# CATALYTIC PYROLYSIS OF WASTE TIRE OVER KL-BASED CATALYSTS: DOUBLE BEDS OF KL AND Y ZEOLITES



Mullika Phopaisarn

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, and Case Western Reserve University 2010

530028

Thesis Title:	Catalytic Pyrolysis of Waste Tire over KL-based Catalysts:
	Double Beds of KL and Y Zeolites
By:	Mullika Phopaisarn
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.

.... Dean

(Asst. Prof. Pomthong Malakul)

**Thesis Committee:** 

(Assoc. Prof. Sirirat Jitkarnka)

FRullo

(Assoc. Prof. Thirasak Rirksomboon)

..... ......

(Dr. Ruengsak Thitiratsakul)

#### ABSTRACT

5171008063:	Petrochemical Technology Program
	Mullika Phopaisarn: Catalytic pyrolysis of waste tire over KL-based
	catalysts: double beds of KL and Y zeolites
	Thesis Advisor: Assoc. Prof. Sirirat Jitkarnka, 132 pp.
Keywords:	Tire/ Pyrolysis/ Platinum/ Acid-base catalysts / Physical mixture

/Packing sequence

Catalysts can assist in waste tire pyrolysis for the production of valuable products. A new type of acid-base catalysts can play an important role on modifying the product yields and the compositions of hydrocarbon products. Therefore, the advantages of high isomerization (KL), aromatization (Pt/KL), and ring opening (Pt/Y) activities could be simultaneously taken by using a combination of these catalysts in a pyrolysis reactor. The influence of the catalyst mixing between acid (Y) and basic (KL) zeolites and the packing sequence in the reactor were studied with the expectation of producing molecules of higher valuable products. The ratio of the two zeolites was varied from 0.25 to 1.0 with a fixed 1% wt of Pt loaded by using incipient wetness impregnation. From the results, it was clear that the yields of light olefins and cooking gas obtained from the physical mixtures (Y + KL) were higher than those of the catalytic pyrolysis with the pure zeolites. Especially, the mixture at the  $Ø_{KL} = 0.25$  gave the highest activity on light olefins and cooking gas production. Moreover, it was found that Pt/KL packed in the first layer with Pt/Y on the second layer at  $Ø_{Pt/KL} = 0.25$  produced the highest saturated hydrocarbon content; thus, this combination can be considered to be a promising catalyst for gas oil production. Furthermore, the single Pt/KL bed gave the highest aromatic content in the maltenes fraction. Therefore, the octane number of its oil is expected to be highly improved.

บทคัดย่อ

นางสาวมัลลิกา เผ่าไพศาล: กระบวนการไพโรไลซิสขางรถยนด์หมดสภาพด้วยตัวเร่ง ปฏิกิริยาซีโอไลท์ชนิดเกแอล: การเรียงของซีโอไลท์ชนิดเกแอลและซีโอไลท์ชนิดวาย (Catalytic pyrolysis of waste tire over KL-based catalysts: double beds of KL and Y zeolites) อ. ที่ปรึกษา: รศ. คร. ศิริรัตน์ จิตการค้า 132 หน้า

ในปัจจุบันตัวเร่งปฏิกิริยาสามารถช่วยในการปรับปรุงผลิตภัณฑ์ที่มีคุณค่าในกระบวนการ ้ไพโรไลซิสของขาง โคยตัวเร่งปฏิกิริยากรค-เบสชนิคใหม่มีบทบาทสำคัญในการปรับเปลี่ยน ปริมาณและองค์ประกอบของสารกระกอบไฮโครคาร์บอนในผลิตภัณฑ์ ดังนั้นการนำเอาข้อคีของ ้ปฏิกิริยาการเปลี่ยนแปลงโครงสร้าง (จากซีโอไลท์ชนิคเคแอล), ปฏิกิริยาการเกิคสารอะโรมาติกส์ ้ (จากแพลตินั่มบนเคแอลซีโอไลท์), และปฏิกิริยาที่เปิดวง (จากแพลตินั่มบนวายซีโอไลท์) มาใช้ให้ เป็นประโยชน์สามารถทำได้โดยการนำเอาดัวเร่งปฏิกิริยาเหล่านี้มาใช้ร่วมกันในเตาปฏิกรณ์ไพ ้โรไลซิส งานวิจัยนี้เป็นการศึกษาผลของการผสมกันระหว่างซีโอไลท์ที่มีความเป็นกรค (วาย) และ เบส (เกแอล) และลำคับของการวางคัวเร่งปฏิกิริยาในเตาปฏิกรณ์ โคยมีความคาคหมายที่จะผลิต ้องค์ประกอบที่มีคุณค่าสูงในผลิตภัณฑ์ ในการทคลองมีการทคสอบผลของการเปลี่ยนแปลง อัตราส่วนของ ซีโอไลท์ชนิคเคแอลจาก 0.25 ถึง 1 พร้อมทั้งกำหนคการบรรจุปริมาณของตัว โลหะแพลตินั่มไว้คงที่ที่ร้อยละ 1 โคยน้ำหนัก ด้วยวิธีการทำให้เอิบชุ่ม จากผลการศึกษาแสดงให้ เห็นอย่างชัดเจนว่า ปริมาณของโอเลฟินส์ชนิดเบาและปริมาณก๊าซหุงต้มที่ได้จากการผสมระหว่าง ้วายและเคแอลซีโอไลท์มีค่ามากกว่าการใช้คัวเร่งปฏิกิริยาเพียงชนิคเดียว โคยเฉพาะอย่างยิ่งคัวเร่ง ที่มีอัตราส่วนของซีโอไลท์เคแอลเท่ากับ 0.25 นั้น สามารถผลิตโอเลฟินส์ชนิดเบาและก๊าซหุงต้ม ้ได้มากที่สุด นอกจากนี้ยังพบอีกว่า เมื่อวางตัวเร่งแพลตินั่มบนเกแอลซีโอไลท์บนชั้นแรก และ ้วางตัวเร่งแพลตินั่มบนวายซีโอไลท์ไว้ในชั้นที่สองในอัตราส่วน 0.25 ทำให้สามารถผลิต สารประกอบไฮโครคาร์บอนอิ่มได้ตัวสูงที่สุด ดังนั้นการนำตัวเร่งปฏิกิริยามาใช้ร่วมกันในลักษณะ นี้ ทำให้ผลิตน้ำมันคีเซลคุณภาพคีได้ นอกจากนี้ตัวเร่งแพลตินั่มบนเคแอลซีโอไลท์ ขังให้ สารประกอบอะ โรมาติกส์ในมัลทีนได้สูงที่สุด ดังนั้นก่าออกเทนของน้ำมันที่ผลิตได้จากตัวเร่งนี้ก็ น่าจะมีค่าสูงขึ้นจากเคิมเช่นกัน

#### ACKNOWLEDGEMENTS

This thesis could not be complete without the assistance and support from all people as follows;

I would like to take this opportunity to give a special thank to my advisors, Assoc. Prof. Sirirat Jitkarnka, who was most responsible for helping me complete the writing of my thesis book and provided the intensive attention, useful recommendation, valuable support and encouragement throughout this work.

Besides my advisors, I would like to thank my thesis committee: Dr. Ruengsak Thitiratsakul, who asked me good questions, creative suggestions, and valuable guidance.

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

Special appreciation is given to all The Petroleum and Petrochemical College's staff, who kindly helped with the analytical instruments and gave the good suggestions in this work.

Last, but not least, I would like to thank all my friends, who shared their friendly cheerful, good suggestions and useful assistance throughout the study period at PPC. Also, Finally, I am deeply indebted to my family for their love, understanding all supports to me all the time.

## **TABLE OF CONTENTS**

	Title P	age	i
	Abstra	ct (in English)	iii
	Abstra	ct (in Thai)	iv
	Ackno	wledgements	v
	Table	of Contents	vi
	List of	Tables	vii
	List of	Figures	xiii
CHA	PTER		
	Ι	INTRODUCTION	1
	II	LITERATURE REVIEW	4
	III	EXPERIMENTAL	17
		3.1 Materials	17
		3.2 Equipment and Chemicals	17
		3.3 Experimental Procedures	18
		3.3.1 Catalyst Preparation	18
		3.3.2 Pyrolysis Process	19
		3.3.3 Product Analysis	21
		3.3.4 Catalyst Characterization	23
	IV	RESULTS AND DISCUSSION	25
		4.1 Catalyst Characterization	25
		4.1.1 Crystal Structure of the Catalysts	25
		4.1.2 Physical Properties and Catalytic Activities	26
		4.2 Effect of Double Beds on Pyrolysis Products	27

V

P	A	G	E
л,	n	U	Ľ

4.2.1	Product Yields		27
4.2.2	Gas Composition		29
	4.2.2.1 Light Olefins and Cook	ing Gas production	30
4.2.3	Oil Products		31
4.2.4	Coke and Sulfur Formation		39
4.3 Effect	of Platinum Loading on Double	Bed Catalysts	41
4.3.1	Pyrolysis Yields		41
4.3.2	Gas Composition	×	44
	4.2.2.1 Light Olefins and Cook	ing Gas production	44
4.3.3	Oil Products	*	46
4.3.4	Coke and Sulfur Formation		51
CONCLU	SIONS AND RECOMMENDA	TIONS	56
5.1 Concl	usions		56
5.1 Recon	nmendations	1	57
REFERE	NCES		58
APPEND	ICES		66
Appendix	A Operating Temperature		66
Appendix	B Yields of Pyrolysis Products		92
Appendix	C Pyrolysis Gas Composition, g	100 g Tires	93
Appendix	D True Boiling Point Distillation	n (°C)	97
Appendix	E Chemical Compositions of Ma	ltenes	123
Appendix	F Carbon Number Distribution c	of Maltenes	125
Appendix	G Petroleum Fractions of Derive	ed Oils	129
Appendix	H Asphaltenes		131

## CURRICULUM VITAE

132

#### **LIST OF TABLES**

TABLE		PAGE
2.1	The structure of KL and Y zeolites	7
3.1	The optimized composition and volumes of mobile phases	
	for maltenes separation	22
3.2	Hammett indicators used for the measurment of basic and	
	acid strength	24
4.1	Physical properties and acid strength of all physical	
	mixtures	27
4.2	Coke and sulfur formation from the different packing	
	styles without platinum loading	40
4.3	Pyrolysis products obtained from the different packing	
	styles of Y and KL zeolites	42
4.4	Pyrolysis product obtained from different packing styles of	
	Pt/Y and Pt/KL zeolites	43
4.5	Petroleum fractions and chemical compositions in the	
	liquid products obtained from the different packing styles	
	of Y and KL zeolites	46
4.6	Petroleum fractions and chemical compositions in the	
	liquid products obtained from the different packing styles	
	of Y and KL zeolites with platinum loading	47
4.7	Coke and sulfur formation from the different packing	
	styles with platinum loading	52
Al	Pyrolysis conditions: non-catalytic pyrolysis	66
A2	Pyrolysis conditions: non-catalytic pyrolysis	67
A3	Pyrolysis conditions: catalytic pyrolysis using KL	68
A4	Pyrolysis conditions: catalytic pyrolysis using KL	69
A5	Pyrolysis conditions: catalytic pyrolysis using Y	70
A6	Pyrolysis conditions: catalytic pyrolysis using Y	71

and the second second

1

A7	Pyrolysis conditions: catalytic pyrolysis using Y and K	
	$(Y + KL \text{ at } \emptyset_{KL} = 0.25)$	72
A8	Pyrolysis conditions: catalytic pyrolysis using Y and KL	
	$(Y + KL \text{ at } \emptyset_{KL} = 0.5)$	73
A9	Pyrolysis conditions: catalytic pyrolysis using Y and KL	
	$(Y + KL \text{ at } \emptyset_{KL} = 0.75)$	74
A10	Pyrolysis conditions: catalytic pyrolysis using Y and KL	
	$(Y> KL at \ Ø_{KL} = 0.25)$	75
AH	Pyrolysis conditions: catalytic pyrolysis using Y and KL	
	$(Y> KL \text{ at } \emptyset_{KL} = 0.5)$	76
A12	Pyrolysis conditions: catalytic pyrolysis using Y and KL	
	$(Y> KL at \ Ø_{KL} = 0.75)$	77
A13	Pyrolysis conditions: catalytic pyrolysis using Y and KL	
	$(KL> Y \text{ at } \emptyset_{KL} = 0.25)$	78
A14	Pyrolysis conditions: catalytic pyrolysis using Y and KL	
	$(KL> Y \text{ at } \emptyset_{KL} = 0.5)$	79
A15	Pyrolysis conditions: catalytic pyrolysis using Y and KL	
	$(KL> Y \text{ at } \emptyset_{KL} = 0.75)$	80
A16	Pyrolysis conditions: catalytic pyrolysis using Pt/KL	81
A17	Pyrolysis conditions: catalytic pyrolysis using Pt/Y	82
A18	Pyrolysis conditions: catalytic pyrolysis using Pt/Y and	
	$Pt/KL (Pt/Y + Pt/KL at Ø_{Pt/KL} = 0.25)$	83
A19	Pyrolysis conditions: catalytic pyrolysis using Pt/Y and	
	$Pt/KL (Pt/Y + Pt/KL at Ø_{Pt/KL} = 0.5)$	84
A20	Pyrolysis conditions: catalytic pyrolysis using Pt/Y and	
	$Pt/KL (Pt/Y + Pt/KL at Ø_{Pt/KL} = 0.75)$	85
A21	Pyrolysis conditions: catalytic pyrolysis using Pt/Y and	
	$Pt/KL$ ( $Pt/Y \rightarrow Pt/KL$ at $\emptyset_{Pt/KL} = 0.25$ )	86

## TABLE

A22	Pyrolysis conditions: catalytic pyrolysis using Pt/Y and	
	$Pt/KL$ ( $Pt/Y \rightarrow Pt/KL$ at $Ø_{Pt/KL} = 0.5$ )	87
A23	Pyrolysis conditions: catalytic pyrolysis using Pt/Y and	
	$Pt/KL (Pt/Y> Pt/KL at Ø_{Pt/KL} = 0.75)$	88
A24	Pyrolysis conditions: catalytic pyrolysis using Pt/Y and	
	Pt/KL (Pt/KL> Pt/Y at $Ø_{Pt/KL} = 0.25$ )	89
A25	Pyrolysis conditions: catalytic pyrolysis using Pt/Y and	
	Pt/KL (Pt/KL> Pt/Y at $Ø_{Pt/KL} = 0.5$ )	90
A26	Pyrolysis conditions: catalytic pyrolysis using Pt/Y and	
	Pt/KL (Pt/KL> Pt/Y at $Ø_{Pt/KL} = 0.75$ )	91
B1	Effects of KL, Y and platinum-supported catalysts	92
B2	Effects of physical mixtures and platinum-supported	
	catalysts	92
B3	Effects of packing sequence (Y> KL) and platinum-	
	supported catalysts	92
B4	Effects of packing sequence (KL> Y) and platinum-	
	supported catalysts	92
C1	Influences of various zeolites	93
C2	Influences of physical mixtures (Y + KL) and	
	corresponding platinum-supported beds (Pt/Y + Pt/KL)	94
C3	Influences of packing sequence (Y> KL) and	
	corresponding platinum-supported beds (Pt/Y> Pt/KL)	95
C4	Influences of packing sequence (KL> Y) and	
	corresponding platinum-supported beds (Pt/KL> Pt/Y)	96
D1	Non-catalytic case	97
D2	Non-catalytic case	98
D3	KL zeolite	99
D4	KL zeolite	100
D5	Y zeolite	101

## TABLE

D6	Y zeolite	102
D7	Physical mixture (Y + KL) at $Ø_{KL} = 0.25$	103
D8	Physical mixture (Y + KL) at $Ø_{KL} = 0.5$	104
D9	Physical mixture (Y + KL) at $Ø_{KL} = 0.75$	105
D10	Packing sequence (Y> KL) at $Ø_{KL} = 0.25$	106
D11	Packing sequence (Y> KL) at $Ø_{KL} = 0.5$	107
D12	Packing sequence (Y> KL) at $Ø_{KL} = 0.75$	108
D13	Packing sequence (KL> Y) at $Ø_{KL} = 0.25$	109
D14	Packing sequence (KL> Y) at $Ø_{KL} = 0.5$	110
D15	Packing sequence (KL> Y) at $Ø_{KL} = 0.75$	111
D16	Pt/KL	112
D17	Pt/Y	113
D18	Physical mixture (Pt/Y + Pt/KL) at $Ø_{Pt/KL} = 0.25$	114
D19	Physical mixture (Pt/Y + Pt/KL) at $Ø_{Pt/KL} = 0.5$	115
D20	Physical mixture (Pt/Y + Pt/KL) at $Ø_{Pt/KL} = 0.75$	116
D21	Packing sequence (Pt/Y> Pt/KL) at $\emptyset_{Pt/KL} = 0.25$	117
D22	Packing sequence (Pt/Y> Pt/KL) at $Ø_{Pt/KL} = 0.5$	118
D23	Packing sequence (Pt/Y> Pt/KL) at $Ø_{Pt/KL} = 0.75$	119
D24	Packing sequence (Pt/KL> Pt/Y) at $Ø_{Pt/KL} = 0.25$	120
D25	Packing sequence (Pt/KL> Pt/Y) at $Ø_{Pt/KL} = 0.5$	121
D26	Packing sequence (Pt/KL> Pt/Y) at $Ø_{Pt/KL} = 0.75$	122
El	Effects of KL, Y and platinum-supported catalysts	123
E2	Effects of physical mixtures and platinum-supported	123
	catalysts	
E3	Effects of packing sequence (Y> KL) and platinum-	123
	supported catalysts	
E4	Effects of packing sequence (KL> Y) and platinum-	124
	supported catalysts	
F1	Influences of various zeolites	125

\*\*\*\*

F2	Influences of physical mixtures (Y + KL) and	
	corresponding platinum-supported beds (Pt/Y + Pt/KL)	126
F3	Influences of packing sequence (Y> KL) and	
	corresponding platinum-supported beds (Pt/Y> Pt/KL)	127
F4	Influences of packing sequence (KL> Y) and	
	corresponding platinum-supported beds (Pt/KL> Pt/Y)	128
Gl	Effects of KL, Y and platinum-supported catalysts	129
G2	Effects of physical mixtures and platinum-supported	
	catalysts	129
G3	Effects of packing sequence (Y> KL) and platinum-	
	supported catalysts	129
G4	Effects of packing sequence (KL> Y) and platinum-	
	supported catalysts	130
H1	Effects of non platinum-supported catalysts	131
H2	Effects of platinum-supported catalysts	131

### **LIST OF FIGURES**

FIGURI	Ξ	PAGE
2.1	Sulfide network formation.	4
2.2	Tire components and main rubber compositions in tire: (a)	5
	diagonal tire, and (b) radial tire.	
2.3	Mixture design for the system of ZSM-5/beta/rhenium.	14
2.4	Direct and two-stage routes for converting pyrolysis gasoline	
	into $C_{2+}$ - <i>n</i> -alkanes, a high-quality synthetic feedstock for	
	steamcrackers.	16
3.1	The order of catalyst packing in the reactor.	19
3.2	An autoclave reactor used in the experiment.	20
3.3	Schematic of the pyrolysis process.	20
4.1	XRD patterns of (a) physical mixtures (Y + KL) and (b)	
	physical mixtures with platinum loading (Pt/Y + Pt/KL) at	
	various weight fractions of KL	26
4.2	G/L ratio at different packing sequences and various weight	
	fractions of KL.	28
4.3	Distribution of gas compositions for the case of physical	
	mixtures of Y and KL zeolites.	29
4.4	Effects of double bed packing and the weight fraction of KL	
	on light olefins production.	30
4.5	Effects of double bed packing and the weight fraction of KL	
	on cooking gas production.	31
4.6	Effect of physical mixing (Y + KL) on petroleum fractions	
	in maltenes.	32
4.7	Effect of packing sequence (Y> KL) on petroleum	
	fractions in maltenes.	33
4.8	Effect of packing sequence (KL> Y) on petroleum	
	fractions in maltenes.	34

### **FIGURE**

4.9	Chemical composition in maltene obtained from the physical	
	mixtures of zeolites (Y + KL) with various weight fractions	
	of KL.	36
4.10	Chemical composition in maltene obtained from the packing	
	sequence (Y> KL) with various weight fractions of KL.	37
4.11	Chemical composition in maltene obtained from the packing	
	sequence (KL> Y) with various weight fractions of KL.	38
4.12	Weight fraction of asphaltene in pyrolytic oils obtained from	
	using the double beds of zeolites.	39
4.13	The $\alpha_{G/L}$ at different styles of double bed packing and	
	various weight fractions of KL.	44
4.14	The $\alpha_{\text{light olefins}}$ at different packing sequences and various	
	weight fractions of KL.	45
4.15	The $\alpha_{\text{cooking gas}}$ at different packing sequences and various	
	weight fractions of KL.	45
4.16	The $\alpha_{Naphtha}$ obtained from different packing styles at various	
	weight fractions of KL.	48
4.17	The $\alpha_{Kerosene}$ obtained from different packing styles at various	
	weight fractions of KL.	48
4.18	The $\alpha_{Gas oil}$ obtained from different packing styles at various	
	weight fractions of KL.	49
4.19	The $\alpha_{Saturated hydrocarbons}$ obtained from different packing styles	
	at various weight fractions of KL.	50
4.20	The $\alpha_{Total aromatic hydrocarbons}$ obtained from different packing	
	styles at various weight fractions of KL.	50
4.21	The $\alpha_{asphaltene}$ at different packing sequences and various	
	weight fractions of KL.	51