

**IMPACT OF ACID ZEOLITES AS ADDITIVES IN Pd-LOADED HBETA
AND HY CATALYSTS ON WASTE TIRE PYROLYSIS PRODUCTS**

Nateetorn Manchantrarat

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

I 28373741

Thesis Title: Impact of Acid Zeolites as Additives in Pd-Loaded HBETA
and HY Catalysts on Waste Tire Pyrolysis Products
By: Nateetorn Manchantrarat
Program: Petroleum Technology
Thesis Advisors: 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.

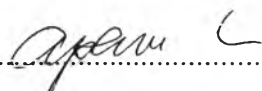


..... College Dean
(Asst. Prof. Pomthong Malakul)

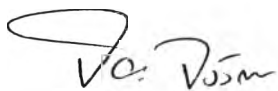
Thesis Committee:



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



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



.....
(Dr. Piya Chongvatana)

ABSTRACT

50373010063: Petroleum Technology Program

Nateetorn Manchantrarat: Impact of Acid Zeolites as Additives in Pd-Loaded HBETA and HY Catalysts on Waste Tire Pyrolysis Products.

Thesis Advisors: Assoc. Prof. Sirirat Jitkarnka, 108 pp.

Keywords: Tire/ Pyrolysis/ Palladium/ Acid zeolites/ Zeolite additive

Addition of one or two acid zeolites as additives into catalysts used in catalytic pyrolysis of waste tire was studied in this work. Pd/HBETA and Pd/HY were used as the main catalysts because of their ability on improving the quality and quantity of light fractions (full range naphtha, and kerosene). Taking advantages of their large pore size, HBETA and HY were selected as a first additive in the main catalysts, aiming to improve cracking performance for the high production of lighter fraction, namely full range naphtha. HZSM-5 zeolite, which has smaller pore diameter and high acid strength, favors the aromatization reaction of light molecules. Therefore, it was used as a second additive in the main pyrolysis catalysts. The amount of Pd was fixed at 1%wt, whereas the additive, varied at 10 %wt, and 20 %wt, was physically mixed with the main catalyst. The obtained products were analyzed via gas chromatograph, liquid chromatograph, and SIMDIST GC, whereas the catalysts were analyzed by SAA and TG-DTA. The results indicated that the addition of HY in Pd/HBETA cannot improve the naphtha fraction because the cracking activity was reduced. However, it can improve the gas oil fractions instead by increasing saturated hydrocarbons in these fractions. On the other hand, the addition of 10 %wt HBETA in Pd/HY can improve the cracking performance of Pd/HY, resulting in the high production of naphtha fraction and valuable gaseous products. The further mixing with the second additive, HZSM-5, in the selected catalysts can improve both quantity and quality of naphtha fraction. These results revealed that the acid properties and pore sizes of zeolites were two important factors influencing the products.

บทคัดย่อ

นทีธร แม่นจันทร์รัตน: ผลกระทบของซีโอไลต์กรดที่ใช้เป็นสารเติมแต่งในตัวเร่งปฏิกิริยาพลาสมาเคียมบนเอชเบต้า และเอชวาย ต่อผลิตภัณฑ์จากกระบวนการไพโรไลซิสยางรถยนต์หมดสภาพ (Impact of Acid Zeolites as Additives in Pd-Loaded HBETA and HY Catalysts on Waste Tire Pyrolysis Products) อ. ที่ปรึกษา : รศ. ดร. ศิริรัตน์ จิตการคำ 108 หน้า

ในงานวิจัยนี้เป็นการศึกษาการเติมซีโอไลต์ที่มีคุณสมบัติเป็นกรดจำนวนหนึ่งหรือสองตัวเพื่อใช้เป็นสารเติมแต่งในตัวเร่งปฏิกิริยาที่ใช้ในกระบวนการไพโรไลซิสยางหมดสภาพพลาสมาเคียมบนซีโอไลต์เอชเบต้าและพลาสมาเคียมบนเอชวายถูกเลือกให้เป็นตัวเร่งปฏิกิริยาหลักเพราะมีความสามารถในการปรับปรุงคุณภาพและปริมาณของน้ำมันส่วนเบา (แนฟทา และน้ำมันก๊าด) และด้วยข้อได้เปรียบจากขนาดของรูพรุนที่ใหญ่ของซีโอไลต์เอชเบต้าและเอชวาย มันจึงถูกเลือกให้เป็นสารเติมแต่งตัวแรกในตัวเร่งปฏิกิริยาหลัก เพื่อที่จะปรับปรุงความสามารถในการแตกสลายโครงสร้างของตัวเร่งปฏิกิริยาให้สามารถผลิตน้ำมันส่วนเบาได้ในปริมาณมากขึ้น โดยเฉพาะอย่างยิ่งน้ำมันในส่วนของแนฟทา ส่วนซีโอไลต์เอชซีเอสเอ็มไฟว์ที่มีขนาดรูพรุนที่เล็กและมีความเป็นกรดที่สูง ซึ่งมักจะเอื้อให้เกิดปฏิกิริยาการรวมตัวกันเป็นอะโรมาติกส์ ดังนั้นมันจึงถูกใช้เป็นสารเติมแต่งตัวที่สองในตัวเร่งปฏิกิริยาหลัก ปริมาณของพลาสมาเคียมถูกจำกัดไว้ที่ร้อยละ 1 โดยน้ำหนัก ในขณะที่สารเติมแต่งถูกผสมกันเชิงกายภาพกับตัวเร่งปฏิกิริยาหลักในปริมาณร้อยละ 10 และ 20 โดยน้ำหนัก สำหรับผลิตภัณฑ์ที่ได้นั้นถูกนำไปวิเคราะห์โดยวิธีก๊าซโครมาโทกราฟีและลิกวิดโครมาโทกราฟี ส่วนตัวเร่งปฏิกิริยาจะถูกนำไปวิเคราะห์ด้วยเครื่องวิเคราะห์พื้นผิว และด้วยเทคนิค TG/DTA จากผลการทดลองพบว่า การเติมเอชวายลงในพลาสมาเคียมบนเอชเบต้าไม่สามารถช่วยเพิ่มปริมาณของแนฟทาได้ เพราะความสามารถในการแตกสลายลดน้อยลง แต่มันสามารถปรับปรุงคุณภาพของน้ำมันในช่วงดีเซลให้ดีขึ้นได้โดยการเพิ่มสารประกอบไฮโดรคาร์บอนอิมตัวน้ำมัน ในขณะที่การเติมสารเติมแต่งเอชเบต้าร้อยละ 10 โดยน้ำหนักในพลาสมาเคียมบนเอชวานั้นสามารถเพิ่มความสามารถในการแตกสลายได้ดีขึ้น ซึ่งส่งผลให้ผลิตแนฟทาและก๊าซที่มีคุณค่าได้ในปริมาณที่สูง การผสมสารเติมแต่งตัวที่สองคือ เอชซีเอสเอ็มไฟว์ลงไปในตัวเร่งปฏิกิริยาที่เลือกมานั้น สามารถเพิ่มได้ทั้งคุณภาพและปริมาณของน้ำมันช่วงแนฟทา ซึ่งผลการทดลองเหล่านี้แสดงให้เห็นว่าคุณสมบัติความเป็นกรดและขนาดรูพรุนของซีโอไลต์เป็นสองปัจจัยที่สำคัญที่ส่งผลกระทบต่อถึงการผลิตผลิตภัณฑ์ต่าง ๆ

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.

This research work could not have been accomplished without the assistance and supports from all these individuals and organizations.

First and foremost, I would like to express my sincerest gratitude to my advisor, Assoc. Prof. Sirirat Jitkarnka, for the valuable guidance, attentive encouragement, and all the helpful supports throughout this thesis work.

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

Unforgettably, appreciation is forwarded to all my family and friends for their cheerful encouragement, understanding and generous supports at all time.

My sincere appreciation also extends to all staff members at The Petroleum and Petrochemical College who have provided helpful assistance and many useful technical supports at various occasions.

Lastly, I am grateful for the scholarship and funding of the thesis work provided by Thailand Research Fund, The Commissions on Higher Education, the Petroleum and Petrochemical College, and the Center of Excellence on Petrochemical and Materials Technology, Thailand.

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	 17
3.1 Materials	17
3.2 Equipments	17
3.3 Chemicals and Solvents	17
3.4 Experimental Procedures	
3.4.1 Catalyst Preparation	18
3.4.2 Reaction Equipment	19
3.4.3 Catalyst Characterization	20
3.4.4 Gas Analysis	21
3.4.5 Oil Analysis	21
 IV RESULTS AND DISCUSSION	 24
4.1 Effect of HY as a First Additive in Pd/HBETA	24
4.1.1 Catalyst Characterization	24
4.1.2 Product Distributions	25
4.1.3 Gas Compositions	26

CHAPTER	PAGE
4.1.4 Liquid Products	28
4.2 Effect of HBETA as a First Additive in Pd/HY	34
4.2.1 Catalyst Characterization	34
4.2.2 Product Distributions	35
4.2.3 Gas Compositions	36
4.2.4 Liquid Products	37
4.3 Effect of HZSM-5 as a Second Additive in Pd/HBETA + 20%wt HY	41
4.3.1 Catalyst Characterization	42
4.3.2 Product Distributions	42
4.3.3 Gas Compositions	43
4.3.4 Liquid Products	44
4.4 Effect of HZSM-5 as a Second Additive in Pd/HY + 20%wt HBETA	49
4.4.1 Catalyst Characterization	49
4.4.2 Product Distributions	49
4.4.3 Gas Compositions	50
4.4.4 Liquid Products	51
 V CONCLUSIONS AND RECOMMENDATIONS	 56
 REFERENCES	 58
 APPENDICES	 61
Appendix A Temperature Profiles	61
Appendix B Yield of Pyrolysis Products	75
Appendix C Gas Products	77
Appendix D Amount of Asphaltene in Pyrolysis Oils	81
Appendix E Chemical Compositions of Maltenes	82
Appendix F True Boiling Point of Maltenes	86

CHAPTER	PAGE
Appendix G True Boiling Point of Maltenes, Saturated Hydrocarbons, Mono-, Di-, Poly-, and Polar-aromatics in Maltenes	90
Appendix H Petroleum Fractions of Derived Oils	104
CURRICULUM VITAE	108

LIST OF TABLES

TABLE	PAGE	
2.1	Structure of zeolites used in this experiment	7
3.1	The optimized compositions and volumes of mobile phases for preparative separation of petroleum maltenes using the chromatographic column	22
4.1	Physical properties of catalysts with varied percentages of HY in Pd/HBETA	25
4.2	True boiling point cuts and carbon ranges of refinery products	28
4.3	Physical properties of catalysts with varied percentages of HBETA in Pd/HY	35
4.4	Physical properties of catalysts with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY	42
4.5	Physical properties of catalysts with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA	49
A1	Pyrolysis conditions: Non-catalytic Pyrolysis	61
A2	Pyrolysis conditions: HBETA catalyst	62
A3	Pyrolysis conditions: HY catalyst	63
A4	Pyrolysis conditions: 1%Pd/HBETA catalyst	64
A5	Pyrolysis conditions: 1%Pd/HBETA+10%HY catalyst	65
A6	Pyrolysis conditions: 1%Pd/HBETA+20%HY catalyst	66
A7	Pyrolysis conditions: 1%Pd/HY catalyst	67
A8	Pyrolysis conditions: 1%Pd/HY+10%HBETA catalyst	68
A9	Pyrolysis conditions: 1%Pd/HY+10%HBETA catalyst (repeated)	69
A10	Pyrolysis conditions: 1%Pd/HY+20%HBETA catalyst	70
A11	Pyrolysis conditions: 1%Pd/HBETA+20%HY +10%HZSM-5 catalyst	71

TABLE	PAGE
A12 Pyrolysis conditions: 1%Pd/HBETA+20%HY +20%HZSM-5 catalyst	72
A13 Pyrolysis conditions: 1%Pd/HY+10%HBETA +10%HZSM-5 catalyst	73
A14 Pyrolysis conditions: 1%Pd/HY+10%HBETA +20%HZSM-5 catalyst	74
B1 Yield of pyrolysis products obtained from pyrolysis with varied percentages of HY in Pd/HBETA	75
B2 Yield of pyrolysis products obtained from pyrolysis with varied percentages of HBETA in Pd/HY	75
B3 Yield of pyrolysis products obtained from pyrolysis with varied percentages of HZSM-5 in Pd/HBETA mixed with 20%HY	76
B4 Yield of pyrolysis products obtained from pyrolysis with varied percentages of HZSM-5 in Pd/HY mixed with 10%HBETA	76
C1 Distribution and yield of gases obtained from pyrolysis with varied percentages of HY in Pd/HBETA	77
C2 Distribution and yield of gases obtained from pyrolysis with varied percentages of HBETA in Pd/HY.	78
C3 Distribution and yield of gases obtained from pyrolysis with varied percentages of HZSM-5 in Pd/HBETA mixed with 20%HY	79
C4 Distribution and yield of gases obtained from pyrolysis with varied percentages of HZSM-5 in Pd/HY mixed with 10%HBETA	80
D1 The amount of asphaltene in pyrolysis oils	81
E1 Chemical compositions of maltenes obtained from pyrolysis with varied percentage of HY in Pd/HBETA	82

TABLE	PAGE
E2 Chemical compositions of maltenes obtained from pyrolysis with varied percentage of HBETA in Pd/HY	83
E3 Chemical compositions of maltenes obtained from pyrolysis with varied percentages of HZSM-5 in Pd/HBETA mixed with 20%HY	84
E4 Chemical compositions of maltenes obtained from pyrolysis with varied percentages of HZSM-5 in Pd/HY mixed with 10%HBETA	85
F1 True boiling point of maltenes obtained from pyrolysis with varied percentages of HY in Pd/HBETA	86
F2 True boiling point of maltenes obtained from pyrolysis with varied percentages of HBETA in Pd/HY	87
F3 True boiling point of maltenes obtained from pyrolysis with varied percentages of HZSM-5 in Pd/HBETA mixed with 20%HY	88
F4 True boiling point of maltenes obtained from pyrolysis with varied percentages of HZSM-5 in Pd/HY mixed with 10%HBETA	89
G1 Pyrolysis conditions: Non-catalytic Pyrolysis	90
G2 Pyrolysis conditions: HBETA catalyst	91
G3 Pyrolysis conditions: HY catalyst	92
G4 Pyrolysis conditions: 1%Pd/HBETA catalyst	93
G5 Pyrolysis conditions: 1%Pd/HBETA+10%HY catalyst	94
G6 Pyrolysis conditions: 1%Pd/HBETA+20%HY catalyst	95
G7 Pyrolysis conditions: 1%Pd/HY catalyst	96
G8 Pyrolysis conditions: 1%Pd/HY+10%HBETA catalyst	97
G9 Pyrolysis conditions: 1%Pd/HY+10%HBETA catalyst (repeated)	98
G10 Pyrolysis conditions: 1%Pd/HY+20%HBETA catalyst	99

TABLE	PAGE
G11 Pyrolysis conditions: 1%Pd/HBETA+20%HY +10%HZSM-5 catalyst	100
G12 Pyrolysis conditions: 1%Pd/HBETA+20%HY +20%HZSM-5 catalyst	101
G13 Pyrolysis conditions: 1%Pd/HY+10%HBETA +10%HZSM-5 catalyst	102
G14 Pyrolysis conditions: 1%Pd/HY+10%HBETA +20%HZSM-5 catalyst	103
H1 Petroleum fractions in derived oils obtained from pyrolysis with varied percentages of HY in Pd/HBETA	104
H2 Petroleum fractions in derived oils obtained from pyrolysis with varied percentages of HBETA in Pd/HY	105
H3 Petroleum fractions in derived oils obtained from pyrolysis with varied percentages of HZSM-5 in Pd/HBETA mixed with 20%HY	106
H4 Petroleum fractions in derived oils obtained from pyrolysis with varied percentages of HZSM-5 in Pd/HY mixed with 10%HBETA	107

LIST OF FIGURES

FIGURE	PAGE
2.1 Private vehicle tire components.	4
2.2 Compositions of tire and tire molecule.	5
3.1 Schematic of experimental pyrolysis system.	19
4.1 G/L ratio obtained from pyrolysis with varied percentages of HY in Pd/HBETA.	25
4.2 Yield of light olefins in the gas products obtained from pyrolysis with varied percentages of HY in Pd/HBETA.	26
4.3 Yield of cooking gases in the gas products obtained from pyrolysis with varied percentages of HY in Pd/HBETA.	27
4.4 Petroleum fractions in derived oils obtained from pyrolysis with varied percentages of HY in Pd/HBETA.	29
4.5 Percentage of asphaltene in pyrolytic oils obtained from pyrolysis with varied percentages of HY in Pd/HBETA.	30
4.6 Chemical compositions of maltenes obtained from pyrolysis with varied percentages of HY in Pd/HBETA.	31
4.7 Distribution of saturated hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HY in Pd/HBETA.	32
4.8 Distribution of total aromatic hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HY in Pd/HBETA.	33
4.9 Coke formation (wt%) on spent catalysts using in pyrolysis with varied percentages of HY in Pd/HBETA.	34
4.10 G/L ratio obtained from pyrolysis with varied percentages of HBETA in Pd/HY.	35
4.11 Yield of light olefins in the gas products obtained from pyrolysis with varied percentages of HBETA in Pd/HY.	36

FIGURE	PAGE
4.12 Yield of cooking gases in the gas products obtained from pyrolysis with varied percentages of HBETA in Pd/HY.	36
4.13 Petroleum fractions in derived oils obtained from pyrolysis with varied percentages of HBETA in Pd/HY.	38
4.14 Percentage of asphaltene in pyrolytic oils obtained from pyrolysis with varied percentages of HBETA in Pd/HY.	38
4.15 Chemical compositions of maltenes obtained from pyrolysis with varied percentages of HBETA in Pd/HY.	39
4.16 Distribution of saturated hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HBETA in Pd/HY.	40
4.17 Distribution of total aromatic hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HBETA in Pd/HY.	40
4.18 Coke formation (wt%) on spent catalysts with varied percentages of HBETA in Pd/HY.	41
4.19 G/L ratio obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.	43
4.20 Yield of light olefins in the gas products obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.	43
4.21 Yield of cooking gases in the gas products obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.	44
4.22 Petroleum fractions in derived oils obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.	45

FIGURE	PAGE
4.23 Percentage of asphaltene in pyrolytic oils obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.	45
4.24 Chemical compositions of maltenes obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.	46
4.25 Distribution of saturated hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.	47
4.26 Distribution of total aromatic hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.	48
4.27 Coke formation (wt%) on spent catalysts with varied percentages of HZSM-5 in 1%Pd/HBETA+20%HY.	48
4.28 G/L ratio obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.	50
4.29 Yield of light olefins in the gas products obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.	51
4.30 Yield of cooking gases in the gas products obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.	51
4.31 Petroleum fractions in derived oils obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.	52
4.32 Percentage of asphaltene in pyrolytic oils obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.	52

FIGURE	PAGE
4.33 Chemical compositions of maltenes obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.	53
4.34 Distribution of saturated hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.	54
4.35 Distribution of total aromatic hydrocarbons in petroleum cuts obtained from pyrolysis with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.	54
4.36 Coke formation (wt%) on spent catalysts with varied percentages of HZSM-5 in 1%Pd/HY+10%HBETA.	55
A1 Temperature profiles of waste non-catalytic pyrolysis.	61
A2 Temperature profiles of waste tire pyrolysis with using HBETA catalyst.	62
A3 Temperature profiles of waste tire pyrolysis with using HY catalyst.	63
A4 Temperature profiles of waste tire pyrolysis with using 1%Pd/HBETA catalyst.	64
A5 Temperature profiles of waste tire pyrolysis with using 1%Pd/HBETA+10%HY catalyst.	65
A6 Temperature profiles of waste tire pyrolysis with using 1%Pd/HBETA+20%HY catalyst.	66
A7 Temperature profiles of waste tire pyrolysis with using 1%Pd/HY catalyst.	67
A8 Temperature profiles of waste tire pyrolysis with using 1%Pd/HY+10%HBETA catalyst.	68
A9 Temperature profiles of waste tire pyrolysis with using 1%Pd/HY+10%HBETA (repeat) catalyst.	69

FIGURE		PAGE
A10	Temperature profiles of waste tire pyrolysis with using 1%Pd/HY+20%HBETA catalyst.	70
A11	Temperature profiles of waste tire pyrolysis with using 1%Pd/HBETA+20%HY+10%HZSM-5 catalyst.	71
A12	Temperature profiles of waste tire pyrolysis with using 1%Pd/HBETA+20%HY+20%HZSM-5 catalyst.	72
A13	Temperature profiles of waste tire pyrolysis with using 1%Pd/HY+10%HBETA+10%HZSM-5 catalyst.	73
A14	Temperature profiles of waste tire pyrolysis with using 1%Pd/HY+10%HBETA+20%HZSM-5 catalyst.	74