

**Potential Use of Modified Catalysts for Production of Valuable Tire Derived
Products**

Yotin Piyawongpinyo


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
2013

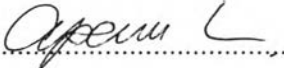
Thesis Title: Potential Use of Modified Catalysts for Production of Valuable Tire Derived Products
By: Yotin Piyawongpinyo
Program: Petrochemical Technology
Thesis Advisor: Assoc. Prof. Sirirat Jitkarnka

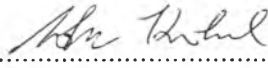
Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.


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

Thesis Committee:


.....
(Assoc. Prof. Sirirat Jitkarnka)


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


.....
(Dr. Natthakorn Kraikul)

ABSTRACT

5471032063: Petrochemical Technology Program
Potential Use of Modified Catalysts for Production of Valuable Tire
Derived Product
Thesis Advisors: Assoc. Prof. Sirirat Jitkarnka 91 pages
Keywords: Pyrolysis, bimetallic catalyst, tire derived oil, sulfur content

Tire derived oil is one of the alternative fuels which can be used to substitute petroleum oil that is continuously running out of the world. In this work, waste tire pyrolysis was chosen to be the way to produce pyrolytic oil. Due to the limit of sulfur in petroleum products and the high price of a noble metal, in this research, NiMo, NiW, CoMo and CoW are chosen as non-noble metals to be used in the pyrolysis of waste tire. The effects of non-noble metals (Ni and Co) modified with Mo and W as second metals and supported on HBETA zeolite for tire pyrolysis were investigated in this work on the quality and compositions of the pyrolytic oil products. The amount of Ni or Co was fixed at 5 %wt with the second metal (Mo or W) varied at 10 %wt and 20%wt. The obtained products were analyzed via gas chromatograph, GC-TOF, column chromatography, and SIMDIST GC, whereas the catalysts were characterized using temperature programmed reduction and X-ray diffraction. The results indicated that the catalyst with 5 wt% of Ni with 20 wt% of Mo on HBETA showed the good activity for pyrolysis process because it gave a high saturated hydrocarbon contents (48.6 wt%) with a low sulfur content (0.82 wt%) in oil. 5 wt% of Co with 20 wt% of W on HBTEA had the highest hydrodesulfurization ability among the other bimetallic catalysts because it can decrease the sulphur content in the tire-derived oil from 1.36 (non-catalytic case) to 0.51.

บทคัดย่อ

โยธิน ปิยะวงศ์ภิญโญ: ศักยภาพในการใช้ตัวเร่งปฏิกิริยาที่ถูกดัดแปลงเพื่อผลิตผลิตภัณฑ์จากกระบวนการไพโรไลซิสยางรถยนต์หมดสภาพ (Potential Use of Modified Catalysts for Production of Valuable Tire Derived Product) อ. ที่ปรึกษา : รศ. ดร. ศิริรัตน์ จิตการคำ 91 หน้า

น้ำมันที่ได้จากยางรถยนต์เป็นหนึ่งในพลังงานทางเลือกที่สามารถนำไปใช้แทนน้ำมันปิโตรเลียมที่กำลังลดลงอย่างต่อเนื่อง ในงานนี้กระบวนการไพโรไลซิสยางรถยนต์หมดสภาพถูกเลือกเป็นวิธีที่จะผลิตน้ำมัน และด้วยการจำกัดปริมาณของกำมะถันในผลิตภัณฑ์ปิโตรเลียมและราคาของโลหะมีตระกูลจึงทำให้งานวิจัยนี้เลือกตัวเร่งปฏิกิริยาชนิดต่างๆที่ประกอบไปด้วย นิกเกิล โมลิบดีนัม นิกเกิลทังสเตน โคบอลต์โมลิบดีนัม และโคบอลต์ทังสเตน ซึ่งเป็นโลหะที่ไม่มีตระกูลมาใช้ในกระบวนการไพโรไลซิสของยางที่หมดสภาพซึ่งศึกษาผลของการเติม โมลิบดีนัมและทังสเตนซึ่งเป็นโลหะตัวที่สองลงไป ในโลหะนิกเกิลและโคบอลต์และตรวจสอบคุณภาพและองค์ประกอบของผลิตภัณฑ์น้ำมันที่ได้ โดยปริมาณของนิกเกิลหรือโคบอลต์ถูกกำหนดให้คงที่ที่ 5% โดยน้ำหนักและเปลี่ยนแปลงปริมาณของโลหะตัวที่สอง (โมลิบดีนัมและทังสเตน) 10% และ 20% โดยน้ำหนัก ผลิตภัณฑ์ที่ได้จะถูกนำมาวิเคราะห์โดยแก๊สโครมาโตกราฟีชนิดต่างๆ ขณะที่ตัวเร่งปฏิกิริยาถูกนำมาวิเคราะห์โดยใช้เครื่อง TPR และ XRD เพื่อวิเคราะห์คุณสมบัติของตัวเร่งปฏิกิริยาจากผลการทดลองพบว่าน้ำมันที่ได้จากการกระบวนการไพโรไลซิสด้วยตัวเร่งปฏิกิริยา 5% โดยน้ำหนักของโคบอลต์กับ 20% โดยน้ำหนักของทังสเตนบนเอชเบต้าซีโอไลต์ มีสารไฮโดรคาร์บอนอิ่มตัวสูง (63.8% โดยน้ำหนัก) และยังสามารถลดปริมาณกำมะถันในน้ำมันได้เยอะสุดโดยลดลงเหลือเพียง 0.51% โดยน้ำหนัก เมื่อเปรียบเทียบกับปริมาณกำมะถันจากปฏิกิริยาที่ไม่ใช้ตัวเร่งปฏิกิริยาซึ่งมีปริมาณกำมะถันถึง 1.36% โดยน้ำหนัก

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my appreciation for those who had been so significantly influential and responsible for my achievement in order to complete this thesis.

First and foremost, I would like to express my sincere thanks to my thesis advisor, Assoc. Prof. Sirirat Jitkarnka for her invaluable help and constant encouragement throughout the course of this research. I am most grateful for her teaching and advice, not only the research methodologies but also many other methodologies in life.

My gratitude is extended to the thesis committee, Assoc. Prof. Apanee Luengnaruemitchai and Dr. Nathakorn Kraikul for their important comments and suggestions.

Unforgettably, I most gratefully acknowledge my parents and my friends for all their support throughout the period of this research.

I would like to thank all staff members at The Petroleum and Petrochemical College who have provided helpful assistance and many useful technical supports at various occasions.

Finally, I am very grateful for the mutual funds of the thesis work provided by The Petroleum and Petrochemical College, The Center of Excellence on Petrochemical and Materials Technology, Thailand research Fund, and The Commission on Higher Education.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	xiii
 CHAPTER	
I INTRODUCTION	1
 II LITERATURE REVIEW	 4
 III EXPERIMENTAL	 15
3.1 Materials and Equipments	15
3.1.1 Materials	15
3.1.2 Equipments	15
3.1.3 Chemicals and Solvents	16
3.2 Methodology	16
3.2.1 Catalyst Preparation	16
3.2.2 Reaction Equipment	17
3.2.3 Catalyst Characterization	18
3.2.4 Product Analysis	19
 IV RESULTS AND DISCUSSION	 22
4.1 Modified Ni/HBETA catalysts	22
4.1.1 Verification of metallic form of modified Ni/HBETA	22

CHAPTER	PAGE
4.1.2 Pyrolysis activity	24
4.1.2.1 Gas to liquid ratio	24
4.1.2.2 Yield of olefins	25
4.1.2.3 Yield of cooking gas	26
4.1.2.4 Liquid composition	27
4.1.2.5 Petroleum fractions	29
4.1.3 Reducibility of modified Ni catalysts and metal-metal interaction	30
4.1.4 Desulfurization ability	32
4.1.4.1 Sulfur distribution	32
4.1.4.2 Sulfur contents	33
4.1.4.3 Type of sulfur compounds	34
4.2 Modified Co/HBETA catalysts	36
4.2.1 Pyrolysis activity	36
4.2.1.1 Gas to liquid ratio	36
4.2.1.2 Yield of olefins	37
4.2.1.3 Yield of cooking gas	38
4.2.1.4 Liquid composition	39
4.2.1.5 Petroleum fractions	41
4.1.3 Reducibility of modified Co catalysts and metal-metal interaction	42
4.1.4 Desulfurization ability	44
4.1.4.1 Sulfur distribution	44
4.1.4.2 Sulfur contents	45
4.1.4.3 Type of sulfur compounds	46
V CONCLUSIONS AND RECOMMENDATIONS	48

CHAPTER	PAGE
REFERENCES	50
APPENDICES	54
Appendix A Temperature Profiles	54
Appendix B Yield of Pyrolysis Products	64
Appendix C The Pyrolysis Gas Compositions	65
Appendix D Amount of Asphaltene in Pyrolysis Oils	66
Appendix E Chemical Compositions of Maltenes	66
Appendix F Petroleum Fractions of Derived Oils	67
Appendix G Sulfur in Derived Oils and sulfur deposition on spent Catalysts	68
Appendix H Sulfur distribution	68
Appendix I Carbon Number Distribution of polar-aromatics	69
Appendix J Amount of sulfur compounds in the range of petroleum fraction	72
Appendix K Type of sulfur compounds from all catalysts	73
CURRICULUM VITAE	91

LIST OF TABLES

TABLE		PAGE
3.1	The optimized compositions and volumes of mobile phases for preparative separation of maltene using the chromatographic column	20
4.1	Reduction peaks of modified Ni/HBETA catalysts in comparison with those of 10Mo/HBETA and 10W/HBETA	31
4.2	Reduction peaks of modified Co/HBETA catalysts in comparison with those of 10Mo/HBETA, 10W/HBETA and 5Ni20Mo/HBETA.	43
A1	Pyrolysis conditions: Non-catalyst	52
A2	Pyrolysis conditions: HBETA catalyst	53
A3	Pyrolysis conditions: 5Ni/HBETA catalyst	54
A4	Pyrolysis conditions: 5Ni10Mo/HBETA catalyst	55
A5	Pyrolysis conditions: 5Ni20Mo/HBETA catalyst	56
A6	Pyrolysis conditions: 5Ni10W/HBETA catalyst	57
A7	Pyrolysis conditions: 5Ni20W/HBETA catalyst	58
A8	Pyrolysis conditions: 5Co/HBETA catalyst	59
A9	Pyrolysis conditions: 5Co20Mo/HBETA catalyst	60
A10	Pyrolysis conditions: 5Co20W/HBETA catalyst	61
B1	Weight percentage of pyrolysis products obtained from Ni/HBETA and NiMo/HBETA catalysts	62
B2	Weight percentage of pyrolysis products obtained from Ni/HBETA and NiW/HBETA catalysts	62
B3	Weight percentage of pyrolysis products obtained from modified Co/HBETA catalysts	62

TABLE	PAGE	
C1	Weight percentage of gas products obtained from Ni/HBETA and NiMo/HBETA catalysts	63
C2	Weight percentage of gas products obtained from the NiW/HBETA and modified Co/HBETA catalysts	63
D1	Amount of asphaltene in pyrolysis oils	64
E1	Chemical compositions of maltenes obtained from Ni/HBETA and NiMo/HBETA catalysts	64
E2	Chemical compositions of maltenes obtained from NiW/HBETA and modified Co/HBETA catalysts	65
F1	Petroleum fractions of derived oils obtained from Ni/HBETA and NiMo/HBETA	65
F2	Petroleum fractions of derived oils obtained from NiW/HBETA and modified Co/HBETA catalysts	65
G1	Sulfur in derived oils and sulfur deposition on spent catalysts	66
H1	Sulfur distribution (%wt) in the pyrolytic products obtained from using each catalyst	66
I1	Carbon Number Distribution of polar-aromatics obtained from Ni/HBETA and NiMo/HBETA catalysts	67
I2	Carbon Number Distribution of polar-aromatics obtained from NiW/HBETA and modified Co catalysts	68
J1	Distribution of sulfur compounds in petroleum fractions from Ni/HBETA and NiMo/HBETA catalysts	70
J2	Distribution of sulfur compounds in petroleum fractions from NiW/HBETA and modified Co/HBETA catalysts	70
K1	Sulfur compounds in oil from the non-catalytic case	71
K2	Sulfur compounds in oil from the HBETA	72
K3	Sulfur compounds in oil from the 5Ni/HBETA	74
K4	Sulfur compounds in oil from the 5Ni10Mo/HBETA	75

TABLE		PAGE
K5	Sulfur compounds in oil from the 5Ni20Mo/HBETA	77
K6	Sulfur compounds in oil from the 5Ni10W/HBETA	80
K7	Sulfur compounds in oil from the 5Ni20W/HBETA	82
K8	Sulfur compounds in oil from the 5Co/HBETA	83
K9	Sulfur compounds in oil from the 5Co20Mo/HBETA	85
K10	Sulfur compounds in oil from the 5Co20W/HBETA	87

LIST OF FIGURES

FIGURE		PAGE
2.1	Components of a tire	4
2.2	Hydrodesulfurization of 4,6-DM-DBT	10
3.1	Diagram of the pyrolysis process	18
4.1(a)	XRD patterns of Ni and NiMo over HBETA catalysts; (*) HBETA, (°) Ni, (+) Mo, (-) NiO, (/) MoO ₂ , and (©) (MoO ₃)	22
4.1(b)	XRD patterns of Ni and NiW over HBETA catalysts; (*) HBETA, (°) Ni, (+) W, (-) NiO, (/) WO, (©) WO ₂ , (®) WO ₃ , and (i) W ₄ O ₁₁	23
4.2	G/L ratio obtained from modified Ni /HBETA catalysts	24
4.3	Yield of ethylene and propylene obtained from modified Ni/HBETA catalysts	25
4.4	Yield of cooking gas obtained from modified Ni/HBETA catalysts	26
4.6	Average carbon number of polar-aromatics fractions obtained from using modified Ni/HBETA catalysts	28
4.7	Petroleum fractions in maltenes obtained from modified Ni/HBETA catalysts	29
4.8	TPR profiles of various bimetallic NiMo catalysts in comparison with that of 10Mo/HBETA	30
4.9	TPR profiles of various bimetallic NiW catalysts in comparison with that of 10W/HBETA	31
4.10	Sulfur distribution in the pyrolytic products obtained from modified Ni/HBETA catalysts	32
4.11	Sulfur contents (%wt) on spent catalysts and in the pyrolytic oils obtained from modified Ni /HBETA catalysts	33
4.12	Sulfur distribution in petroleum fractions obtained from 5Ni20Mo/HBETA	34

FIGURE		PAGE
4.13	G/L ratio obtained from modified Co/HBETA	36
4.14	Yield of ethylene and propylene obtained from modified Co/HBETA catalysts	37
4.15	Yield of cooking gas obtained from modified Co/HBETA catalysts	38
4.16	Chemical compositions in maltenes from modified Co/HBETA catalysts	39
4.17	Average carbon number of polar-aromatics fraction obtained from using modified Co/HBETA catalysts	40
4.18	Petroleum fractions in maltenes obtained from modified Co/HBETA catalysts	41
4.19	TPR profiles of various modified Co/HBETA catalysts, 10Mo/HBETA, and 5Ni20Mo/HBETA	42
4.20	TPR profiles of various modified Co/HBETA catalysts, 10W/HBETA, and 5Ni20Mo/HBETA	43
4.21	Sulfur distribution in the pyrolytic products obtained from using modified Co catalysts on HBETA zeolite	44
4.22	Sulfur contents (%wt) on spent catalysts and in the pyrolytic oils obtained from modified Co catalysts	45
4.23	Sulfur distribution in petroleum fractions obtained from 5Co20Mo/HBETA and 5Co20W/HBETA in comparison with 5Ni20Mo/HBETA	46