts   | 41  |
| 4.4   | XRD patterns of the reduced Pd-supported catalysts                                   | 42  |
| 4.5   | XRD patterns of NiMo-supported catalysts   | 44  |

| FIGURE |  | PAGE |
|--------|--|------|
| 4.6    | TPO profiles of studied catalyst after reaction; a)                                  |      |
|        | Pd-supported catalysts and b) NiMo-supported catalysts                               | 46   |
| 4.7    | Chromatograms of standard chemicals: a) n-pentadecane,                               |      |
|        | n-hexadecane, n-heptadecane, n-octadecane, b) hexadecanol,                           |      |
|        | octadecanol, palmitic acid, stearic acid, oleic acid,                                |      |
|        | c) monoolein, monolinolein, monostearin, monopalmitin,                               |      |
|        | d) diolein, dilinolein, distearin, dipalmitin, e) triolein, trilinolein,             |      |
|        | tristearin, tripalmitin.   | 49   |
| 4.8    | Chromatogram of 10 vol% beef fat in n-dodecane                                       | 51   |
| 4.9    | Chromatograms of feed and products obtained over                                     |      |
|        | Pd/Al <sub>2</sub> O <sub>3</sub> at different time on stream. Reaction condition:   |      |
|        | 500 psig, 325 °C, LHSV of 1 h <sup>-1</sup> , and H <sub>2</sub> /feed molar         |      |
|        | ratio of 30.   | 52   |
| 4.10   | Conversion and selectivity as a function of time on                                  |      |
|        | stream of Pd/Al <sub>2</sub> O <sub>3</sub> (reaction condition: 500 psig, 325 °C,   |      |
|        | LHSV of 1 h <sup>-1</sup> , and H <sub>2</sub> /feed molar ratio of 30).             | 54   |
| 4.11   | Conversion and selectivity as a function of time on                                  |      |
|        | stream of Pd/F-Al <sub>2</sub> O <sub>3</sub> (reaction condition: 500 psig, 325 °C, |      |
|        | LHSV of 1 h <sup>-1</sup> , and H <sub>2</sub> /feed molar ratio of 30).             | 55   |
| 4.12   | Conversion and selectivity as a function of time on stream                           |      |
|        | of Pd/KL (reaction condition: 500 psig, 325 °C, LHSV                                 |      |
|        | of 1 h <sup>-1</sup> , and H <sub>2</sub> /feed molar ratio of 30).                  | 56   |
| 4.13   | Conversion and selectivity as a function of time on stream                           |      |
|        | of Pd/SiO <sub>2</sub> (reaction condition: 500 psig, 325 °C, LHSV                   |      |
|        | of 1 h <sup>-1</sup> , and H <sub>2</sub> /feed molar ratio of 30).                  | 56   |
| 4.14   | Conversion and selectivity as a function of time on stream                           |      |
|        | of Pd/C (reaction condition: 500 psig, 325 °C, LHSV of 1 h <sup>-1</sup> ,           |      |
|        | and H <sub>2</sub> /feed molar ratio of 30).   | 57   |

| FIGUF | RE   | PAGE |
|-------|--|------|
| 4.15  | Conversion and selectivity as a function of time on  |      |
|       | stream of Pd/TiO <sub>2</sub> (reaction condition: 500 psig, 325 °C,                       |      |
|       | LHSV of 1 h <sup>-1</sup> , and H <sub>2</sub> /feed molar ratio of 30).                   | 58   |
| 4.16  | Conversion and selectivity as a function of time on stream                                 |      |
|       | of NiMo/Al <sub>2</sub> O <sub>3</sub> (reaction condition: 500 psig, 325 °C, LHSV         |      |
|       | of 1 h <sup>-1</sup> , and H <sub>2</sub> /feed molar ratio of 30).                        | 60   |
| 4.17  | Conversion and selectivity as a function of time on stream                                 |      |
|       | of NiMo/F-Al <sub>2</sub> O <sub>3</sub> (reaction condition: 500 psig, 325 °C,            |      |
|       | LHSV of 1 h <sup>-1</sup> , and H <sub>2</sub> /feed molar ratio of 30).                   | 61   |
| 4.18  | Conversion and selectivity as a function of time on stream                                 |      |
|       | of NiMo/C (reaction condition: 500 psig, 325 °C, LHSV                                      |      |
|       | of 1 h <sup>-1</sup> , and H <sub>2</sub> /feed molar ratio of 30).                        | 62   |
| 4.19  | Conversion and selectivity as a function of time on stream                                 |      |
|       | of NiMo/TiO <sub>2</sub> (reaction condition: 500 psig, 325 °C, LHSV                       |      |
|       | of 1 h <sup>-1</sup> , and H <sub>2</sub> /feed molar ratio of 30).                        | 62   |
| 4.20  | Conversion and selectivity as a function of time on stream                                 |      |
|       | of NiMo/SiO <sub>2</sub> (reaction condition: 500 psig, 325 °C, LHSV                       |      |
|       | of 1 h <sup>-1</sup> , and H <sub>2</sub> /feed molar ratio of 30).                        | 63   |
| 4.21  | Conversion and selectivity as a function of time on  |      |
|       | stream of NiMo/CeO <sub>2</sub> -ZrO <sub>2</sub> (reaction condition:                     |      |
|       | 500 psig, 325 °C, LHSV of 1 h <sup>-1</sup> , and H <sub>2</sub> /feed molar ratio of 30). | 63   |