

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

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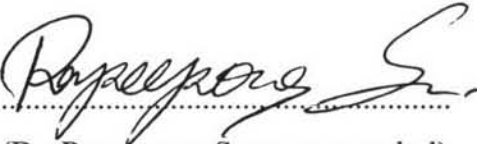
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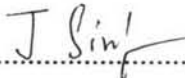
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ABSTRACT

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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: การกำจัดสารประกอบกำมะถันออกจากร้ำมันเชื้อเพลิงโดยการดูดซับบนโซเดียมเอ็กซ์ซีโอไลท์ในระบบแบบต่อเนื่อง (Continuous Removal of Thiophenic Sulfur Compounds from Transportation Fuels by Using X Zeolite) อ. ที่ปรึกษา: ผศ. ดร. ปมทอง มาลากุล ณ อุรุยา, ดร. โชพี จูเลียน และ ดร. รพีพงศ์ สุวรรณวารงูร 94 หน้า ISBN 974-9937-42-2

ปัจจุบันกฎระเบียบด้านสิ่งแวดล้อมที่เข้มงวดทำให้น้ำมันเชื้อเพลิงที่มีกำมะถันในปริมาณต่ำเป็นพิเศษเป็นที่ต้องการมากขึ้น ในช่วงที่ผ่านมากกระบวนการดูดซับจึงได้รับความสนใจในการกำจัดสารประกอบกำมะถันประเภทที่กำจัดได้ยากซึ่งไม่สามารถกำจัดได้โดยวิธีไฮโดรดีซัลเฟอร์ไรเซชัน (Hydrodesulfurization) งานวิจัยนี้เป็นการศึกษาการดูดซับสารประกอบกำมะถันประเภทไทโอฟิน 3 ชนิด คือ 3-เมทิลไทโอฟิน เบนโซไทโอฟิน และไคเบนโซไทโอฟินในระบบแบบต่อเนื่องโดยใช้ตัวดูดซับ คือ โซเดียมเอ็กซ์ซีโอไลท์ (NaX zeolite) และใช้ดีเคนและไอโซออกเทน เป็นแบบจำลองของน้ำมันเชื้อเพลิงดีเซลและแก๊สโซลีนตามลำดับ โดยศึกษาผลกระทบของความเข้มข้นตั้งต้นของสารประกอบกำมะถันและชนิดของสารประกอบกำมะถันที่มีผลต่อกราฟการเบรคทลู ผลการทดลองแสดงให้เห็นว่าเมื่อความเข้มข้นตั้งต้นของสารประกอบกำมะถันในสารละลายสูงขึ้น ความชันของกราฟการเบรคทลูมีแนวโน้มเพิ่มขึ้น แต่ระยะเวลาในการเบรคทลูจะสั้นลง เมื่อเปรียบเทียบระยะเวลาในการเบรคทลูของสารประกอบกำมะถันทั้ง 3 ชนิดพบว่าลดลงตามลำดับดังนี้ เบนโซไทโอฟิน > 3-เมทิลไทโอฟิน > ไคเบนโซไทโอฟิน สำหรับการพัฒนาแบบจำลองทางคณิตศาสตร์เพื่อทำนายกราฟการเบรคทลูของการดูดซับของสารประกอบกำมะถันบนโซเดียมเอ็กซ์ซีโอไลท์นั้น ได้พิจารณาทั้งการแพร่ผ่านของสารประกอบกำมะถันทั้งภายในหลอดดูดซับและภายในซีโอไลท์ ผลที่ได้จากแบบจำลองทางคณิตศาสตร์สอดคล้องกับผลการทดลองภายใต้สภาวะต่างๆ นอกจากนี้ได้ทำการศึกษาการฟื้นฟูสภาพและการนำตัวดูดซับกลับมาใช้ใหม่ที่อุณหภูมิ 400 องศาเซลเซียส ซึ่งพบว่าสามารถฟื้นฟูความสามารถในการดูดซับของโซเดียมเอ็กซ์ซีโอไลท์ได้ดีในกรณีของ 3-เมทิลไทโอฟิน และเบนโซไทโอฟิน แต่ยังไม่มีประสิทธิภาพดีพอสำหรับไคเบนโซไทโอฟิน

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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 ($m^3 \text{ mole}^{-1}$)
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 ($g \text{ mole}^{-1}$)
MW_{sulfur}	molecular weight of sulfur ($g \text{ mole}^{-1}$)
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 number
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 ($^{\circ}\text{C}$)
Q	volumetric flow rate of feed stream ($\text{cm}^3 \text{min}^{-1}$)
V_{bA}	molar volume of solute ($\text{cm}^3 \text{mole}^{-1}$)
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_p	voidage of pellet
μ_B	viscosity of solvent (centipoise)
ρ_{fuel}	fuel density at room temperature (g cm^{-3})
\emptyset	association parameter
τ	tortuosity factor