활성탄을 이용한 이산화탄소, 에탄올 혼합물에서의 이산화탄소 순수정제

김병헌, 이재익, 이광순*, 서성섭[1]

서강대학교 화공생명공학과, [1]홍익대학교 화공생명공학과

(kslee@sogang.ac.kr*)

Purification of high pressure CO_2 from CO_2/EtOH mixture by adsorption with activated carbon

Byunghun Kim, Jaeik Lee, Kwang Soon Lee*, Sung-Sup Suh[1]

Department of Chemical and Biomolecular Engineering, Sogang University, Korea

[1]Department of Chemical and Biomolecular Engineering, Hong-ik University. Korea

(kslee@sogang.ac.kr*)

INRTRODUCTION

Supercritical CO_2 has some unique and ideal properties as a green solvent, and has been employed for extraction of specialty materials in food, bio-chemical, and other related industries. Since CO_2 is known as the main cause of the greenhouse effect, its recovery and purification has become an important issue. The purpose of the present work is to develop a purification process for CO_2 which is recovered from a supercritical CO_2 extraction process, using adsorptive separation technology. EtOH was assumed to be the major impurity and activated carbon was used as the adsorbent. Adsorption isotherms were determined through experiments for each component and simulation study has been conducted for column design.

EXPERIMENTS

A volumetric-type static adsorption apparatus in Fig. 1 was used to determine the equilibrium isotherms of CO_2 and EtOH, respectively. Adsorption data on activated carbon were obtained at 303.15, 313.15, and 323.15 K and at pressures up to 60 bar for CO_2, and at pressures up to one half the vapor pressure for EtOH. In the experiments, molar amount of the adsorbed phase is represented by

$$n_{ads} = (n_{L1} - n_{L2}) - (n_{A2} - n_{A1}) \quad (1)$$

where n_L and n_A denote moles of gas in the loading cell and the adsorption cell, respectively; subscripts 1 and 2 represent 'before' and 'after' gas supply to the adsorption cell, respectively. It typically took one to two hours for CO_2 and EtOH to reach the adsorption equilibrium after the gas supply begins, and n_{A2} was measured after then.

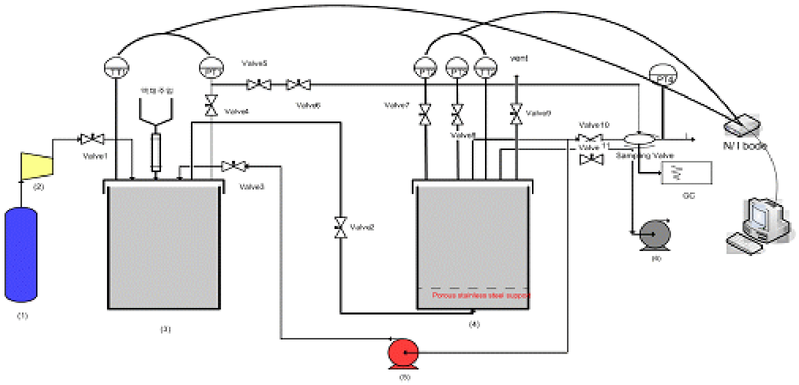

Fig. 1. Experimental apparatus for measurement of gas adsorption : (1) gas supply cylinder, (2) syringe pump, (3) loading cell, (4) adsorption cell, (5) circulation pump, (6) vacuum pump.

MODELING OF ADSORPTION COLUMN

The column model was set up for binary gas mixture. Mass balance for a single component, total mass balance, and energy balance were considered with the equation of state, isotherm relations, and Ergun equation for the pressure and gas velocity relationship. The resulting equations are written as below:

$$\frac{\partial y_1}{\partial t}=\frac{D_{ax}}{L^2}\frac{\partial^2 y_1}{\partial z^2}+\left(\frac{D_{ax}}{L^2}\frac{1}{C}\frac{\partial C}{\partial z}-\frac{1}{aL^2}\frac{\partial P}{\partial z}\right)\frac{\partial y_1}{\partial z}+\frac{1}{C}\frac{(1-\varepsilon)}{\varepsilon}\rho_s\left(k_1(q_1^*-q_1)+k_2(q_2^*-q_2)\right)y_1-\frac{1}{C}\frac{(1-\varepsilon)}{\varepsilon}\rho_s k_1(q_1^*-q_1) \tag{2}$$

$$\frac{\partial q_i}{\partial t}=k_i(q_i^*-q_i) \tag{3}$$

$$\frac{\partial C}{\partial t}+\frac{(1-\varepsilon)}{\varepsilon}\rho_s\sum_{i=1}^{2}\frac{\partial q_i}{\partial t}=-u\frac{\partial C}{\partial z}-C\frac{\partial u}{\partial z} \tag{4}$$

$$\frac{\partial T}{\partial t}=\frac{1}{C_f+((1-\varepsilon)/\varepsilon)C_s}\left(\frac{\lambda_L}{L^2}\frac{\partial^2 T}{\partial z^2}-C_f\frac{1}{aL^2}\frac{\partial P}{\partial z}\frac{\partial T}{\partial z}-C_f\frac{1}{aL^2}\frac{\partial^2 P}{\partial z^2}T+\frac{(1-\varepsilon)}{\varepsilon}\rho_s\left(-\Delta H_1 k_1(q_1^*-q_1)-\Delta H_2 k_2(q_2^*-q_2)\right)\right) \tag{5}$$

The above PDEs were reduced to a set of ODEs using CSCM with five equally distributed internal collocation points over [0,1] with far-side boundary condition at z=5 for numerical simulation. [4]

RESULTS AND DISCUSSION

The data from adsorption equilibrium experiments are presented in Fig. 2. The marks and lines indicate experimental data and fitting results to the Langmuir – Freundlich isotherm, which is represented by

$$q=q_{\max}\frac{b\,P^{1/n}}{1+b\,P^{1/n}} \tag{7}$$

The Langmuir – Freundlich isotherm parameters for CO_2 were estimated as in Table 2.

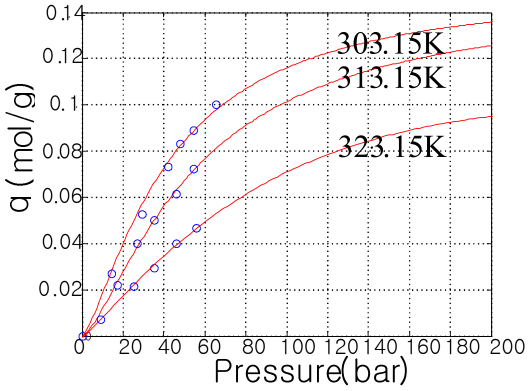

Fig. 2. Adsorption isotherm of CO_2 on activated carbon of 20 to 40 mesh at 303.15~323.15 K.

Table 2. Langmuir–Freundlich isotherm parameters for CO2 on activated carbon.

Temp.	q_{max} (mol/g)	b (1/atm)	n
303.15K	0.1469	0.0035	0.7135
313.15K	0.1196	0.0048	0.8620
323.15K	0.0912	0.0096	0.7316

Experimental results for EtOH are shown in Fig. 3. Due to the linear relationship between the pressure and adsorbed amount, Henry's law $q = HC$ was considered to fit the data. The resulting Henry's constants are given in Table 3 .

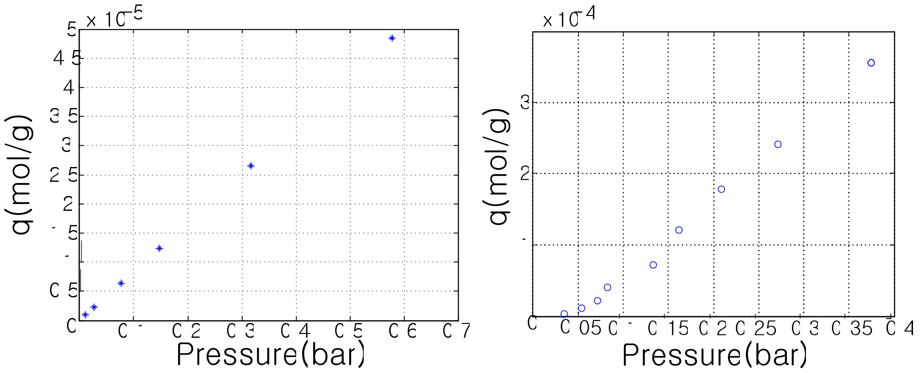

Fig. 3. Adsorption isotherm of EtOH on activated carbon at 303.15 and 313.15K, respectively.

Table 3. Henry's constants for EtOH adsorption on activated carbon.

.	303.15K	313.15K
Henry constant(m^3/kg)	0.020698	0.00221

Figures 4 and 5 demonstrates the estimated breakthrough curves for EtOH when the gas mixture with EtOH mole fraction of 0.2 is fed at 1.1 bar at the column inlet. It is assumed that the column is initially saturated with CO_2 at 1 bar. Detailed simulation conditions are given in Table 4. It is shown that under the concerned column dimension and operating conditions, pure CO_2 can be produced for the first 20min during the adsorption step.

Table 4. Simulation conditions for the operation with carbon dioxide/ethanol.

P_{feed} (atm)	T_{feed} (K)	$y_{co2,feed}$	P_{inter} (atm)	T_{inter} (K)	$y_{co2,inter}$
1.1	303	0.8	1	303	1

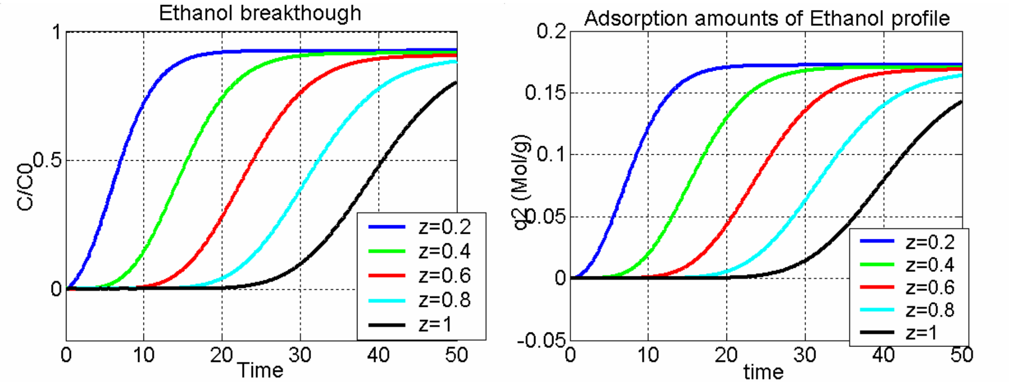

Fig. 4. Breakthrough curve and adsorption amounts of EtOH in the activated carbon bed versus the time.

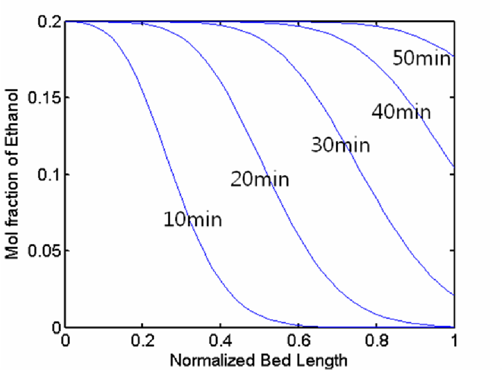

Fig. 5. Breakthrough curve of EtOH in the activated carbon bed versus the distance.

REFERENCES

[1] R. B. Bird, W. E. Stewart, and E. N. Lightfoot "Transport Phenomena", 2nd.Ed, Wiley, 2001.

[2] H. S. Fogler, "Elements of Chemical Reaction Engineering", 4 nd Ed, Prentice-Hall International, 2005.

[3] W. Yun and K. S. Lee, " The use of cubic spline and far-side boundary condition for the collocation solution of a transient convection-diffusion problem". Korean J. chem.. Eng., 24, (2007) 204-208.

[4] J. A. Delgado, M. A. Uguina, J. L. Sotelo, and B. Ruiz, "Modeling of the fixed-bed adsorption of methane/nitrogen mixtures on silicalite pellets", Separation and Purification Technology 50., (2006) 192-203.

[감사] 이 논문은 홍익대학교 교수연구년기간(2008.9.1 -2009.8.31)중 연구되었음.