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PRODUCTION OF PURE ETHANOL FROM AZEOTROPIC SOLUTION
BY PRESSURE SWING ADSORPTION

Mr. Pit Pruksathorn

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Chemical Technology

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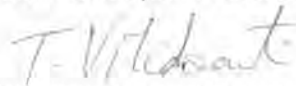
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กระบวนการดูดซับแบบความดันสลับเป็นหนึ่งในวิธีการที่ได้รับการสนใจอย่างมากใน
กระบวนการแยกน้ำ โดยเฉพาะในอุตสาหกรรมการผลิตเอทานอลเพื่อนำไปเป็นเชื้อเพลิง ถึงแม้จะมีงาน
ศึกษาวิจัยที่เกี่ยวข้องกับแบบจำลองทางคณิตศาสตร์หรือการทดลองการดูดซับน้ำบนตัวดูดซับซีโอไลต์
3เอที่บรรจุในเครื่องปฏิกรณ์แบบเบดนิ่ง ยังไม่มีงานวิจัยใดที่ศึกษาการดูดซับด้วยกระบวนการดูดซับ
แบบความดันสลับอย่างแท้จริง จุดประสงค์ของงานวิจัยนี้ทำขึ้นเพื่อศึกษากระบวนการดูดซับแบบ
ความดันสลับโดยใช้หอดูดซับคู่และศึกษาผลของปัจจัยสำคัญต่างๆที่มีต่อประสิทธิภาพของการผลิตเอ
ทานอลบริสุทธิ์จากสารละลายคงจุดเดือดของดูดซับแบบความดันสลับ งานวิจัยนี้ยังได้ทำการศึกษา
รวมไปถึงกลไกและแบบจำลองทางจลนพลศาสตร์ของการดูดซับน้ำบนซีโอไลต์ 3เอ การทดลองใน
หอดูดซับแบบเบดนิ่งดำเนินไปด้วยวิธีแฟกทอเรียลเพื่อหาตัวแปรที่มีนัยสำคัญต่อเวลาเบรคทูและ
ความสามารถในการดูดซับของหอดูดซับ ทั้งนี้ตัวแปรที่ทำการศึกษานั้นได้แก่อุณหภูมิเริ่มต้นของหอดูดซับ
ความเข้มข้นของสารป้อนและอัตราการป้อนของสารตั้งต้นเข้าสู่หอดูดซับ จากการทดลองพบว่า
ไอโซเทอร์มแบบแลงเมียร์มีความเหมาะสมที่สุดในการอธิบายกลไกการดูดซับน้ำโดยซีโอไลต์ 3เอใน
การแยกน้ำออกจากสารละลายเอทานอล โดยอธิบายได้ด้วยสมการ $q = (8.18C) / (1+42.83C)$.
นอกจากนี้การทดลองในส่วนของกระบวนการดูดซับแบบความดันสลับ ได้มีการศึกษาหาภาวะที่
เหมาะสมที่สุดในการเตรียมเอทานอลบริสุทธิ์จากสารละลายคงจุดเดือดในลักษณะที่จะใช้ได้จริงใน
ระบบอุตสาหกรรม ตัวแปรที่ทำการศึกษารวมไปถึงความเข้มข้นของสารป้อน อัตราเร็วของสารป้อน
อุณหภูมิขณะดูดซับ ระยะเวลา ความดันขณะดูดซับและคายซับโดยอาศัยการจัดการทดลองแบบแฟก
ทอเรียลและการวิเคราะห์ผลเชิงสถิติ จากนั้นเสนอแบบจำลองเพื่อทำนายประสิทธิภาพการดูดซับโดย
ทำคูลมวลในหอดูดซับแบบความดันสลับ ผลของการวิจัยในหอดูดซับแบบนี้จะช่วยในการออกแบบ
ระบบดูดซับแบบความดันสลับ นอกจากนี้การทดลองได้รับความสำเร็จเนื่องจากสามารถผลิตเอทา
นอลความเข้มข้นสูงได้อย่างต่อเนื่องในปริมาณที่น่าพอใจและสามารถขยายผลไปสู่ภาคอุตสาหกรรม
ได้

ภาควิชา.....เคมีเทคนิค.....ลายมือชื่อนิสิต.....
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Pressure swing adsorption (PSA) is attractive for final separation in the process of water removal especially for fuel ethanol production. Despite many researches on simulation and experimental works on adsorption of water on 3A zeolite in a fixed bed, none have studied a process with the actual PSA system. The purpose of this research was to study the PSA process with two adsorbers and effects of several parameters. The research also included analysis of kinetic and thermodynamic data of ethanol-water adsorption on commercial 3A zeolites in a single fixed bed. Two-level factorial design experiment was used in this research work to preliminary screen the influence and interaction among each factor. Effects of important parameters such as initial temperature, feed concentration and feed rate were investigated. It was proven that Langmuir isotherm could best predict the experimental results with the corresponding equation of $q = (8.18C)/(1+42.83C)$. In the PSA pilot test, the principal factors, which had effects on the performance, were feed rate, feed concentration, adsorption pressure and the cycle time. Prediction of the process efficiency in terms of ethanol recovery and enrichment was proposed in the form of regression models. The results of the study in a fixed bed adsorber could help designing a pilot scale PSA unit. The experiments proved to be successful in terms of continuously producing high concentration ethanol with high percentage of ethanol recovery. With further simulation works the process could be scaled up for an industrial use.

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NOMENCLATURES

ϵ_p	= Particle porosity
ϵ_e	= External porosity
ϕ_{cs}	= Diameter of the bed (cm)
ρ_B	= Density of the bed (g/cm^3)
ρ_p	= Particle density (g/cm^3)
ρ_f	= Fluid density (g/cm^3)
ρ_b	= Bulk density (g/cm^3)
μ	= Fluid viscosity (Pa.s)
u_s	= Fluid superficial velocity (cm/s)
τ	= Tortuosity (correction factor > 1 to account for the tortuous nature of pore structure).
A_{cs}	= Cross sectional area of the bed (cm^2)
c_f	= Concentration of the solute in the feed (%vol)
C_{pf}	= Fluid heat capacities (kJ/kg.K)
C_{ps}	= Adsorbent heat capacities (kJ/kg.K)
d_p	= Pore diameter (\AA)
D_{AB}	= Diffusion coefficient of adsorbate in fluid
E	= Enrichment of the product (% in ethanol volume)
H_{cs}	= Height of the bed (cm)
k	= Mass transfer coefficient
k_1	= Rate constant
L_B	= Total bed length (cm)
LUB	= Length of unused bed (cm)
LES	= Length of equilibrium section (cm)
M_0	= Amount of feeding fluid (mL)

- M_f = Product amount in the recipient, for operation cycle (mL)
 MTZ = Mass transfer zone (cm)
 P_d = Desorption pressure (bar)
 P_{Hf} = Adsorption pressure (bar)
 q_0 = Maximum solid-phase concentration of the adsorbed solute ($g_{water}/g_{adsorbent}$)
 q_{ref} = Loading per unit mass of adsorbent that is in equilibrium with the feed concentration ($g_{water}/g_{adsorbent}$)
 Q_f = Volumetric flow rate of feed (mL/min)
 R = Crossover ratio
 R = Percentage of ethanol recovery (%)
 Re = Reynolds number
 S = Total mass of adsorbent in the bed (g)
 S_g = Specific surface area (m^2/g)
 Sc = Schmidt number
 t_{br} = Breakthrough time (seconds)
 T = Initial bed temperature ($^{\circ}C$)
 v_{super} = Superficial velocity (cm/s)
 v_{inter} = Interstitial velocity (cm/s)
 $V_B = V_{cs}$ = Volume of the bed (cm^3)
 X_{res} = Residual loading in the bed prior to the adsorption step
 X_f = Concentration of the product in the recipient at steady state
 (% in ethanol volume)
 X_0 = Concentration of the feeding fluid (% in ethanol volume)
 Y = Molar ratio of adsorbate to the carrier fluid (i denotes inlet, o denotes outlet)