

**COMPETITIVE ADSORPTION OF C<sub>8</sub> AROMATICS AND TOLUENE  
ON KY AND KBaX ZEOLITES**



Mr. Varoon Varanyanond

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

2001

ISBN 974-13-0704-7

12

2562

I 19689457

**Thesis Title:** Competitive Adsorption of C<sub>8</sub> Aromatics and Toluene on KY and KBaX Zeolites  
**By:** Mr. Varoon Varanyanond  
**Program:** Petrochemical Technology  
**Thesis Advisor:** Dr. Santi Kulprathipanja  
Dr. Pramoch Rangsunvigit  
Dr. Pomthong Malakul

---

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

*K. Bunyakiat*  
..... College Director  
(Assoc. Prof. Kunchana Bunyakiat)

**Thesis Committee:**

*Santi Kulprathipanja*  
.....  
(Dr. Santi Kulprathipanja)

*Pramoch*  
.....  
(Dr. Pramoch Rangsunvigit)

*Pomthong Malakul*  
.....  
(Dr. Pomthong Malakul)

*Piya Ouraipryvan*  
.....  
(Mr. Piya Ouraipryvan)

## บทคัดย่อ

วรุณ วารัญญานนท์ : การดูดซับแบบแข่งขันระหว่างอโรมาติกส์คาร์บอนแปดอะตอมกับโทลูอินของซีโอไลต์โพแทสเซียมวายและโพแทสเซียมแบเรียมเอ็กซ์ (Competitive Adsorption of  $C_8$  Aromatics and Toluene on *KY* and *KBaX* Zeolites) อ. ที่ปรึกษา : ดร. สันติ กุลประทีปปัญญา ดร. ปราโมช รังสรรค์วิจิตร ดร. ปมทอง มาลากุล ณ อยุธยา 124 หน้า ISBN 974-13-0704-7

งานวิจัยศึกษาการดูดซับระหว่างพาราไซลีน ออโทไซลีน เมตาไซลีน และเอทิลเบนซีนกับโทลูอินในสถานะของเหลวบนซีโอไลต์โพแทสเซียมวาย และโพแทสเซียมแบเรียมเอ็กซ์ที่อุณหภูมิคงที่ และได้ทำการศึกษาผลกระทบของความเข้มข้นของสารตั้งต้น อุณหภูมิระหว่างการดูดซับ และปริมาณน้ำในซีโอไลต์ ที่ความเข้มข้นของสารตั้งต้นสูงพบว่าซีโอไลต์ทั้งสองชนิดดูดซับพาราไซลีนได้มากที่สุด รองลงมาได้แก่เอทิลเบนซีน เมตาไซลีนและ ออโทไซลีน ตามลำดับ ลักษณะดังกล่าวสามารถอธิบายได้โดยความเป็นกรดของซีโอไลต์ ซีโอไลต์ที่มีความเป็นกรดอ่อนสามารถดูดซับพาราไซลีนได้ดีกว่า เนื่องจากความเป็นเบสของสารลดลงจากเมตาไซลีน ออโทไซลีน เอทิลเบนซีน และพาราไซลีน ดังนั้นซีโอไลต์โพแทสเซียมวายซึ่งมีความเป็นกรดอ่อนกว่าซีโอไลต์โพแทสเซียมแบเรียมเอ็กซ์จึงมีความสามารถในการดูดซับพาราไซลีนได้ดีกว่า สำหรับความจุในการดูดซับซีโอไลต์โพแทสเซียมวายมีความสามารถสูงกว่าซีโอไลต์โพแทสเซียมแบเรียมเอ็กซ์ ค่าความจุในการดูดซับและค่าซีเล็คติวิตีต่อพาราไซลีนของซีโอไลต์ทั้งสองชนิดลดลงเมื่ออุณหภูมิระหว่างการดูดซับ หรือปริมาณน้ำในซีโอไลต์สูงขึ้น แบบจำลองทางคณิตศาสตร์ของการดูดซับสามารถนำไปใช้เป็นตัวแทนข้อมูลจากการทดลองได้ดี นอกจากนี้ยังพบว่าค่าซีเล็คติวิตีต่อพาราไซลีนที่ได้จากการทดลองการดูดซับแบบแข่งขันของสารทุกตัวพร้อมกันมีค่าสูงกว่าค่าที่ได้จากการทดลองของสารแต่ละตัว

## ABSTRACT

4271027063: PETROCHEMICAL TECHNOLOGY PROGRAM

Varoon Varayanond: Competitive Adsorption of C<sub>8</sub> Aromatics and Toluene on KY and KBaX Zeolites

Thesis Advisors: Dr. Santi Kulprathipanja, Dr. Pramoch Rangsunvigit, and Dr. Pomthong Malakul, 124 pp ISBN 974-13-0704-7

Keywords: Xylene Separation/ Adsorption/ Zeolite/ Faujasite/ Water Content/ Adsorptive Separation

Liquid phase adsorption of four isomers of C<sub>8</sub> aromatics (*p*-xylene, *m*-xylene, *o*-xylene, and ethylbenzene) with toluene as a desorbent on *KY* and *KBaX* zeolites at constant temperature was studied. Effects of each C<sub>8</sub> aromatic concentration, operating temperature, and water content in the zeolites on the adsorption of each C<sub>8</sub> aromatic were investigated. At high concentration, both zeolites adsorbed preferentially *p*-xylene, followed by ethylbenzene, *m*-xylene, and *o*-xylene at the studied water contents and temperatures. However, at low concentration, although the zeolites also adsorbed *p*-xylene the most, no definite trend was observed for the other aromatics. Additionally, *KY* zeolite had higher capacity and *p*-xylene selectivity than *KBaX* zeolite over the range of concentration. As the operating temperature increased, the zeolite capacity and *p*-xylene selectivity decreased. Moreover, the higher water content in the zeolite, the lower zeolite capacity and *p*-xylene selectivity. The statistical model provided good agreement to the single component adsorption data. In addition, the selectivity from multi-component pulse tests on *KY* zeolite was higher than that from the single component result.

## ACKNOWLEDGEMENT

This work has been a very invaluable and enjoyable experience. This work can not be successful without the help of a number of graceful persons.

First of all, I am deeply indebted to Dr. Santi Kulprathipanja, my US advisor, for serving as my thesis advisor, for his precious advice, constructive criticism, and reliable suggestions. Also, for his strong support and encouragement that he gave throughout this work. I would like to forward my appreciation to Ms. Apinya Kulprathipanja, whose kindness has engraved deeply in my heart.

Out of a sense of gratefulness, I would like to express my deepest gratitude to Dr. Pramoch Rangsunvigit, my Thai advisor, not only for his excellent guidance and assistance, but also for his patience in listening and proofreading my thesis. He also makes this thesis fascinating.

I would also like to thank Dr. Pomthong Malakul, my co-advisor, for his admirable support. He provided very useful suggestions and also proofreading the thesis.

Unforgettable appreciation is forwarded to the Petroleum and Petrochemical College staff who contributed in various degrees to the success of this thesis.

I would like to extend special thanks to the UOP LLC for a great support during my graduate studies.

I have benefited greatly from my discussions with a number of individuals, in particular Ms. Worrarat Rattanawong, Mr. Yune D.T. Le, Mr. Darryl Johnson, Ms. Linda Cheng, and Mr. Greg Maher.

Finally, I would like to take this opportunity to thank my family and all my friends for their help, trust, cheerfulness, and encouragement.

## TABLE OF CONTENTS

	<b>PAGE</b>
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	viii
List of Figures	x
<b>CHAPTER</b>	
<b>I INTRODUCTION</b>	<b>1</b>
<b>II BACKGROUND AND LITERATURE SURVEY</b>	<b>3</b>
2.1 Background	3
2.1.1 Adsorption	3
2.1.2 Selectivity	4
2.1.3 Zeolite	4
2.1.4 General Statistical Model	6
2.2 Literature Survey	7
<b>III EXPERIMENTAL</b>	<b>14</b>
3.1 Materials	14
3.2 Experiment	15
3.2.1 Single Component Adsorption Experiment	15
3.2.2 Multi-Component Pulse Test	16

<b>CHAPTER</b>	<b>PAGE</b>
<b>IV RESULTS AND DISCUSSION</b>	21
4.1 Effect of Zeolite	21
4.2 Effect of Operating Temperature	23
4.3 Effect of Water Content in Zeolite	24
4.4 Adsorption of Toluene	24
4.5 Modeling of the Experimental Data	25
4.6 The Multi-Component Pulse Test on KY Zeolite	26
<b>V CONCLUSIONS AND RECOMMENDATIONS</b>	112
<b>REFERENCES</b>	114
<b>APPENDICES</b>	116
<b>APPENDIX A</b> Modeling Parameters	116
<b>APPENDIX B</b> Additional References	122
<b>CURRICULUM VITAE</b>	124

## LIST OF TABLES

TABLE	PAGE
3.1 Chemical used in the experiment	14
3.2 Properties of the <i>KBaX</i> and <i>KY</i> zeolites from the BET analysis	14
3.3 GC conditions for the analysis	16
3.4 Samples preparation for <i>p</i> -xylene	18
3.5 Samples preparation for <i>m</i> -xylene	18
3.6 Samples preparation for <i>o</i> -xylene	18
3.7 Samples preparation for ethylbenzene	18
4.1 Selectivity from the single component experiment of <i>p</i> -xylene on <i>KY</i> zeolite LOI=1.2%	28
4.2 Selectivity from the single component experiment of <i>p</i> -xylene on <i>KY</i> zeolite LOI=2.4%	28
4.3 Selectivity from the single component experiment of <i>p</i> -xylene on <i>KY</i> zeolite LOI=4.4%	28
4.4 Selectivity from the single component experiment of <i>p</i> -xylene on <i>KBaX</i> zeolite LOI=1.2%	29
4.5 Selectivity from the single component experiment of <i>p</i> -xylene on <i>KBaX</i> zeolite LOI=2.5%	29
4.6 Selectivity from the single component experiment of <i>p</i> -xylene on <i>KBaX</i> zeolite LOI=4.5%	29
4.7 Selectivity from the pulse test of <i>p</i> -xylene on <i>KY</i> zeolite LOI=1.2%	30
4.8 Selectivity from the pulse test of <i>p</i> -xylene on <i>KY</i> zeolite LOI=2.4%	30



<b>TABLE</b>	<b>PAGE</b>
4.9 Selectivity from the pulse test of <i>p</i> -xylene on <i>KY</i> zeolite LOI=4.4%	30
A-1 Parameters of the adsorption model for <i>KY</i> zeolite LOI=1.2%	116
A-2 Parameters of the adsorption model for <i>KY</i> zeolite LOI=2.4%	117
A-3 Parameters of the adsorption model for <i>KY</i> zeolite LOI=4.4%	118
A-4 Parameters of the adsorption model for <i>KBaX</i> zeolite LOI=1.2%	119
A-5 Parameters of the adsorption model for <i>KBaX</i> zeolite LOI=2.5%	120
A-6 Parameters of the adsorption model for <i>KBaX</i> zeolite LOI=4.5%	121

**LIST OF FIGURES**

<b>FIGURE</b>	<b>PAGE</b>
2.1 Secondary Building units and commonly occurring polyhedral units in zeolite framework structure	12
2.2 Schematic representation showing framework structure of zeolite faujasite	13
3.1 Experimental setup for single component adsorption experiment	19
3.2 Experimental setup of a pulse test unit	20
4.1 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=1.2% at 40 °C	31
4.2 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=1.2% at 65 °C	32
4.3 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=1.2% at 90 °C	33
4.4 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=2.4% at 40 °C	34
4.5 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=2.4% at 65 °C	35
4.6 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=2.4% at 90 °C	36
4.7 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=4.4% at 40 °C	37
4.8 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=4.4% at 65 °C	38
4.9 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=4.4% at 90 °C	39

FIGURE	PAGE
4.10 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=1.2% at 40 °C	40
4.11 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=1.2% at 65 °C	41
4.12 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=1.2% at 90 °C	42
4.13 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=2.5% at 40 °C	43
4.14 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=2.5% at 65 °C	44
4.15 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=2.5% at 90 °C	45
4.16 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=4.5% at 40 °C	46
4.17 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=4.5% at 65 °C	47
4.18 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=4.5% at 90 °C	48
4.19 Adsorption of <i>p</i> -xylene and toluene on KY and <i>KBaX</i> zeolites LOI=1.2% at 40 °C	49
4.20 Adsorption of <i>p</i> -xylene and toluene on KY and <i>KBaX</i> zeolites LOI=1.2% at 65 °C	50
4.21 Adsorption of <i>p</i> -xylene and toluene on KY and <i>KBaX</i> zeolites LOI=1.2% at 90 °C	51
4.22 Adsorption of <i>p</i> -xylene and toluene on KY and <i>KBaX</i> zeolites LOI=2.4% at 40 °C	52

FIGURE	PAGE
4.23 Adsorption of <i>p</i> -xylene and toluene on KY and <i>KBaX</i> zeolites LOI=2.4% at 65 °C	53
4.24 Adsorption of <i>p</i> -xylene and toluene on KY and <i>KBaX</i> zeolites LOI=2.4% at 90 °C	54
4.25 Adsorption of <i>p</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=4.4% at 40 °C	55
4.26 Adsorption of <i>p</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=4.4% at 65 °C	56
4.27 Adsorption of <i>p</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=4.4% at 90 °C	57
4.28 Adsorption of <i>o</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=1.2% at 40 °C	58
4.29 Adsorption of <i>o</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=1.2% at 65 °C	59
4.30 Adsorption of <i>o</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=1.2% at 90 °C	60
4.31 Adsorption of <i>o</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=2.4% at 40 °C	61
4.32 Adsorption of <i>o</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=2.4% at 65 °C	62
4.33 Adsorption of <i>o</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=2.4% at 90 °C	63
4.34 Adsorption of <i>o</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=4.4% at 40 °C	64
4.35 Adsorption of <i>o</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=4.4% at 65 °C	65

FIGURE	PAGE
4.36 Adsorption of <i>o</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=4.4% at 90 °C	66
4.37 Adsorption of <i>m</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=1.2% at 40 °C	67
4.38 Adsorption of <i>m</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=1.2% at 65 °C	68
4.39 Adsorption of <i>m</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=1.2% at 90 °C	69
4.40 Adsorption of <i>m</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=2.4% at 40 °C	70
4.41 Adsorption of <i>m</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=2.4% at 65 °C	71
4.42 Adsorption of <i>m</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=2.4% at 90 °C	72
4.43 Adsorption of <i>m</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=4.4% at 40 °C	73
4.44 Adsorption of <i>m</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=4.4% at 65 °C	74
4.45 Adsorption of <i>m</i> -xylene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=4.4% at 90 °C	75
4.46 Adsorption of ethylbenzene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=1.2% at 40 °C	76
4.47 Adsorption of ethylbenzene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=1.2% at 65 °C	77
4.48 Adsorption of ethylbenzene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=1.2% at 90 °C	78

FIGURE	PAGE
4.49 Adsorption of ethylbenzene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=2.4% at 40 °C	79
4.50 Adsorption of ethylbenzene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=2.4% at 65 °C	80
4.51 Adsorption of ethylbenzene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=2.4% at 90 °C	81
4.52 Adsorption of ethylbenzene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=4.4% at 40 °C	82
4.53 Adsorption of ethylbenzene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=4.4% at 65 °C	83
4.54 Adsorption of ethylbenzene and toluene on <i>KY</i> and <i>KBaX</i> zeolites LOI=4.4% at 90 °C	84
4.55 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=1.2% at 40 °C	85
4.56 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=1.2% at 65 °C	86
4.57 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=1.2% at 90 °C	87
4.58 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=2.4% at 40 °C	88
4.59 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=2.4% at 65 °C	89
4.60 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=2.4% at 90 °C	90
4.61 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=4.4% at 40 °C	91

FIGURE	PAGE
4.62 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=4.4% at 65 °C	92
4.63 Adsorption of the C <sub>8</sub> aromatics on the <i>KY</i> zeolite LOI=4.4% at 90 °C	93
4.64 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=1.2% at 40 °C	94
4.65 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=1.2% at 65 °C	95
4.66 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=1.2% at 90 °C	96
4.67 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=2.5% at 40 °C	97
4.68 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=2.5% at 65 °C	98
4.69 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=2.5% at 90 °C	99
4.70 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=4.5% at 40 °C	100
4.71 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=4.5% at 65 °C	101
4.72 Adsorption of the C <sub>8</sub> aromatics on the <i>KBaX</i> zeolite LOI=4.5% at 90 °C	102
4.73 Pulse test on <i>KY</i> zeolite LOI=1.2% at 40 °C	103
4.74 Pulse test on <i>KY</i> zeolite LOI=1.2% at 65 °C	104
4.75 Pulse test on <i>KY</i> zeolite LOI=1.2% at 90 °C	105
4.76 Pulse test on <i>KY</i> zeolite LOI=2.4% at 40 °C	106
4.77 Pulse test on <i>KY</i> zeolite LOI=2.4% at 65 °C	107

<b>FIGURE</b>	<b>PAGE</b>
4.78 Pulse test on <i>KY</i> zeolite LOI=2.4% at 90 °C	108
4.79 Pulse test on <i>KY</i> zeolite LOI=4.4% at 40 °C	109
4.80 Pulse test on <i>KY</i> zeolite LOI=4.4% at 65 °C	110
4.81 Pulse test on <i>KY</i> zeolite LOI=4.4% at 90 °C	111