CONTINUOUS REMOVAL OF THIOPHENIC SULFUR COMPOUNDS FROM TRANSPORTATION FUELS BY USING X ZEOLITE

Jittima Kaewboran

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
2006

ISBN 974-9937-42-2

Thesis Title:	Continuous Removal of Thiophenic Sulfur Compounds from Transportation Fuels by Using X Zeolite
By:	Jittima Kaewboran
Program:	Petroleum Technology
Thesis Advisors:	Asst. Prof. Pomthong Malakul
	Dr. Sophie Jullian
	Dr. Rapeepong Suwanwarangkul

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

Nantaya Yanumet ..... College Director
(Assoc. Prof. Nantaya Yanumet)

Thesis Committee:

....
(Asst. Prof. Pomthong Malakul) (Dr. Sophie Jullian)

....
(Dr. Rapeepong Suwanwarangkul) (Asst. Prof. Apanee Luengnaruemitchai)

.....
(Dr. Siriporn Jongpatiwut)

ABSTRACT

4773004063: Petroleum Technology
Jittima Kaewboran: Continuous Removal of Thiophenic Sulfur Compounds from Transp ortation Fuels by Using X Zeolite
Thesis Advisors: Asst. Prof. Pomthong Malakul, Dr. Sophie Jullian, and Dr. Rapeepong Suwanwarangkul 94 pp. ISBN 974-9937-42-2
Keywords: Adsorption/ Diesel/ Gasoline/ Sulfur Removal/ Zeolite

Recently, new laws and regulations concerning environmental impacts have driven an increase in the demand of ultra low sulfur fuels. Over the years, the adsorption process has proven to be an efficient process for removing a small amount of refractory sulfur compounds (ppm level), which is difficult to treat by the conventional hydrodesulfurization process (HDS). In this research, continuous liquid adsorption of three model sulfur compounds, i.e., 3-methylthiophene (3-MT), benzothiophene (BT) and dibenzothiophene (DBT), using NaX zeolites were studied in a packed column. Iso-octane and decane were used to represent gasoline and diesel, respectively. The effects of initial sulfur concentration and types of sulfur compounds on the adsorption breakthrough curve were examined. The result shows that at higher initial feed concentration, the slope of the breakthrough curve is steeper and the breakthrough time is shorter. Whereas, the breakthrough of the three types of sulfur compounds are found to arrange in the order of BT>3-MT>DBT. The mathematical model of sulfur adsorption on NaX zeolite was developed to predict breakthrough profiles. It considers diffusion along the column and inside the adsorbent particles. The breakthrough curve obtained from the model agrees well with the experimental data. In addition, the desorption of sulfur compounds was also studied by heating the column at 400°C. The desorptions of adsorbed 3-MT and BT were successfully achieved. NaX zeolite can be recovered almost all of the original capacity but it is not effective for DBT desorption.

บทคัดย่อ

จิตติมา แก้วโบราณ: การกำจัดสารประกอบกำมะถันออกจากน้ำมันเชื้อเพลิงโดยการดูดซับบนโซเดียมเอ็กซ์ซีโอไลท์ในระบบแบบต่อเนื่อง (Continuous Removal of Thiophenic Sulfur Compounds from Transportation Fuels by Using X Zeolite) อ. ที่ปรึกษา: ผศ. ดร. ปมทอง มาลากุล ณ อยุธยา, ดร. โซฟี จูเลียน และ ดร. รพีพงศ์ สุวรรณวรางกูร 94 หน้า ISBN 974-9937-42-2

ปัจจุบันกฎระเบียบด้านสิ่งแวดล้อมที่เข้มงวดทำให้น้ำมันเชื้อเพลิงที่มีกำมะถันในปริมาณต่ำเป็นพิเศษเป็นที่ต้องการมากขึ้น ในช่วงที่ผ่านมากระบวนการดูดซับจึงได้รับความสนใจในการกำจัดสารประกอบกำมะถันประเภทที่กำจัดได้ยากซึ่งไม่สามารถกำจัดได้โดยวิธีไฮโดรดีซัลเฟอร์ไรเซชั่น (Hydrodesulfurization) งานวิจัยนี้เป็นการศึกษาการดูดซับสารประกอบกำมะถันประเภทไทโอฟีน 3 ชนิด คือ 3-เมทิลไทโอฟีน เบนโซไทโอฟีน และไดเบนโซไทโอฟีน ในระบบแบบต่อเนื่องโดยใช้ตัวดูดซับ คือ โซเดียมเอ็กส์ซีโอไลท์ (NaX zeolite) และใช้ดีเคนและไอโซออกเทน เป็นแบบจำลองของน้ำมันเชื้อเพลิงดีเซลและแก๊สโซลีนตามลำดับ โดยศึกษาผลกระทบของความเข้มข้นตั้งต้นของสารประกอบกำมะถันและชนิดของสารประกอบกำมะถันที่มีผลต่อกราฟการเบรคทรู ผลการทดลองแสดงให้เห็นว่าเมื่อความเข้มข้นตั้งต้นของสารประกอบกำมะถันในสารละลายสูงขึ้น ความชันของกราฟการเบรคทรูมีแนวโน้มเพิ่มขึ้น แต่ระยะเวลาในการเบรคทรูจะสั้นลง เมื่อเปรียบเทียบระยะเวลาในการเบรคทรูของสารประกอบกำมะถันทั้ง 3 ชนิดพบว่าลดลงตามลำดับดังนี้ เบนโซไทโอฟีน>3-เมทิลไทโอฟีน>ไดเบนโซไทโอฟีน สำหรับการพัฒนาแบบจำลองทางคณิตศาสตร์เพื่อทำนายกราฟการเบรคทรูของการดูดซับของสารประกอบกำมะถันบนโซเดียมเอ็กซ์ซีโอไลท์นั้นได้พิจารณาทั้งการแพร่ผ่านของสารประกอบกำมะถันทั้งภายในหอดูดซับและภายในซีโอไลท์ ผลที่ได้จากแบบจำลองทางคณิตศาสตร์สอดคล้องกับผลการทดลองภายใต้สภาวะต่างๆ นอกจากนี้ได้ทำการศึกษาการฟื้นฟูสภาพและการนำตัวดูดซับกลับมาใช้ใหม่ที่อุณหภูมิ 400 องศาเซลเซียส ซึ่งพบว่าสามารถฟื้นฟูความสามารถในการดูดซับของโซเดียมเอ็กซ์ซีโอไลท์ได้ดีในกรณีของ 3-เมทิลไทโอฟีน และเบนโซไทโอฟีน แต่ยังไม่มีประสิทธิภาพดีพอสำหรับไดเบนโซไทโอฟีน

ACKNOWLEDGEMENTS

This thesis can not be successful without the participation and support from the following individuals and organization. First of all, I would like to express my deepest appreciation to Asst. Prof. Pomthong Malakul, Dr. Rapeepong Suwanwarangkul, my thesis advisors, for their enlighten, suggestions, invaluable guidance, understanding and strong encouragement throughout the course of this research. This thesis would never have been completed without their consistent help. The others that could not be forgotten in this work is Dr. Sophie Jullian. I would like give special thanks to her for valuable suggestions and comments on this research.

I would also thank Asst. Prof. Apanee Luengnaruemitchai and Dr. Siriporn Jongpatiwut for kindly serving on my thesis commitee.

I would like to extend my sincere thank to all of my professors who guided me through their courses, establishing the knowledge needed for this thesis.

It is pleasure to acknowledge the Petroleum and Petrochemical College for their support in laboratory facilities and all of the staff of the college for their helpful assistance.

I am grateful for the partial scholarship and partial funding of the thesis work provided by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium).

I would like to express my special thank to the Environmental Engineering Association of Thailand (EEAT) for partial financial support.

Finally, I would like to take this opportunity to thank PPC Ph.D students and all my PPC friends. I had the most enjoyable time working with all of them. And also unforgettable thanks are forwarded to my family for their endless support, love and understanding.

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		x
List of Symbols		xii
CHAPTER		
I	**INTRODUCTION**	1
II	**BACKGROUND AND LITERATURE SURVEY**	3
	2.1 Fuel and Sulfur Composition	3
	2.2 Removal of Sulfur Compounds by Hydrodesulfurization (HDS)	7
	2.3 Removal of Sulfur Compounds by Adsorption	8
	2.3.1 Fundamental of Adsorption	8
	2.3.2 Adsorbents and Selectivity for Sulfur Compounds	10
	2.3.3 Zeolite	12
	2.3.4 Fixed Bed Adsorption	16
	2.3.5 Desorption of Sulfur Compounds and Regeneration of Adsorbent	18
	2.4 Mathematical Modeling of a Fixed Bed Adsorber	19
III	**EXPERIMENTAL**	22
	3.1 Materials and Equipment	22
	3.1.1 Materials	22

CHAPTER **PAGE**

3.1.2 Equipment 23
3.2 Methodology 23
3.2.1 Preparation of the Adsorbents 23
3.2.2 Preparation of the Simulated Transportation Fuels 24
3.2.3 Experimental Setup and Investigation 24
3.2.4 Calculation Method of Breakthrough Curve 26

IV MATHEMATICAL MODEL 28
4.1 Model Description 28
4.2 Model Assumptions 29
4.3 Governing Equations 30
4.3.1 Mass Balance in Fixed Bed Adsorber 30
4.3.2 Mass Balance at any Radial Direction of Pellet 31
4.3.3 Mass Balance at any Radial Direction of Crystal 31
4.3.4 Adsorption Isotherm 32
4.4 Numerical Implementation 34
4.4.1 Discretization Technique 34
4.4.2 Programming Algorithm for MATLAB™ 35

V RESULTS AND DICUSSION 37
5.1 Adsorption of Sulfur Compounds on NaX Zeolite 37
5.1.1 Effect of Initial Concentration of Sulfur Compounds on Adsorption by NaX 36
5.1.2 Effect of Type of Sulfur compounds on Adsorption by NaX 39
5.2 Desorption of Sulfur Compounds from Used Adsorbent by Heating Technique 43
5.3 Mathematical Models for the Adsorption of Sulfur Compounds on NaX Zeolite 48

CHAPTER PAGE

5.3.1 Program Testing 49
5.3.2 Comparison of Experimental and Theoretical Breakthrough Curves 51

VI **CONCLUSIONS AND RECOMMENDATIONS** 56
6.1 Conclusions 56
6.2 Recommendations 57

REFERENCES 58

APPENDICES 62
Appendix A Calculation and Sample of Calculation 62
Appendix B Experimental Data 68
Appendix C Bed Voidage 87
Appendix D Correlations Relating to the Model 88
Appendix E Simulation Program for MATLAB Model 90
Appendix F Simulation Parameters 92

CURRICULUM VITAE 94

LIST OF TABLES

TABLE		PAGE
2.1	Some characteristics of crude oils	4
2.2	Type of organic sulfur and properties	5
2.3	Composition of commercial diesel fuel	6
2.4	Correlations proposed to describe the adsorption isotherm	10
3.1	Properties of NaX zeolite used in this experiment	22
3.2	Physical properties of sulfur compounds and simulated transportation fuels	23
3.3	GC conditions for the analysis	25
4.1	Initial and boundary condition for solving	34
5.1	The breakthrough capacities of thiophenic sulfur compounds on NaX (5 ppmw)	42
5.2	The saturation capacities of thiophenic sulfur compounds on NaX (95% of initial sulfur concentration)	43
5.3	Adjusted parameters for generating breakthrough curves of sulfur adsorption	54
5.4	The effective diffusivity of each types of sulfur compounds inside the adsorbent particle	55

LIST OF FIGURES

FIGURE		PAGE
2.1	Hydrocarbon composition and boiling ranges for major refined products	7
2.2	Adsorption isotherms	9
2.3	Schematic representation of (a) framework structure of zeolite X and Y, (b) cation sites in type X and Y	13
2.4	Idealized breakthrough curve of a fixed bed adsorber	17
3.1	Schematic diagram of experimental setup	24
3.2	Breakthrough curve for adsorption process	27
4.1	Adsorber geometry considered in the model development	29
4.2	Discretization of fixed bed adsorber	34
4.3	Programming algorithm for the model development	36
5.1	The effect of influent concentration of 3-methylthiophene on adsorption by NaX	38
5.2	The effect of influent concentration of benzothiophene on adsorption by NaX	38
5.3	The effect of influent concentration of dibenzothiophene on adsorption by NaX	39
5.4	The effect of type of sulfur compounds at 200 ppmw on adsorption by NaX	40
5.5	The effect of type of sulfur compounds at 500 ppmw on adsorption by NaX	41
5.6	The effect of type of sulfur compounds at 1000 ppmw on adsorption by NaX	41
5.7	The effect of type of sulfur compounds at 1800 ppmw on adsorption by NaX	42
5.8	The effect of desorption of 3-methylthiophene by heating on NaX capacity (desorption time 1 hr at 400°C)	44

FIGURE **PAGE**

5.9	The effect of desorption of 3-methylthiophene by heating on NaX capacity (desorption time 3 hrs at 400°C)	44
5.10	The effect of desorption of benzothiophene by heating on NaX capacity (desorption time 1 hr at 400°C)	45
5.11	The effect of desorption of benzothiophene by heating on NaX capacity (desorption time 3 hrs at 400°C)	46
5.12	The effect of desorption of dibenzothiophene by heating on NaX capacity (desorption time 3 hrs at 400°C)	47
5.13	The effect of desorption of dibenzothiophene by heating on NaX capacity (desorption time 6 hrs at 400°C)	47
5.14	Comparison of the mathematical breakthrough curves developed using MATLAB™ and FEMLAB™ at 200 ppmw of BT	49
5.15	Comparison of the mathematical breakthrough curves developed using MATLAB™ and FEMLAB™ at 500 ppmw of 3-MT.	50
5.16	Comparison of the mathematical breakthrough curves developed using MATLAB™ and FEMLAB™ at 1000 ppmw of 3-MT	50
5.17	Comparison of the mathematical breakthrough curves developed using MATLAB™ and FEMLAB™ at 1800 ppmw of DBT	51
5.18	Comparison between experimental and mathematical breakthrough curves of 3-MT adsorption on NaX zeolite	52
5.19	Comparison between experimental and mathematical breakthrough curves of BT adsorption on NaX zeolite	52
5.20	Comparison between experimental and mathematical breakthrough curves of DBT adsorption on NaX zeolite	53
5.21	The adjusted parameters at various sulfur concentration	54

LIST OF SYMBOLS

SYMBOL

A	cross sectional area of column (m^2)
c_b	adsorbate concentration in mobile phase (mole m^{-3})
c_p	adsorbate concentration in macropores of the pellet (mole m^{-3})
C_i	total sulfur concentration in the feed (ppmw)
$C(t)$	effluent total sulfur concentration (ppmw) at any time
d_p	average pellet diameter (m)
D	combined diffusivity inside the macro-pores of the zeolites pellet ($m^2\ s^{-1}$)
D_{AB}	molecular diffusivity ($m^2\ s^{-1}$)
D_c	diffusivity of the adsorbate within the crystal ($m^2\ s^{-1}$)
D_k	Knudsen diffusivity ($m^2\ s^{-1}$)
D_L	axial dispersion coefficient ($m^2\ s^{-1}$)
D_p	effective diffusivity inside the pores ($m^2\ s^{-1}$)
k	adsorption equilibrium constant ($m^3\ mole^{-1}$)
k_a	adsorption rate constant (s^{-1})
k_d	desorption rate constant (s^{-1})
K	equilibrium or partition coefficient between macro and micro-pores volume
K_m	average mass transfer coefficient ($m\ s^{-1}$).
$m_{adsorbent}$	weight of adsorbent bed (g)
M_B	molecular weight of solvent ($g\ mole^{-1}$)
MW_{sulfur}	molecular weight of sulfur ($g\ mole^{-1}$)
N_R	molar diffusion flux in the radial direction of the pellet ($mol\ m^{-2}\ s^{-1}$)
n	Freundlich exponent
Pe_{Mp}	molecular mass Peclet numbe
q	amount of adsorbed (mole g^{-1} adsorbent)

SYMBOLS

q_c	concentration of the adsorbate inside the crystal (mol m^{-3})
$\bar{q}_c$	average concentration of the adsorbate inside the crystal (mol m^{-3})
q_{max}	maximum amount of adsorbed (mole g^{-1} adsorbent)
r	radial co-ordinate in the crystal (m)
R	radial co-ordinate in the particle (m)
R_c	crystal radius (m)
Re	Reynold number
R_p	pellet radius (m)
Sc	Schmidt number
Sh	Sherwood number
t	time (s)
T	temperature (^oC)
Q	volumetric flow rate of feed stream (cm^3 min^{-1})
V_{bA}	molar volume of solute (cm^3 $mole^{-1}$)
v_z	interstitial fluid velocity (m s^{-1})
X_i	total sulfur fraction (by weight) in the feed
z	distance measure from column inlet (m)

GREEK LETTERS

ε_b	voidage of adsorbent bed
ε_b	voidage of pellet
μ_B	viscosity of solvent (centipoise)
ρ_{fuel}	fuel density at room temperature (g cm^{-3})
ø	association parameter
τ	tortuosity factor