2탑 PSA공정을 이용한 수소의 분리에 관한 연구

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Experimental and Theoretical study on PSA process for separation of H_2

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Introduction

Recently hydrogen is highly required in the areas such as fuel cell preparation and semiconductor process, and a demand for hydrogen in the petrochemical industry has still been increasing. Also, hydrogen is regarded as a renewable and clean energy source. Mostly, hydrogen used in several industries has been produced from steam reforming of light hydrocarbon, partial oxidation of heavy hydrocarbon, recovery from coke oven gas and water electrolysis etc.

Adsorption has become an important tool for gas separation, particularly by pressure swing adsorption(PSA) process. PSA process has attracted increasing of its low energy requirements as well as low capital investment costs. Many more sophisticated PSA processes have been developed and commercialized since the introduction of the Skarstrom cycle. And, many researchers have extensively studied on separation of hydrogen using PSA process.

In this study, an experimental and theoretical study was performed for separation of H_2/CH_4 mixture(8:2) by pressure swing adsorption(PSA) process with activated carbon adsorbent. For the optimized adsorption condition of PSA, the effects of adsorption pressure, adsorption time, P/F ratio, and pressure equalization step time were investigated by simulation and were compared with experimental results.

Theory

The mathematical model adopted is a non-isothermal, non-adiabatic, bulk separation model with a nonlinear multicomponent equilibrium isotherm. The assumption used to derive the model included the following: (i) the flow pattern is described by the axially dispersed plug flow model, (ii) thermal equilibrium is assumed between fluid and particle instantaneously, (iii) the mass transfer rate is

represented by a linear driving force(LDF) model, (iv) the gas phase behaves an ideal gas mixture, and (v) radial concentration and temperature gradients are negligible. Applying an ideal gas law, the component mass balance and overall mass balance for the bulk gas phase of an adsorption bed can be written as follows:

$$-D_L\frac{\partial^2 y_i}{\partial z^2}+\frac{\partial y_i}{\partial t}+u\frac{\partial y_i}{\partial z}+\frac{RT}{P}\frac{1-\varepsilon}{\varepsilon}\rho_P\left(\frac{\partial \bar{q}}{\partial t}-y_i\sum_{j=1}^{n}\frac{\partial \overline{q_j}}{\partial t}\right)=0 \tag{1}$$

$$\begin{aligned}&-D_L\frac{\partial^2 P}{\partial z^2}+\frac{\partial P}{\partial t}+P\frac{\partial u}{\partial z}+u\frac{\partial P}{\partial z}-PT\left(-D_L\frac{\partial^2 (1/T)}{\partial z^2}+\frac{\partial (1/T)}{\partial t}+u\frac{\partial (1/T)}{\partial z}\right)+\\&\frac{1-\varepsilon}{\varepsilon}\rho_p RT\sum_{j=1}^{n}\frac{\partial \overline{q_j}}{\partial t}=0\end{aligned} \tag{2}$$

the energy balance for the gas and solid phases of an adsorption bed and for the wall of an adsorption bed are given by

$$-K_L\frac{\partial^2 T}{\partial z^2}+\left(\alpha\rho_g C_{pg}+\rho_B C_{ps}\right)\frac{\partial T}{\partial t}+\rho_g C_{pg}\varepsilon u\frac{\partial T}{\partial z}-\rho_B\sum_i^n Q_i\frac{\partial \bar{q}}{\partial t}+\frac{2h_i}{R_{B_i}}\left(T-T_w\right)=0 \tag{3}$$

$$\rho_w C_{pw}A_w\frac{\partial T_w}{\partial t}=2\pi R_{B_i}h_i\left(T-T_w\right)-2\pi R_{B_0}h_0\left(T_w-T_{atm}\right) \tag{4}$$

The sorption rate into the adsorbent, $\partial\overline{q_i}/\partial t$, could be described by the LDF model. The LDF model is following:

$$\frac{\partial \overline{q_i}}{\partial t}=k_i\left(q_i^*-\overline{q_i}\right),\quad k_i=\frac{15D_{ei}}{R_p{}^2} \tag{5}$$

The Langmuir-Freundlich(L-F) isotherm was used to predict the adsorption equilibrium, and this isotherm was extended to predict the multicomponent isotherm by the loading ratio correlation(LRC) equation.

$$q_i=\frac{q_{mi}B_iP_i^{1/n_i}}{1+\sum_{j=1}^{n}B_jP_j^{1/n_j}} \tag{6}$$

Experiment

Activated carbon (Calgon Co.) was chosen as an adsorbent. Prior to measurement, the adsorbent was kept at 423.15K in a drying vacuum oven more than 12hr to remove impurities. The adsorption bed was fabricated from the stainless steel pipe of 4.089cm I.D, 120cm length and 0.405cm wall thickness. Five thermocouples were installed at 20, 40, 60, 80 and 100cm from bed end to track the thermal wave front. Feed and purge flow rates were controlled by mass flow controllers. Recovery and purity were calculated by measuring the amount of gas flowing into and out of a PSA system using gas flowing into and out of a PSA system using a mass flow meter and a wet gas meter. The metering valve installed at a pressure equalization line was used to control the flow rate and the step time during a pressure equalization step.

The experiments were conducted at nonisothermal and nonadiabatic condition. First of all, we determined the time sequence, and then investigated the P/F ratio and adsorption pressure to find the optimum condition to give the recovery more than 85% and the purity more than 99%.

Results and Discussions

Adsorption isotherm. Figure. 1 showed the adsorption isotherms of single component for pure H_2 and CH_4 onto activated carbon at 293.15K temperature and pressures up to 20atm. The experimental data were correlated by the Langmuir-Freundlich equation. The parameters for the Langmuir-Freundlich equation were obtained and they were used to find the parameters of LRC equation.

Adsorption/desorption dynamics of adsorption column. It is important to understand the characteristics of adsorbent and adsorbate interactions in terms of thermodynamics and kinetics. So, we conducted the breakthrough and regeneration experiments at various flow rates and pressures to understand the adsorption and desorption dynamics. Figure. 2 showed the breakthrough experiment results of the effect of feed flow rate at 8atm. And, figure. 3 showed the breakthrough experiment results of the effect of pressure at 11.8LPM. The slower the flow rate, the longer the breakthrough time and, the higher the pressure, the longer the breakthrough time. Figure. 4 showed the regeneration experiment results of the effect of purge flow rate at 1.2atm. if the faster the purge flow rate, the regeneration time lessened.

PSA process. We selected the two-bed and six-step PSA process that consists of feed, adsorption, pressure equalization, blow down, purge and pressure equalization. And, the experiments were conducted for H2/CH4(8:2) binary system with activated carbon adsorber. Generally, the recovery and the purity of some component were affected by adsorption time, adsorption pressure, P/F ratio and pressure equalization time. But, we investigated the effect of P/F ratio at condition fixed step time and adsorption pressure.

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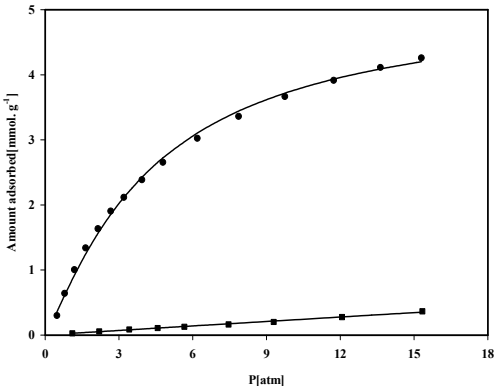

Figure 1. Measured and fitted isotherms of :•,CH_4 and ■,H2 onto activated carbon at 293.15K

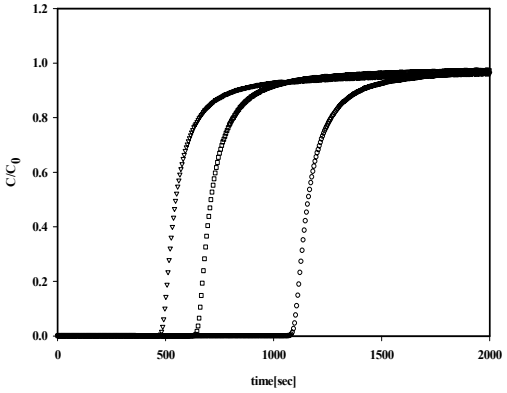

Figure 2. Breakthrough experiment result of CH_4 and H_2 system- the effect of flow rate; ○, 9.7LPM ; □, 1.8LPM; ▽; 16.5 LPM

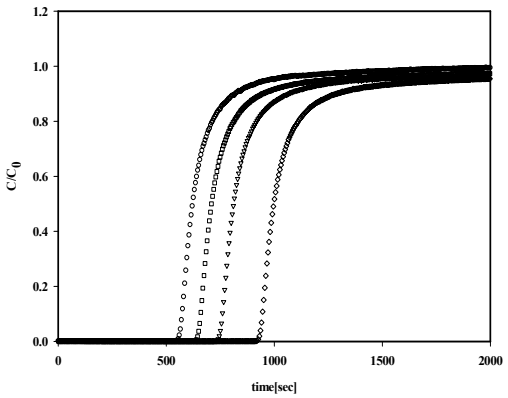

Figure 3. Breakthrough experiment result of CH_4 and H_2 system- the effect of pressure ; ○, 6atm; □, 8atm; ▽, 10atm; ◇, 12atm

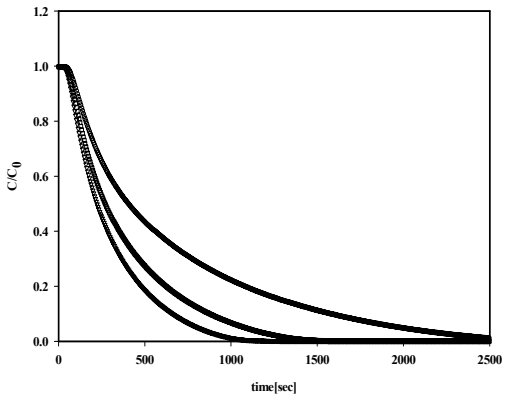

Figure 4. Regeneration experiment result of CH_4 and H_2 system- the effect of purge rate; ○, 1.5LPM; □, 2.5LPM; ▽, 3.5 LPM