CO₂ Recovery from Flue Gas by PSA Process using Activated Carbon

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Abstract—An experimental study was performed for the recovery of CO₂ from flue gas of the electric power plant by pressure swing adsorption process. Activated carbon was used as an adsorbent. The equilibrium adsorption isotherms of pure component and breakthrough curves of their mixture (CO₂ : N₂ : O₂ = 17 : 79 : 4 vol%) were measured. Pressure equalization step and product purge step were added to basic 4-step PSA for the recovery of strong adsorbates. Through investigation of the effects of each step and total feed rate, highly concentrated CO₂ could be obtained by increasing the adsorption time, product purge time, and evacuation time simultaneously with full pressure-equalization. Based on the basic results, the 3-bed, 8-step PSA cycle with the pressure equalization and product purge step was organized. Maximum product purity of CO₂ was 99.8% and recovery was 34%.

Key words: CO₂, PSA, Adsorption, Recovery, Activated Carbon

INTRODUCTION

As the increase of the fuel consumption, CO₂ concentration in atmosphere becomes higher, which causes the global warming problems. In order to reduce it various researches have been performed. One approach is to replace the fossil energy with alternate energy source. However, the consumption of fossil energy will increase for a moment. The other approach is to recover CO₂ from the plant and to utilize it by the conversion of CO₂ to other chemicals. This method can be easily applied for the reduction of CO₂ emission in the near future.

The major sources of the CO₂ emission are power plant, steel plant, cement plant, chemical plant, and fermentation plant. It is easy to separate and recover CO₂, when the concentration of emission gas is more than 25%. In case of the power plant, the CO₂ concentration is relatively low, 10-17%, so it is known to be difficult to recover it economically [Kim et al., 1992; Lee et al., 2000]. However, power plant is the major source of the CO₂ emission, and it is very important to develop a process for recovery of low concentration CO₂.

PSA (Pressure Swing Adsorption) process is one of the possible processes to separate gases economically. It has been reported that the equilibrium separation by activated carbon is better than the kinetic separation by carbon molecular sieve [Kikinides et al., 1993]. In case of the equilibrium separation, zeolite 13X is better than the activated carbon [Chue et al., 1995]. Comparison of the adsorbents and prediction of the process was performed by simulation of the process [Chung et al., 1998; Jang et al., 1998; Kim et al., 1995; Kim et al., 1998; Kim and Suh, 1999; Shin and Suh, 1998; Suh et al., 1996; Yang et al., 1998], so experimental studies would be necessary to validate the results.

In this study, a PSA unit with 3 bed was constructed. 8-step process including pressure equalization and product purge step was designed, and the effect of step time was observed. Activated carbon was used as an adsorbent because it is much cheaper than zeolite and it is negligibly affected by the moisture contents in the feed. The feed gas mixture was 17% CO₂, 79% N₂, and 4% O₂. The adsorption amount of each gas was measured, and the breakthrough curve with mixture gas was observed. Based on the isotherm data, cyclic operation experiment was performed.

EXPERIMENTAL SECTION

The adsorption isotherms of CO₂, N₂, and O₂ were measured at 288-328 K with a volumetric apparatus [Sorial et al., 1983]. Activated carbon (Samchunri, Korea) was used as an adsorbent. The physical properties are listed in Table 1. Breakthrough experiment was performed at 1.5 atm with the flow rate of 4.7-20.0 SLPM (standard liter per minute). Before experiment the adsorbent was activated at 323 K for 6 h under He flow. A schematic drawing of PSA experimental apparatus is shown in Fig. 1, and the dimensions of adsorption bed are listed in Table 2.

The flow rates of gases were controlled by mass flow controller (Brooks Co., 5850I). The feed gases were mixed in a mixer to make a desired concentration. Adsorption bed, tubes, and connectors were made by stainless steel 316, and the adsorption bed was wrapped with heating jacket to heat the adsorbent during the activation step. Pressure transmitters were installed at the inlet and outlet of the adsorption bed to measure the bed pressure during operation. Thermocouples were located at 16, 35, 54, and 73 cm from the bottom.

<table>
<thead>
<tr>
<th>Table 1. Physical properties of activated carbon</th>
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<tr>
<td>Particle size (mesh)</td>
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<tr>
<td>BET surface area (m²/g)</td>
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<tr>
<td>Total pore volume (ml/g)</td>
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<tr>
<td>Average pore diameter (A)</td>
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</table>
of the bed, which was assigned as TC1-TC4. Pneumatic valves (Kitz Co.) were controlled by PLC (programmable logic controller, Siemens Co.). Feed pressure during adsorption was controlled by back pressure regulator (Tescom Co., 44-2362-24). Adsorbed gases were desorbed under vacuum with vacuum pump (ULVAC Co., DA-60D). The product gases were analyzed by mass spectrometer (Balzers Co., TCP 015) and the flow rate of the product gas was measured by wet test meter (GCA Co., 63115).

The pressure of the bed was controlled at 1.5 atm during adsorption, and the pressure during desorption step was measured at 0.1 atm. The cyclic operation steps were composed of: (I) pressurization, (II) adsorption, (III) cocurrent blowdown, (IV) cocurrent pressure equalization, (V, VI) product purge, (VII) vacuum desorption, and (VIII) countercurrent pressure equalization. The operation schedule is shown in Fig. 2. Upper illustration in Fig. 2 represented a sequential flow pattern of each column. During the pressurization step the feed gas flew into the bed from the bottom and the pressure was increased from 0.5 to 1.5 atm. The CO\textsubscript{2} was adsorbed on activated carbon at 1.5 atm during adsorption step. The pressure was decreased to 1.0 atm during the cocurrent blowdown step, and N\textsubscript{2} in the void space flew out of the bed. This bed was then connected to the vacuum pump to decrease the pressure to 0.1 atm and to obtain pure CO\textsubscript{2}. Part of the CO\textsubscript{2} was stored in the product tank for a product purge gas and the remaining CO\textsubscript{2} was obtained as a product. This gas was connected to the mass spectrometer for the analysis and to the wet test meter for flow rate measurement. This bed connected to the bed that finished the cocurrent blowdown step to increase the pressure to 0.5 atm. The bed continued the next cycle. The experimental conditions in this study are summarized in Table 3.

### ADSORPTION ISOTHERMS OF PURE GASES

The adsorption isotherms of N\textsubscript{2}, O\textsubscript{2}, and CO\textsubscript{2} on activated carbon was measured at the temperature range of 15-55°C and the pressure range of 0-2 atm. The adsorption amount of CO\textsubscript{2} is more than 5 times than those of N\textsubscript{2} and O\textsubscript{2} as shown in the adsorption isotherms of Figs. 3-5. The mixture gases could be separated from the difference of adsorption amounts. In case of CO\textsubscript{2} the adsorption amount decreased with the increase of pressure [Han, 1985], but it increased linearly with the pressure for N\textsubscript{2} and O\textsubscript{2} [Sircar et al., 1995; Berlier et al., 1996]. This told us that the low-pressure range was suitable for the PSA separation because it had a large difference in the adsorption amount. Langmuir-Freundlich model of Eq. (2) predicted the isotherm better than Langmuir model of Eq. (1) for all gases.

\[
q = q_{m} \frac{bp}{1+bp} \quad \text{(1)}
\]

\[
q = q_{m} \frac{bp^{n}}{(1+bp^{n})} \quad \text{(2)}
\]

### BREAKTHROUGH CURVES OF MIXTURE GASES

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This experiment is focused on the changes of CO\textsubscript{2} concentration. The breakthrough curves were measured with the mixture gas of 17\% CO\textsubscript{2}, 79\% N\textsubscript{2}, and 4\% O\textsubscript{2} at 1.5 atm as shown in Fig. 6 where \( C_0/C \) was measured with time change. Here, \( C_0 \) was the concentration of CO\textsubscript{2} in feed and \( C \) is in product. The breakthrough time became short as flow rate increased. The shape of the curves did not change at the flow rate below 15.2 SLPM, but the mass transfer zone became very sharp at the flow rate of 20 SLPM.

The temperature changes at the entrance of the bed was bigger than the changes at the outlet of the bed as shown in Fig. 7, where \( T_{C1} \) was the temperature at the entrance and \( T_{C4} \) was the temperature at the outlet. The breakthrough time of CO\textsubscript{2} was related to the temperature change at \( T_{C4} \), so the temperature change occurred due to the adsorption of CO\textsubscript{2}. Usually the adsorption of gases on the adsorbent is an exothermic process, so the amount of adsorption is proportional to the temperature increase of the system [Yang, 1987; Ruthven et al., 1994]. It could be analyzed that the adsorption amount of CO\textsubscript{2} at the entrance of the bed was bigger than that at the outlet from the data of temperature changes, and this was due to the adsorption of N\textsubscript{2}. In the beginning of the adsorption step CO\textsubscript{2} and N\textsubscript{2} adsorbed at the same time at the entrance of the bed, which caused the temperature increase high. However, at the outlet of the bed N\textsubscript{2} adsorbed first and the gas flow carried the heat out of the bed. As the concentration front moved to the outlet of the bed, most

Table 3. Operating conditions for PSA experiment*

<table>
<thead>
<tr>
<th>Run</th>
<th>Feed flow rate (SLPM)</th>
<th>Step time (sec)</th>
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<tbody>
<tr>
<td>A</td>
<td>10.0</td>
<td>PR 40 AD 162 CD 7 PE 209 EV - PU -</td>
</tr>
<tr>
<td>B</td>
<td>10.0</td>
<td>PR 40 AD 162 CD 7 PE 209 EV 209</td>
</tr>
<tr>
<td>C</td>
<td>10.0</td>
<td>PR 22 AD 180 CD 7 PE 209 EV 0</td>
</tr>
<tr>
<td>D</td>
<td>10.0</td>
<td>PR 22 AD 180 CD 7 PE 209 EV 209</td>
</tr>
<tr>
<td>E</td>
<td>4.7</td>
<td>PR 60 AD 142 CD 7 PE 209 EV 209</td>
</tr>
<tr>
<td>F</td>
<td>15.2</td>
<td>PR 18 AD 184 CD 7 PE 209 EV 209</td>
</tr>
<tr>
<td>G</td>
<td>20.0</td>
<td>PR 15 AD 187 CD 7 PE 209 EV 209</td>
</tr>
<tr>
<td>H</td>
<td>10.0</td>
<td>PR 24 AD 178 CD 7 PE 209 EV 209</td>
</tr>
<tr>
<td>I</td>
<td>10.0</td>
<td>PR 26 AD 176 CD 7 PE 209 EV 209</td>
</tr>
<tr>
<td>J</td>
<td>10.0</td>
<td>PR 22 AD 240 CD 7 PE 269 EV 210</td>
</tr>
<tr>
<td>K</td>
<td>10.0</td>
<td>PR 22 AD 240 CD 7 PE 269 EV 150</td>
</tr>
<tr>
<td>L</td>
<td>10.0</td>
<td>PR 22 AD 240 CD 7 PE 269 EV 269</td>
</tr>
<tr>
<td>M</td>
<td>10.0</td>
<td>PR 22 AD 240 CD 7 PE 269 EV 240</td>
</tr>
<tr>
<td>N</td>
<td>10.0</td>
<td>PR 22 AD 240 CD 7 PE 269 EV 269</td>
</tr>
<tr>
<td>O</td>
<td>10.0</td>
<td>PR 22 AD 300 CD 7 PE 329 EV 329</td>
</tr>
<tr>
<td>P</td>
<td>10.0</td>
<td>PR 22 AD 360 CD 7 PE 389 EV 389</td>
</tr>
<tr>
<td>Q</td>
<td>10.0</td>
<td>PR 22 AD 480 CD 7 PE 509 EV 509</td>
</tr>
</tbody>
</table>

*adsorption pressure: 1.5 atm; evacuation pressure: 0.1 atm

Fig. 2. Simplified flow schedule for CO\textsubscript{2} concentration from flue gas.

Fig. 3. Adsorption isotherm of CO\textsubscript{2} on activated carbon.
of the adsorbed N₂ was replaced by CO₂. Part of the adsorption heat of CO₂ was used to desorb N₂, so the temperature increase at the outlet of the bed was lower than that at the entrance. These phenomena can be explained by the temperature profiles in Fig. 7, which have two peaks. The first small peak is due to the N₂ adsorption and the second large peak is due to the CO₂ adsorption. The amount of O₂ was only 4% and the adsorption isotherm was very similar to N₂, so the effect of O₂ could be neglected.

Another breakthrough experiment was done with 83% He and 17% CO₂ to check the effect of N₂ adsorption. The temperature profile had only one peak as shown in Fig. 8, because He did not absorb. From the comparison of Fig. 7 and 8 it could be concluded that the first small peak in Fig. 7 was due to the adsorption of N₂. It is implied from Fig. 7 that fairly large amount of N₂ adsorbed on the surface of activated carbon, which decreased the purity of CO₂ product. In this experiment cocurrent blowdown step [Doong and Yang, 1986] and cocurrent pressure equalization was included to make the purity of CO₂ higher.

RESUL TS OF CYCLIC OPERATION

The results of cyclic operation were compared on the basis of recovery, purity, and productivity. The recovery was defined by the amount of a gas in the product divided by the amount of same gas in the feed. If the cyclic operation contained product purge step, the amount of product purge gas was excluded in the calculation. The analysis of the product was performed at the final end of the process, so the product purge gas was not counted in this experiment. The purity was defined by the amount of one gas in the product divided by the amount of total gas in the product. The productivity was defined by the amount of a gas in the product per unit adsorbent and unit time.

In order to make an optimum process, the purity and the recovery of CO₂ was compared at 10 SLPM with 162 sec of pressuriza-
tion time, 40 sec of adsorption time, 7 sec of cocurrent blowdown time, and 209 sec of vacuum desorption time. If the pressure equa-
lization step was included in the process, the operation time was
changed to 180 sec of pressurization time, 22 sec of adsorption time,
7 sec of cocurrent blowdown time, and 209 sec of vacuum desorp-
tion time. Product purge time was equal to the vacuum desorption
time, and pressure equalization time was set to 11 sec (run A-D in
Table 3).

When the operation cycle was composed of 4 steps, i.e., pres-
surization, adsorption, cocurrent blowdown, and vacuum desorp-
tion, the purity of CO₂ was 48.8% and the recovery was 72.5%. If
the product purge step were added to the process to obtain strongly
adsorbed gas as a product [Doong and Yang, 1986; Baksh and Yang,
1990; Sircar, 1988], the purity was increased to 70.2% and the re-
covery was decreased to 53.1%. When the cocurrent pressure equa-
lization step was included, the purity was 68.8% and the recovery
was 73.9%. When both product purge and pressure equalization
was added to the process, the purity was 91.2% and the recovery
was 46.1%. The comparison of various PSA processes was sum-
marized in Fig. 9.

The differences in purity and recovery at various conditions came
from the effect of N₂ adsorption. The amount of desorbed N₂ de-
pended on the depressurization condition. When cocurrent depre-
surization was simply included, small amount of N₂ was desorbed.
In this case including product purge could not increase the purity
any more. In order to improve the performance and reduce the com-
pression work, countercurrent pressure equalization was added. Dur-
ing the pressure equalization step, the bed after a depressurization
step was connected to a bed after a evacuation step and the pres-
sure was reduced to 0.5 atm. In the pressure equalization step, there
were to ways of connecting the two beds. One way was connect-
ing the top of one bed to the bottom of the other bed, and the other
was connecting the top of two beds. It was concluded from the ex-
periments that the latter was effective way of increasing the prod-
uct recovery. The N₂ concentration was higher at the top of the bed
than the bottom, so mostly N₂ was desorbed from the bed during
the pressure equalization step and the CO₂ concentration inside the
bed was increased. The outlet gas was fed to the top of the bed in
which the pressure increased from 0 to 0.5 atm.

In order to increase the product purity, pressure equalization and
product purge steps were included together. During the pressure
equalization step the pressure of the bed decreased to 0.5 atm and a
lot of N₂ was desorbed. Following product purge step replaced the
adsorbed N₂ to CO₂, which increased the purity of the CO₂.

1. Effect of Feed Flow Rate

In order to find out optimum feed flow rate for the process, purity
and recovery of CO₂ were measured according to the flow rate.
Countercurrent depressurization, pressure equalization, and vacuum
evacuation time were set to 7 sec, 11 sec, and 209 sec, respectively.
Purge time was same as the vacuum evacuation time. Pressuriza-
tion and adsorption times were set to 60 sec and 142 sec at 4.7
SLPM of feed flow rate, 22 sec and 180 sec at 10 SLPM, 18 sec
and 184 sec at 15.2 SLPM, and 15 sec and 187 sec at 20 SLPM,
respectively (run D-G). CO₂ purity did not increase above 10 SLPM
of feed flow rate as shown in Fig. 10. CO₂ productivity increased
up to 15 SLPM of feed flow rate. When the adsorption time was constant, increasing feed flow rate caused high CO₂ purity due to the increase of adsorption zone.

2. Effect of Pressure Equalization

The purity and recovery of CO₂ were measured according to the change of the pressure equalization time. The flow rate was fixed at 10 SLPM. Adsorption pressure was also fixed at 1.5 atm. Final pressure of pressure equalization step was controlled by equalization and pressurization time (run D, H, I, B). In this experimental condition, the pressure of both columns was fully equalized over 10 sec of pressure equalization time. The purity of CO₂ was increased as the equalization pressure was decreased as shown in Fig. 11. The recovery of CO₂ was increased according to the increase of the equalization pressure, but it showed maximum recovery at 0.6 atm. As the equalization pressure became low, more CO₂ could be adsorbed on activated carbon during the next product purge step because of increasing pressure drop between column pressure and atmospheric pressure. The temperature changes of next purge step showed us whether this phenomenon was true. Fig. 12 showed the temperature changes during the product purge step according to the pressure changes at the pressure equalization step. The temperature of TC1 and TC2 increased at 1.0 and 0.61 atm, and the temperature of TC3 increased at 0.55 and 0.5 atm. This means that the amount of purge gas was large at 0.5 and 0.55 atm of pressure equalization pressure.

3. Effect of Product Purge

The purity and recovery of CO₂ according to the changes of the product purge time was shown in Fig. 13 at the condition that total flow rate was 10 SLPM, pressurization time was 22 sec, adsorption time was 240 sec, depressurization time was 7 sec, pressure equalization time was 11 sec, and vacuum desorption time was 269...

![Fig. 11. Effect of final pressure of pressure equalization step on the purity and recovery of CO₂.](image1)

![Fig. 12. Temperature changes of the adsorption bed at difference final pressure during the pressure equalization step.](image2)

![Fig. 13. Effect of product purge step on the purity and recovery of CO₂.](image3)

![Fig. 14. Temperature changes of the adsorption bed at the various product purge step time.](image4)
From the breakthrough test, adsorption characteristics of gas pressure equalization increased the CO$_2$ purity. The maximum and the vacuum adsorption time. The decrease of the pressure after increased as the increase of the adsorption time, the product purge decreases the recovery. Fig. 15 shows that the purity of CO$_2$ is 99.8% increase of the adsorption zone, which increases the CO$_2$ purity and decreased the product recovery. At the product purge time of 269 sec, the CO$_2$ purity of the purge gas was 94.6%, and that of the effluent gas was 17%, which meant that there was an exchange between N$_2$ and CO$_2$. sec (run J-N). The increase of the product purge time increased the product purity and decreased the product recovery. At the product purge time of 269 sec, the CO$_2$ purity of the purge gas was 94.6% and that of the effluent gas was 17%, which meant that there was an exchange between N$_2$ and CO$_2$.

Fig. 14 shows the changes of the temperature in the adsorption bed according to the product purge time. When there was not a product purge, the temperature change in the bed was small. As the product purge was added, the bed temperature increased. When the product purge time was longer than 209 sec, the temperature at TC4 started to increase. This tells us that the increase of the purge time makes the CO$_2$ adsorption zone wide.

The increase of the adsorption time (run D, N, O-Q) makes the increase of the adsorption zone, which increases the CO$_2$ purity and decreases the recovery. Fig. 15 shows that the purity of CO$_2$ is 99.8% and the recovery is 34% at the adsorption time of 480 sec and the product purge time and the vacuum desorption time of 509 sec.

CONCLUSION

The PSA process using activated carbon was applied to the recovery of CO$_2$ from the power plant. The adsorption isotherm of CO$_2$, N$_2$, and O$_2$ was measured with the volumetric adsorption method at the temperature of 15-55 °C and the pressure of 0-2 atm. The amount of CO$_2$ adsorption was 5 times higher than N$_2$ and O$_2$.

The mixture gas was composed of 17% CO$_2$, 79% N$_2$, and 4% O$_2$. From the breakthrough test, adsorption characteristics of gas mixture for cyclic PSA operation could be understood. The optimum feed rate was decided from the breakthrough curve at the flow rate of 4.7-20 SLPM. The adsorption pressure was 1.5 atm and the dimension of adsorption column was 90 cm length and 4.1 cm inner diameter. The temperature change in the bed was measured with the thermocouple, which gave us the information of the adsorption zone.

The PSA process with 3-bed and 8-step was operated including pressure equalization and product purge step. The CO$_2$ purity was increased as the increase of the adsorption time, the product purge and the vacuum adsorption time. The decrease of the pressure after the pressure equalization increased the CO$_2$ purity. The maximum CO$_2$ purity was 99.8% at the recovery of 34%.

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REFERENCES


