CATALYTIC PYROLYSIS OF WASTE TIRE USING COBALT- AND IRON-MODIFIED CATALYSTS

Suttipong Muenpol

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

2014

4 0 gc 1947

Thesis Title:

Catalytic Pyrolysis of Waste Tire Using Co- and Fe-

modified Catalysts

By:

Suttipong Muenpol

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.

(Asst. Prof. Pomthong Malakul)

Thesis Committee:

(Assoc. Prof. Sirirat Jitkarnka)

(Assoc. Prof. Apanee Luengnaruemitchai)

(Asst. Prof. Bussarin Ksapabutr)

ABSTRACT

5571032063: Petrochemical Technology Program

Suttipong Muenpol: Catalytic Pyrolysis of Waste Tire Using Co- and

Fe- modified Catalysts

Thesis Advisor: Assoc. Prof. Sirirat Jitkarnka, 117 pp.

Keywords: Waste tire/ Catalytic Pyrolysis/ Fe/ Co/ HBeta/ HMOR/ HZSM-5/

KL

Pyrolysis of waste tire not only an alternative technique to handle waste tire problem, but also can recover worthy products such as petrochemicals, and light olefins, for examples, from waste tire. In order to increase the value of pyrolysis products, a catalyst is used in this process. In this work, the effects of Fe- and Comodified catalysts on waste tire-derived products were studied. 5 wt.% Co and Fe supported on different zeolites; namely, HMOR, HBeta, HZSM-5, and KL, were tested for waste tire pyrolysis. The results showed that using both Fe-loaded catalysts and Co-loaded catalysts can enhance the production of valuable hydrocarbons, which are benzene, toluene, xylenes, styrene, cumene, and cyclohexane, except 5%Co/HBeta and 5%Fe/HBeta. In addition, 5%Fe/HMOR was the best catalyst for producing benzene, xylenes and cyclohexane. 5%Fe/HZSM-5 produced the highest yield of cumene, 5%Co/KL produced the highest yield of toluene, and HBeta can be used to produce ethylbenzene. Moreover, Fe-loaded catalysts gave a higher amount of total petrochemicals than Co-loaded catalysts. It can be concluded that Fe-loaded catalysts exhibited a better petrochemical production than Co-loaded catalysts. In addition, sulfur content in oils was reduced with using all catalysts. Namely, sulfur in oils was reduced with using pure zeolites, and further reduced with using both Coloaded catalysts and Fe-loaded catalysts. Furthermore, the lowest sulfur in oil (0.728 wt.%) was achieved from using 5%Fe/HZSM-5.

บทคัดย่อ

สุทธิพงษ์ หมื่นพล: การปรับปรุงตัวเร่งปฏิกิริยาโคบอลต์และใอรอนในปฏิกิริยาไพ โรไลซิสยางรถยนต์หมคสภาพ (Catalytic Pyrolysis of Waste Tire Using Co- and Fe-modified Catalysts) อ. ที่ปรึกษา : รศ. คร. ศิริรัตน์ จิตการค้า 117 หน้า

กระบวนการไพโรไลซิสยางรถยนต์เสื่อมสภาพเป็นี้ทางเลือกหนึ่งที่ใช้ในการจัดการกับ ปัญหาขยะยางรถยนต์ นอกจากนี้ทำให้ได้ผลิตภัณฑ์ที่มีมูลค่ากลับมาใช้ใหม่ เช่น สารปิโตรเคมี และสารโอเลฟิน ในงานวิจัยนี้เป็นการศึกษาผลกระทบที่เกิดจากการปรับปรุงตัวเร่งปฏิกิริยา โคบอลต์และใอรอน ต่อผลิตภัณฑ์ที่เกิดจากปฏิกิริยาไพโรไลซิสยางรถยนต์หมคสภาพโคยใช้ โลหะโคบอลต์ และโลหะไอรอนปริมาณร้อยละ 5 โคยน้ำหนัก บนซีโอไลต์ชนิคต่างๆ ได้แก่ เอชมอร์, เอชเบต้า, เอชซีเอสเอ็มไฟว์ และ เคเอล ผลการทคลองพบว่า การปรับปรุงตัวเร่งปฏิกิริยา ใอรอนและ โคบอลต์ทุกตัว ยกเว้น โคบอลต์บนซี โอ ไลต์ชนิคเอชเบต้าและ ใอรอนบนซี โอ ไลต์ชนิค เอชเบต้า นั้นสามารถเพิ่มการผลิตสารไฮโครคาร์บอนที่มีมูลค่าได้เพิ่มขึ้นซึ่งได้แก่ เบนซีน, โทล อื่น, ไซลื่น, สไตรีน, คิวมีน และ ไซโคลเฮกเซน นอกจากนี้ยังพบว่าตัวเร่งปฏิกิริยาไอรอนบนซึ่ โอไลต์ชนิค เอชซีเอ์สเอ็มไฟว์สามารถใช้ผลิตเบนซีน, ไซลีน และไซโคลเฮกเซน ได้ในปริมาณสูง ที่สุด ตัวเร่งปฏิกิริยาใอรอนบนซีโอไลต์ชนิดเอชซีเอสเอ็มไฟว์สามารถใช้ผลิตคิวมีนได้สูงที่สุด ตัวเรงปฏิกิริยาโคบอลต์บนซีโอไลต์ชนิดเคเอลสามารถผลิตโทลูอีนในปริมาณสูงที่สุด และซี โอใลต์ชนิคเอชเบเต้ผลิตเอทิลเบนซีนได้มากที่สุด แต่โคยรวมพบว่าการใช้ตัวเร่งปฏิกิริยาที่ ปรับปรุงตัวด้วยใอรอนสามารถใช้ผลิตสารปิโตรเคมีได้อย่างมีประสิทธิภาพมากกว่าการใช้ตัวเร่ง ปฏิกิริยาที่ปรับปรุงค้วยโคบอลต์ นอกจากนี้ยังพบอีกว่าปริมาณกำมะถันในน้ำมันลคลงเมื่อใช้ ตัวเร่งปฏิริยาในทุกกรณี โคยเมื่อใช้ซีโอไลต์พบว่าปริมาณกำมะถันในน้ำมันลคลง และลคลงมาก ขึ้นเมื่อใช้ตัวเร่งปฏิกิริยาจากการปรับปรุงตัวเร่งปฏิกิริยาโคบอลต์และใอรอน โคยตัวเร่งปฏิกิริยา ไอรอนบนซี โอ ไลต์ชนิคเอชซีเอสเอ็มไฟว์สามารถปริมาณกำมะถันในน้ำมันได้มากที่สุด

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 Asst. Prof. Bussarin Ksapabutr 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 funding of the thesis work provided by Thailand Research Fund, the Petroleum and Petrochemical College, and the Center of Excellence on Petrochemical and Materials Technology, Thailand.

TABLE OF CONTENTS

			PAGE
	Title	Page	i
	Acce	eptance Page	ii
	Abst	ract (in English)	iii
	Abst	ract (in Thai)	iv
	Ackr	nowledgements	v
	Tabl	e of Contents	vi
	List	of Tables	X
	List	of Figures	xii
		•	
Cŀ	HAPTE:	R	
	I	INTRODUCTION	1
	II	LITERATURE REVIEW	3
		2.1 Petrochemicals	3
		2.1.1 Olefins	3
		2.1.2 Aromatics	4
		2.2 Sulfur Compounds and Sulfur Removal	4
		2.3 Waste Tire Pyrolysis Products	5
		2.3.1 Non-catalytic Pyrolysis	5
		-2.3.2 Catalytic Pyrolysis	7
		2.4 Noble Metals in Catalytic Pyrolysis	8
		2.5 Non-noble Metal in Catalytic Pyrolysis	10
		2.5.1 Cobalt Catalysts	10
		2.5.2 Iron Catalysts	13
	III	EXPERIMENTAL	18
		3.1 Materials and Equipments	18
		3.1.1 Waste tire samples	18

CHAPTER		PAGE
	3.1.2 Equipment	18
	3.1.3 Chemicals and Solvents	18
	3.2 Experimental Procedures	19
	3.2.1 Catalyst Preparation	19
	3.2.2 Reaction Equipment	19
	3.2.3 Catalyst Characterization	20
	3.2.4 Product Analysis	21
IV	IMPACT OF ZEOLITE PROPERTIES ON STRUCTURE	23
	OF HYDROCARBON COMPOUNDS IN WASTE	
	TIRE-DERIVED OILS	
	4.1 Abstract	23
	4.2 Introduction	23
	4.3 Experimental	25
	4.4 Results and Disscussion	26
	4.4.1 Catalyst Characterization	26
	4.4.2 Comparison between Acid and Non-acid Supports	26
	4.4.3 Comparison between the Pore Channel of Zeolite	32
	4.4.4 Comparison between Two Pore Sizes of Zeolites	38
	4.5 Conclusions	43
	4.6 Acknowledgements -	43
	4.7 References	44
V	EFFECTS OF ZEOLITIC SUPPORT PROPERTIES	48
	ON SULFUR SPECIES AND DISTRIBUTION IN	
	TIRE-DERIVED PRODUCTS	
	5.1 Abstract	48
	5.2 Introduction	48
	5.3 Experimental	50
	5.4 Results and Discussion	52

CHAPTER		PAGE	
	5.5 Conclusions	55	
	5.6 Acknowledgements	56	
	5.7 References	56	
VI	EFFECTS OF IRON SUPPORTED ON ZEOLITES ON	57	
	STRUCTURE OF HYDROCARBON CONPOUNDS AND		
	PETROCHEMICALS IN WASTE TIRE-DERIVED OILS		
	6.1 Abstract	57	
	6.2 Introduction	58	
	6.3 Experimental	60	
	6.4 Results and Discussion	62	
	6.5 Conclusions	68	
	6.6 Acknowledgements	69	
	6.7 References	69	
VII	EFFECT OF COBALT SUPPORTED ON ZEOLITES ON	79	
	STRUCTURE OF HYDROCARBON COMPOUNDS AND		
	PETROCHEMICALS IN TIRE-DERIVED OILS		
	7.1 Abstract	79	
	7.2 Introduction	79	
	7.3 Experimental	-81	,
	7.4 Results and Discussion	82	
	7.5 Conclusions	90	
	7.6 Acknowledgements	90	
	7.7 References	91	
VIII	CONCLUSIONS AND RECOMMENDATIONS	101	
	REFERENCES	103	

CHAPTER			PAGE
	APPENDICE	ES	109
	Appendix A	Yield of Pyrolysis Products	109
	Appendix B	Gas Products	110
	Appendix C	Liquid Products	111
	Appendix D	Sulfur Content in Pyrolysis Products	115
	Appendix E	Surface Area and Pore Volume of Catalysts	116
1.40			
	CHIDDICHI	IIM VITAE	117

LIST OF TABLES

TABL	TABLE	
2.1	Properties of zeolites used in the experiments	16
2.2	Experimental design for effects of zeolite	17
2.3	Experimental design of metal-loaded part	17
4.1	Sulfur content on spent catalysts and in oils obtained from	
	KL and HMOR catalysts -	31
4.2	Sulfur content on spent catalysts and in oils obtained from	
	HBeta and HMOR catalysts	37
4.3	Sulfur content on spent catalysts and in oils obtained from	
	HBeta and HZSM-5 catalysts	42
4.4	Surface and Pore Volume of Catalysts	46
4.5	Yield of gas components obtained from waste tire pyrolysis	47
4.6	Petrochemicals obtained from waste tire pyrolysis using HMOR,	
	HBeta, HZSM-5, and KL	47
5.1	Sulfur content on spent catalysts and in oils obtained from	
	HBeta and HMOR	53
5.2	Sulfur content on spent catalysts and in oils obtained from	
	HBeta and HZSM-5	54
6.1	Valuable hydrocarbons (wt.% in maltenes) obtained from zeolites	
	(HMOR, HBeta, HZSM-5, and KL) and Fe-loaded zeolites	76
6.2	Decreases in mono-aromatic species found in oils obtained	
	from using HMOR and 5%Fe/HMOR	77
6.3	Decreases in mono-aromatic species found in oils obtained	
	from using HZSM-5 and 5%Co/HZSM-5	77
6.4	Decreases in mono-aromatic species found in oils obtained	
	from using KL and 5%Fe/KL	77
6.5	Decreases in mono-aromatic species found in oils obtained	
	from using HBeta and 5%Fe/HBeta	78

TABLE		PAGE
7.1	Amount of gasoline (wt.%) in oil	97
7.2	Valuable hydrocarbons (wt.% in maltenes) obtained from zeolites	
	(HMOR, HBeta, HZSM-5, and KL) and Co-loaded zeolites	98
7.3	Decreases in mono-aromatic species found in oils obtained	
	from using HMOR and 5%Co/HMOR	98
7.4	Decreases in mono-aromatic species found in oils obtained	
	from using HZSM-5 and 5%Co/HZSM-5	- 99
7.5	Decreases in mono-aromatic species found in oils obtained	
	from using KL and 5%Co/KL	99
7.6	Decreases in mono-aromatic species found in oils obtained	
	from using HBeta and 5%Co/HBeta	100

LIST OF FIGURES

FIGUI	FIGURE		
3.1	Diagram of the pyrolysis process.		21
4.1	Petroleum fractions in maltenes obtained from HMOR		
	and KL catalysts.		27
4.2	Concentration of chemical components in maltenes		
	obtained from HMOR and KL catalysts.		28
4.3	Concentration of petrochemicals in (a)maltenes and (b)		
	gasoline obtained from KL and HMOR catalysts.		30
4.4	Overall distribution of sulfur in pyrolysis products		
	obtained from KL and HMOR catalysts.		31
4.5	Yield of sulfur species in maltenes obtained from KL		
	and HMOR.		32
4.6	Petroleum fractions in maltenes obtained from HMOR		
	and HBeta catalysts.		33
4.7	Concentration of chemical components in maltenes		
	obtained from HMOR and HBeta catalysts.		34
4.8	Concentration of petrochemicals in (a) maltenes and (b)		
	gasoline obtained from HMOR and HBeta catalysts.		35
4.9	Overall distribution of sulfur in pyrolysis products		
	obtained from HMOR and HBeta catalysts.		36
4.10	Yield of sulfur species in maltenes obtained from HMOR		
	and HBeta catalysts.		38
4.11	Petroleum fractions in maltenes obtained from HZSM-5		
	and HBeta catalysts.		39
4.12	Concentration of chemical components in maltenes		
	obtained from HBeta and HZSM-5 catalysts.		40
4.13	Concentration of petrochemicals in (a) maltenes and (b)		
	gasoline obtained from HBeta and HZSM-5 catalysts.		41

FIGUI	FIGURE	
4.14	Overall distribution of sulfur in pyrolysis products	
	obtained from HBeta and HZSM-5 catalysts.	42
4.15	Yield of sulfur species among sulfur compounds in	
	maltenes obtained from HZSM-5 and HBeta.	43
4.16	XRD pattern of (a) HBeta, (b) HZSM-5, (c) HMOR,	
	and (d) KL.	46
5.1	Overall distribution of sulfur in pyrolysis products	Ÿ
	obtained from HBeta and HMOR.	52
5.2	Yield of sulfur species in maltenes obtained from HMOR	
	and HBeta.	53
5.3	Overall distribution of sulfur in pyrolysis products	
	obtained from HBeta and HZSM-5.	54
5.4	Yield of sulfur species in maltenes obtained from	
	HZSM-5 and HBeta.	55
6.1	H ₂ -TPR profiles: (a) 5%Fe/HBeta, (b) 5%Fe/HMOR, (c)	
	5%Fe/HZSM-5, and (d) 5%Fe/KL.	72
6.2	XRD pattern of (a) 5%Fe/HBeta, (b) 5%Fe/HMOR, (c)	
	5%Fe/HZSM-5, and (d) 5%Fe/KL.	73
6.3	Yield of pyrolysis products obtained from using pure	
	zeolites (KL, HBeta, HMOR, and HZSM-5) and 5%Fe-	
	promoted catalysts.	74
6.4	Gas compositions obtained from using pure zeolites (KL,	
	HZSM-5, HMOR, and HBeta) and 5%Fe-promoted	
	catalysts.	74
6.5	Petroleum fractions in maltenes obtained from using pure	
	zeolites (KL, HZSM-5, HMOR, and HBeta) and 5%Fe	
	supported on zeolites.	63

FIGU	GURE	
6.6	Components in gasoline (wt.%): (a) the non-catalyst case, (b) HMOR, (c) 5%Fe/HMOR, (d) KL, (e)	
	5%Fe/KL, (f) HZSM-5, (g) 5%Fe/HZSM-5, (h) HBeta,	
6.77	and (i) 5%Fe/HBeta.	75
6_7		
	catalyst, (b) HMOR, (c) 5%Fe/HMOR, (d) KL, (e)	
	5%Fe/KL, (f) HZSM-5, (g) 5%Fe/HZSM-5, (h) HBeta,	. -
<i>(</i> 0	and (i) 5%Fe/HBeta.	65
6.8	Concentration of chemical components in maltenes	
	obtained from using pure zeolites (KL, HZSM-5, HMOR,	
	and HBeta) and 5%Fe-promoted catalysts.	66
6.9	Sulfur content in oils obtained from using pure zeolites	
	(KL,HZSM-5, HMOR, and HBeta) and 5%Fe-promoted	
	catalysts.	67
6.10	Yield of sulfur species in maltenes obtained from using	
	pure zeolites (KL, HZSM-5, HMOR, and HBeta) and	
	5%Fe-promoted catalysts.	70
6.11	Overall distribution of sulfur in pyrolysis products	
	obtained from using, pure zeolites (KL, HZSM-5,	
	HMOR, and HBeta) and 5%Fe-promoted catalysts.	76
7.1	XRD pattern of (a) 5%Co/HBeta, (b) 5%Co/HMOR, (c)	
	5%Co/HZSM-5, and (d).5%Co/KL.H ₂ -TPR profiles: (a)	
	5%Co/HBeta, (b) 5%Co/HMOR, (c) 5%Co/HZSM-5,	
	and (d) 5%Co/KL.	93
7.2	H ₂ -TPR profiles: (a) 5%Co/HBeta, (b) 5%Co/HMOR,	
	(c) 5%Co/HZSM-5, and (d) 5%Co/KL.	94
7.3	Yield of pyrolysis products obtained from using pure	
	zeolites (KL, HBeta, HMOR, and HZSM-5) and 5%Co-	
	promoted catalysts	95

FIGUE	FIGURE	
7.4	Gas compositions obtained from using pure zeolites (KL,	
	HZSM-5, HMOR, and HBeta) and Co-promoted	
	catalysts.	95
7.5	Petroleum fractions in maltenes obtained from using pure	
	zeolites (KL, HZSM-5, HMOR, and HBeta) and 5%Co-	
	promoted catalysts.	84
7.6	Components in gasoline (wt.%): (a) the non-catalyst	
-	case, (b) HMOR, (c) 5%Co/HMOR, (d) KL, (e)	
	5%Co/KL, (f) HZSM-5, (g) 5%Co/HZSM-5, (h) HBeta,	
	and (i) 5%Co/HBeta.	96
7.7	Petrochemicals (wt.% in gasoline) obtained from (a) the	
	non-catalyst case, (b) HMOR, (c) 5%Co/HMOR, (d)	
	KL, (e) 5%Co/KL, (f) HZSM-5, (g) 5%Co/HZSM-5,	
	(h) HBeta, and (i) 5%Co/HBeta.	85
7.8	Concentration of chemical components in maltenes	
	obtained from using pure zeolites (KL, HZSM-5, HMOR,	
	and HBeta) and 5%Co-promoted catalysts.	87
7.9	Overall distribution of sulfur in pyrolysis products	
	obtained from using pure zeolites (KL, HZSM-5, HMOR,	
	and HBeta) and 5%Co-promoted catalysts.	97