# DEACTIVATION MODELING FOR THE ADSORPTION ISOTHERM OF DEACTIVATED ADSORBENTS USED IN NATURAL GAS DEHYDRATION PROCESS

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### ABSTRACT

# 4871028063: PETROCHEMICAL TECHNOLOGY PROGRAM Wanaporn Khaikham: Deactivation Modeling for the Adsorption Isotherm of Deactivated Adsorbents used in Natural Gas Dehydration Process. Thesis Advisors: Asst. Prof. Sirirat Jitkarnka, Asst. Prof. Kitipat Siemanond, Dr. Thana Sornchamni and Mr. Sudhibhumi Pumhiran 94 pp. Keywords: Adsorption/ Activated alumina/ Molecular sieve zeolite 4A/

Hydrothermal steaming/ Deactivation/ Adsorption isotherm/ Breakthrough Curve/ Natural gas dehydration

Two types of adsorbents, activated alumina and molecular sieve zeolite 4A, used in the natural gas dehydration process were studied for their adsorption behaviour, both static and dynamic along the adsorption process. Deactivation by hydrothermal steaming was employed for deactivating the adsorbents. The effect of the deactivated adsorbents on the adsorption capacity was then studied. The results showed a decrease in the specific surface area of activated alumina, when hydrothermally steamed at 300 to 550°C, from 200.2 to 124.0 m<sup>2</sup>/g. The adsorption capacity of the activated alumina decreased linearly with surface area. The adsorption capacity of the molecular sieve zeolite was also decreased by steaming, but not in a linear fashion. SEM analysis indicated a decrease in average crystal size from about 2 to 1 microns with the increase of steaming time. The adsorption isotherms of fresh and deactivated adsorbents were examined at 25°C, 1atm, and it was found that Freundlich model gave good agreement for alumina, and Aranovich and Donohue (A-D) for Toth model fitted the data of molecular sieve zeolite. Also, the adsorption isotherms are used in a previously developed mathematical model to predict the breakthrough time of the multi-layered adsorber. From the dynamic adsorption of a packed column with the fresh and deactivated adsorbents, it was found the breakthrough time of the deactivated bed was shorter than the fresh one. The predicted breakthrough time agrees well with the experimental one.

# บทคัดย่อ

วรรณพร ค่ายคำ : การศึกษาการเสื่อมสภาพของตัวดูดซับและการสร้างแบบจำลอง ทางคณิตศาสตร์สำหรับไอโซเทอร์มของตัวดูดซับที่เกิดการเสื่อมสภาพในกระบวนการกำจัดน้ำ จากก๊าซธรรมชาติโดยใช้ตัวดูดซับ ( Deactivation Modeling for the Adsorption Isotherm of Deactivated Adsorbents used in Natural Gas Dehydration Process) อ. ที่ปรึกษา : ผศ. คร. ศิริรัตน์ จิตการค้า, ผศ. คร. กิติพัฒน์ สีมานนด์, คร. ธนา ศรชำนิ และนายสุทธิภูมิ พุ่มหิรัญ 94 หน้า

การศึกษาการดูคซับน้ำออกจากก๊าซธรรมชาติโคยใช้ตัวดูคซับสองชนิค คือ อลูมินา และ 4A ซีโอไลท์ ในขณะที่ตัวดูดซับเกิดการเสื่อมสภาพเนื่องมาจากกระบวนการผ่านความร้อนและไอ น้ำ (Hydrothermal Steaming) โดยได้ศึกษาเชิงกายภาพถึงผลของการเสื่อมสภาพของตัวดูดซับที่มี จากการศึกษาพบว่าตัวดูดซับอลูมินาเมื่อผ่านความร้อนและไอน้ำในช่วง ต่อค่าการคคซับน้ำ อุณหภูมิ 300 ถึง 550 องศาเซลเซียส จะส่งผลให้พื้นที่ผิวลคลงจาก 200.2 เหลือเพียง 124.0 ตาราง เมตรต่อกรัมตามลำคับ และค่าการคูคซับน้ำก็ลคลงเป็นความสัมพันธ์แบบเส้นตรงตามจำนวน พื้นที่ผิวที่ลคลงนี้ด้วย สำหรับตัวดูดซับ 4A ซีโอไลท์ จากการศึกษาพบว่าตัวดูดซับชนิดนี้เกิดการ เสื่อมสภาพจากกระบวนการผ่านความร้อนและไอน้ำเช่นเคียวกัน แต่ความสัมพันธ์ระหว่างค่าการ เสื่อมสภาพต่อค่าการดูคซับของตัวดูคซับชนิคนี้ไม่เป็นแบบเส้นตรง ทั้งนี้ผลการวิเคราะห์โดย เครื่องสแกนนิ่งอิเล็คตรอนไมโครสโคป (SEM) ชี้ให้เห็นว่าขนาดของผลึกซีโอไลท์ 4A ที่ เสื่อมสภาพมีขนาคลคลงจากประมาณ 2 เป็น 1 ไมครอน นอกจากนี้ยังได้ทำการศึกษาหาไอโซเท อร์มของการดูดซับน้ำที่อุณหภูมิ 25 องศาเซลเซียส ความดัน 1 บรรยากาศ ของตัวดูดซับแต่ละ ชนิดทั้งยังไม่ได้เสื่อมสภาพและเมื่อเสื่อมสภาพแล้ว พบว่าสมการ Freundlich สามารถอธิบาย ไอโซเทอร์มของอลูมินาได้อย่างแม่นยำ และในส่วนของซีโอไลท์สมการของ Aranovich-Donohue ที่ปรับปรุงใช้กับสมการของ Toth นั้นสามารถอธิบายไอโซเทอร์มได้เป็นอย่างคีด้วย ซึ่งค่าคงที่ ้งองไอโซเทอร์มที่ได้จะถูกนำมาใช้ในแบบจำลองทางคณิตศาสตร์สำหรับหอดูคซับน้ำที่บรรจุตัว

ของ เอ เซเพอรมท เดงะถูกนามาเข เนแบบงาถองกางคณตศาลตรถาหรบทอดูดขบนาทบรรงุตร ดูดซับหลายชนิดอยู่ภายใน (หอดูดซับแบบมัลติเลเยอร์) ที่ถูกสร้างและพัฒนามาแล้วในงานก่อน หน้านี้ เพื่อนำมาใช้ในการทำนายเวลาเบรคทรูในเชิงทฤษฎีได้ และจากการทคลองพบว่า คุณลักษณะและแนวโน้มของกราฟเบรคทรูในทางทฤษฎีที่ได้จากการทำนายโดยแบบจำลองทาง คณิตศาสตร์สามารถทำนายความสามารถในการดูดซับน้ำได้อย่างแม่นยำ

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## LIST OF SYMBOLS

# SYMBOL

a, b, t, d	adsorption constant
c	adsorbate concentration in fluid phase, (mol/l)
С	total concentration, (mol/l)
$D_L$	axial dispersion coefficient, (cm <sup>2</sup> /s)
К	overall mass transfer coefficient, (l/s)
Р	water vapor pressure, (kP)
q*	equilibrium value of q
t	time, (s)
Т	temperature, (K)
v	interstitial velocity of fluid, (cm/s)
Z	distance measure from column inlet, (cm)

### **GREEK LETTERS**

ε	bed void fraction
ρ	density of mixing gas, (g/cm.s)
$\sigma_{\scriptscriptstyle AB}$	collision diameter from Lennard-Jones potential
$\Omega_{_{AB}}$	collision integral