

4탑 PSA 공정의 의한 SMR off-gas로부터 수소 정제

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Hydrogen Purification by the Four-Bed Pressure Swing Adsorption Process from Steam Methane Reforming Off-Gas

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Abstract : The four-bed PSA process using a layered bed of activated carbon and zeolite 5A was studied to produce a high purity hydrogen product from SMR off-gas. At a desired product purity (99.999%+), the recovery increased with decreasing the linear velocity. However, the difference of the increasing of the recovery became smaller with the decreasing of the linear velocity and then was similar from below the linear velocity 3.9 cm/s. When the adsorbents, the feed gas composition, and the operating conditions are given, the residence time is mainly a function for design of the PSA bed size. The minimum residence time exists to obtain the maximum recovery at desired product purity.

Nomenclature

A_w : cross sectional area [cm^2]
 C : concentration of adsorbate [mol/g]
 C_{pg} : gas heat capacity [$\text{cal/g} \cdot \text{K}$]
 C_{ps} : particle heat capacity [$\text{cal/g} \cdot \text{K}$]
 D_L : mass axial dispersion coefficient [cm^2/s]
 D_e : molecular diffusivity [cm^2/s]
 h : heat transfer coefficient [$\text{cal}/\text{cm}^2 \cdot \text{s} \cdot \text{K}$]
 i : component
 k : dual site langmuir model parameter
 K : equilibrium constant
 P : pressure [atm]
 q : equilibrium moles adsorbed [mol/g]
 Q : average isosteric heat of adsorption [cal/mol]
 t : time [sec]
 T : temperature [K]
 T_w : wall temperature [K]
 u : interstitial velocity [cm/s]
 z : axial position in a adsorption bed [cm]
 ϵ : interparticle void fraction
 ρ : density [cm^3/g]

subscrip

PSA : pressure swing adsorption
SMR : steam methane reforming

1. Introduction

Pressure swing adsorption (PSA) is a well-known method for the separation of bulk gas mixtures and for the purification of gas streams containing undesirable impurities. There has been a tremendous growth in PSA during the past four decades through the modification of established process and the development of new adsorbents. The current technology to separate hydrogen from steam reforming (SMR) off-gas is PSA. The resulting hydrogen-rich gas is then purified to

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produce to produce a 99.99%+ H₂ stream by a PSA process. As hydrogen is separated from SMR off-gas using the PSA process, layered beds consisting of different adsorbents, such as activated carbon and zeolite, have been used. The performance in the PSA process is usually defined as the purity and recovery of hydrogen obtained by executing both experiments and mathematical modeling. The high purity and recovery of the H₂ PSA processes are largely due to an effective operation of multi-bed PSA processes including several pressure equalizations, backfill, and layered adsorption bed.^(1,2)

In the present study, hydrogen separation by the four-bed PSA process using the layered beds of activated carbon and zeolite 5A was investigated experimentally and theoretically to recover high purity H₂ from steam reforming gas. Aspen Adsorb (Aspen Tech. Inc.) was then utilized for the estimation and the simulation of the PSA process cycles. The simulation results obtained were analyzed numerically by using a non-isothermal dynamic model incorporating mass, energy and momentum balance. All experiments were carried out to parametrically analyze the PSA process variables such as total cycle time, linear velocity and residence time.

2. Mathematical model

The non-isothermal and non-adiabatic dynamic model including mass, energy, and momentum balance was used to simulate a PSA process with the following assumption^(3,4): (i) ideal gas law applies; (ii) the flow pattern can be described by the axial dispersion plug flow model; (iii) the solid and gas phase reach thermal equilibrium instantaneously; (iv) the mass transfer rate can be represented by a linear driving force (LDF) rate expression; and (v) radial concentration and temperature gradients are negligible. The mathematical models are summarized in Table 1. The governing partial differential equations were solved in space and the resulting ordinary differential equations are solved using Aspen ADSIM from Aspen Technology Inc.

3. Experimental

In this study, the adsorbents used activated carbon (Calgon Co.) and zeolite 5A (W. R. Grace Co.). The physical properties of the adsorbents and bed are listed in Table 2. Before the experiment, the adsorbents were regenerated for more than 24 hours at 573 K in a drying vacuum oven. The feed composition based on the steam methane reforming (SMR) off-gas (72.2% H₂, 21.6% CO₂, 2.03% CO, 4.17% CH₄) was used.

The schematic diagram of the experimental apparatus is shown in Fig. 1. The four adsorption beds were made of stainless steel and packed with activated carbon and zeolite 5A. The activated carbon layer height is 100 cm at the feed end and the zeolite 5A layer height is 70 cm above activated carbon layer.

To obtain high-purity hydrogen from SMR off-gas, a four-bed ten-step PSA process cycle was experimented

and simulated. Table 3 presents the cycle steps and time schedules. In every experimental run, the adsorption pressure and the purge pressure were set to 9 atm, and 1.3 atm, respectively.

Table 1. PSA adsorption model

(a) Total mass balance

$$-D_L \frac{\partial^2 C}{\partial z^2} + \frac{\partial u C}{\partial z} + \frac{\partial C}{\partial t} + \frac{1-\epsilon}{\epsilon} \rho_P \sum_{i=0}^n \frac{\partial q_i}{\partial t} = 0$$

(b) Mass transfer

$$\frac{\partial q_i}{\partial t} = k_i (q_i^* - \bar{q}_i)$$

(c) Energy balance for the gas and solid phase

$$-K_{Li} \frac{\partial^2 T}{\partial z^2} + (\epsilon_i \rho_g C_{pg} + \rho_B C_{ps}) \frac{\partial T}{\partial t} + \rho_g C_{pg} \epsilon u \frac{\partial T}{\partial z} - \rho_B \sum_i^n Q_i \frac{\partial q_i}{\partial t} + \frac{2h_i}{R_{Bi}} (T - T_w) = 0$$

(d) Energy balance around the wall of the column

$$\rho_w C_{pw} A_w \frac{\partial T_w}{\partial t} = 2\pi R_B h_i (T - T_w) - 2\pi R_{Bo} h_o (T - T_{atm})$$

(e) Momentum balance (Ergun equation)

$$\frac{dP}{dz} = - \left[\frac{150 \times 10^{-5} \mu_g (1-\epsilon_b)^2}{4R_b^2 \epsilon_b^3} u + \frac{1.75 \times 10^{-5} M_w \rho_g (1-\epsilon_b)}{2R_b \epsilon_b^3} u^2 \right]$$

(f) Dual-site Langmuir isotherm

$$q_i = \frac{k_{1i} (k_{2i} \exp[k_{3i}/T_s] P_i)}{1 + \sum_i (k_{2i} \exp[k_{3i}/T_s] P_i)} + \frac{k_{4i} (k_{5i} \exp[k_{6i}/T_s] P_i)}{1 + \sum_i (k_{5i} \exp[k_{6i}/T_s] P_i)}$$

Table 2. Physical properties of adsorbents and bed

Description	Value	
	Activated Carbon	Zeolite 5A
Layer	Activated Carbon	Zeolite 5A
Length	100 cm	70 cm
Inside diameter	3.84 cm	
Outside diameter	4.86 cm	
Heat capacity of column	0.12 cal/g·K	
Density of column	7.83 g/cm ³	
Internal heat transfer coefficient	0.0385 kJ/s·m ² ·K	
External heat transfer coefficient	0.0142 kJ/s·m ² ·K	
Bulk density	0.532 g/cm ³	0.744 g/cm ³
External void fraction	0.433	0.357

Table 3. Cycle step for the PSA process

Cycle Times (sec)	$t_c/24$	$t_c/4$	$t_c/24$	$t_c/6$	$t_c/24$	$t_c/24$	$t_c/6$	$t_c/24$	$t_c/24$	$5t_c/24$
Bed A	AD	AD & PP	EQI-BD	PP	EQII-BD	BD	PU	EQII-PR	EQI-PR	BF
Bed B	EQI-PR	BF	AD	AD & PP	EQI-BD	PP	EQII-BD	BD	PU	EQII-PR
Bed C	BD	PU	EQII-PR	EQI-PR	BF	AD	AD & PP	EQI-BD	PP	EQII-BD
Bed D	EQI-BD	PP	EQII-BD	BD	PU	EQII-PR	EQI-PR	BF	AD	AD & PP

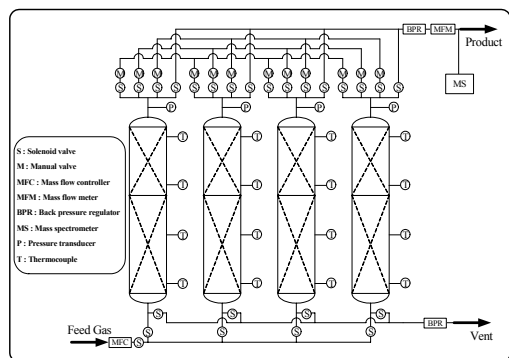


Fig. 1. Schematic diagram of four-bed PSA process.

4. Results and discussion

4.1 Effects of total cycle time and linear velocity

The effect of total cycle time on the performance of a PSA process was studied with varying linear velocity under the adsorption pressure 9 atm. As shown in Fig. 2 (linear velocity 5.2 cm/s), the product purity was high (99.999%+) until a total cycle time of 200 sec and then decreased. A longer total cycle time resulted in lower product purities, as the bed was more contaminated. However, the recovery increases with increasing the total cycle time. This increase in the recovery results from a small of hydrogen remaining in the bed, as the bed was contaminated by the impurities.

The recovery is important to operate the PSA process efficiently. To obtain the high recovery at same process, the linear velocity must increase. However, as the linear velocity increase, the mass transfer zones of impurities are broadened so that the recovery decreases at the given purity.⁽⁵⁾ In order to obtain high recovery, the PSA process experimented and simulated with the various linear velocities and cycle times. The experimental results are shown in Fig. 3-4 with the simulation. With all the linear velocity, the trend of the purity and recovery was similar with the increasing of the total cycle time. However, the recovery was different at high purity (99.999%+). When the linear velocity decreased from 5.2 to 4.7 cm/s, the recovery increased from 66.36 to 73.88 % at high purity (99.999%+). The recovery increased from 73.88 to 75.93 %, as the linear velocity

decreased from 4.7 to 3.9 cm/s. But the difference of the increasing of the recovery became smaller with decreasing the linear velocity. Also, when the linear velocity decreased from 3.9 to 3.14 cm/s, the recovery was similar 75.93% (3.9 cm/s), 75.43% (3.14 cm/s).

4.2 Effect of residence time

The design of the PSA process is complex because of the large number of variables and parameters involved, for example, adsorbent type, adsorbent particle size, bed length/diameter ratio, gas flow velocity, residence time, type of the PSA operating cycle, duration of the steps in the PSA cycle, number of beds, feed gas pressure, feed gas composition, product purity, recovery, and product throughput. When the adsorbents, the feed gas composition and operating condition are given, the residence time is mainly function for design of the PSA

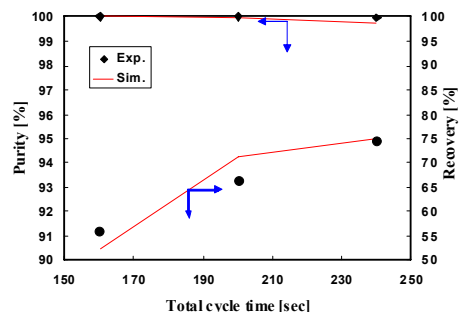


Fig. 2. PSA process performance using different total cycle time at linear velocity 5.22 cm/s.

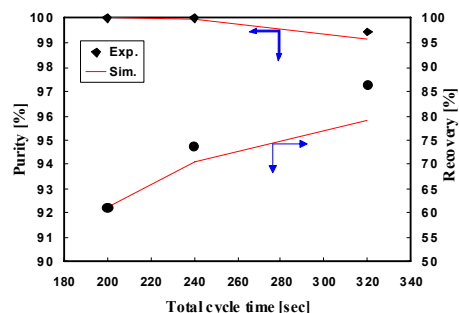


Fig. 3. PSA process performance using different total cycle time at linear velocity 4.70 cm/s.

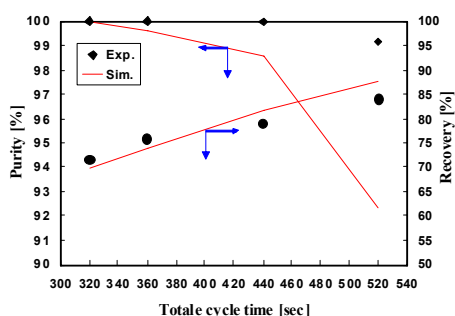


Fig. 4. PSA process performance using different total cycle time at linear velocity 3.90 cm/s.

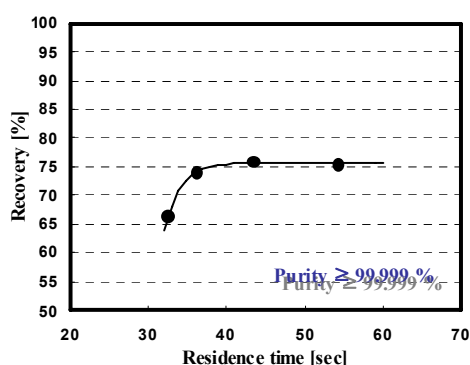


Fig. 5. Recovery with the residence time at product purity 99.999%+.

process. The residence time in a bed is defined as the ratio of the bed volume to the volumetric feed gas flow rate expressed at the bed volumes per unit time.⁽⁶⁾

Fig. 5 shows the experimental results obtained with different residence times with desired product purity (99.999%+) when the bed volume and the adsorption pressure are fixed. The recovery increased about 8 % when the residence time increased from 32.6 to 36.2 sec. The increase of the residence time means that the contact time between the adsorbents and the impurities is increased. As the contact time is decreased in an existing PSA unit, the amount of the impurities through the adsorbents is increased due to increasing the feed flow rate. Thus, the mass transfer zones of impurities are broadened and the recovery is decreased at given product purity. On the other hand, the recovery increased about 2% when the residence time increased from 36.2 to 43.6 sec. Specially, when the residence time increased from 43.6 to 54.2 sec, the recovery was not increased. This implies that the minimum residence time exists to obtain the maximum recovery at fixed product purity (99.999%+).

5. Conclusion

The four-bed ten-step PSA process using a layered bed of activated carbon and zeolite 5A were studied to produce a high purity hydrogen product from SMR

off-gas. The non-isothermal, bulk separation PSA model adopted the linear driving force approximation for the particle uptake and the adsorption isotherm used the Dual-site Langmuir. All the experimental results were in agreement with the values predicted by the theoretical model. It was possible to obtain hydrogen of 99.999%+ purity with 75%+ recovery.

When the total cycle time increased, the recovery increased. The product purity decreased because the impurities reached the product end of the bed and then broke through until the second pressure equalization step. At all the linear velocity, the trend of the purity and recovery was similar with the increasing of total cycle time.

When the adsorbents, the feed gas composition, and the operating conditions are given, the residence time is mainly a function for design of the PSA size. The recovery increased with increasing the residence time at given product purity because of the contact time between the impurities and the adsorbents is increased. The difference of increasing the recovery became smaller with increasing the residence time and then the recovery was not increased more than 43.6 sec of the residence time. The minimum residence time exists to obtain the maximum recovery at desired product purity.

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