

## ECONOMICAL CO<sub>2</sub> CAPTURE FROM FOSSIL FLUE UTILIZATION

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*This paper presented an experimental study for CO<sub>2</sub> capture from flue gas by pressure swing adsorption process (PSA). Capture of carbon dioxide from a binary mixture (N<sub>2</sub>/CO<sub>2</sub>) simulating flue gas was performed by PSA, using selective adsorbents (zeolite-X, carbon molecular sieve, activated carbons). One PSA process consists of three adsorption beds. The process was tested by varying the operation parameters: pressures of adsorption and vacuum evacuation steps. As a typical result, a high purity CO<sub>2</sub> (≈99%) can be produced with recoveries of 50% and 65% from feed gases containing 15-25 vol.% CO<sub>2</sub> respectively. By the other process of two stage PSA, CO<sub>2</sub> can be concentrated from feed gas to product of 99% with much higher capture (>80%). The obtained results prove that the capture of CO<sub>2</sub> from the fossil fuel industry by PSA process is to find cost-effective solutions that will reduce the release of CO<sub>2</sub> into the atmosphere and can contribute to cleaning of environment.*

**Keywords:** CO<sub>2</sub>, PSA, Adsorption, Pollution, Environment

### 1. Introduction

The emission of carbon dioxide (CO<sub>2</sub>) and other pollutants which result from burning fossil fuels has been identified as the major contributor to global warming and climate change [1-3]. However, for the immediate term over the next 10 – 20 years at least, the world will continue to rely on fossil fuels as the source of primary energy. The challenge for the fossil fuel industry is to find cost-effective solutions that will reduce the release of CO<sub>2</sub> and other pollutants into the atmosphere [2-5].

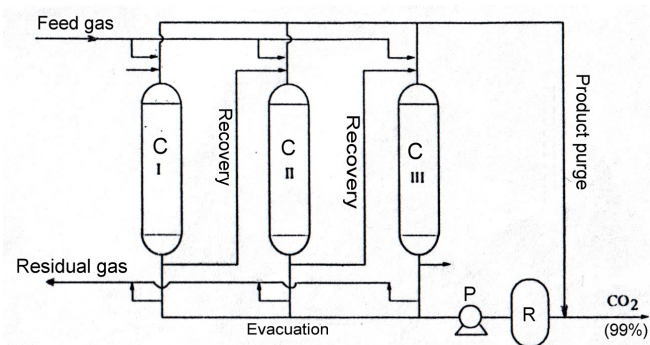
For the purpose of CO<sub>2</sub> separation from flue gas, three separation techniques using absorption, adsorption and membranes are available [6-8]. Up to now CO<sub>2</sub> is recovered from the various streams by an absorption process using ethanolamines as chemical agents [3]. The process has been applied to a large industrial plant. However the absorption process may not be attractive for the recovery of CO<sub>2</sub> from flue gas streams because of the high operating costs and the sensitivity of chemical agents. Therefore a new alternative process for CO<sub>2</sub> separation is adsorption. It is easy to separate and recover CO<sub>2</sub>, when the concentration of emission gas is more than 25%. In case of the power plant, the CO<sub>2</sub> concentration is relatively low 10-18%, so it is known to be difficult to

recover it economically. However, power plant is the major source of the CO<sub>2</sub> emission and it is very important to develop a process for recovery of low concentration CO<sub>2</sub>. PSA (Pressure Swing Adsorption) process is one of the possible processes to separate gases economically [4-6]. The CO<sub>2</sub> recovery by adsorption from flue gas has been studied by using wide pore carbon molecular sieves (CMS), activated carbon (AC), and zeolite and a number of PSA process concepts were patented. The PSA process can concentrate CO<sub>2</sub> to high purity from flue gas, but at a low recovery ratio.

In this paper, two CO<sub>2</sub> PSA processes are examined. One PSA consists of three adsorption beds charged with zeolite 5A and a binary gas mixture (CO<sub>2</sub>/N<sub>2</sub>) containing 15 and 25% of CO<sub>2</sub> was tested to obtain CO<sub>2</sub> with high purity. The other process is a two stage PSA, which differs by the number of the adsorption beds and by the operation sequence per cycle, was developed for further increase in CO<sub>2</sub> recovery.

## 2.Experimental part

Two different small scale units were achieved and tested in the laboratory. Unit I consists of three adsorption columns, a vacuum pump, pneumatic valves, a pressure regulator and product tank. Unit II for two stage PSA contains three adsorption columns for the first stage PSA and two adsorption columns for the second PSA stage. The schematic flow diagram of unit I is shown in Figure 1.



**Figure 1.** Schematic diagram of a PSA unit with three adsorption columns: C-adsorption column; P-vacuum pump; R-gas reservoir

Each of adsorption column in unit I is 1m in height and 70 mm in diameter, containing 1200 g of zeolite 5A. The flow rates of gases were controlled by mass flow controller. Pneumatic valves were controlled by programmable logic controller (PLC). Thermocouples were located at 15, 50 and 85 cm from the bottom of the adsorption bed. Feed pressure during adsorption was controlled by pressure regulator. Adsorbed gases were desorbed under vacuum with vacuum

pump. The product gases were analyzed by GC method using a chromatograph type Varian CP-3800.

A detail description of the operation of the unit is presented below. Three adsorption columns are operated in two different cycle sequences as shown in Fig.2.

C I	PR	AD	CD	PE	Product Purge			Vacuum			PE
C II	Product Purge			Vacuum			PE	PR	AD	CD	PE
C III	Vacuum			PE	PR	AD	CD	PE	Product Purge		

**Figure 2.** Simplified flow schedule for CO<sub>2</sub> recovery from flue gas:(PR-pressurization; AD-adsorption; CD-cocurrent depressurization; PE-pressure equalization)

The cyclic operation steps were composed of: pressurization (PR); adsorption (AD); cocurrent depressurization (CD); pressure equalization (PE); product purge, vacuum desorption, and countercurrent pressure equalization. Step (PR )-cocurrent pressurization: The adsorption column which is initially at the lowest pressure level in a cycle is brought to adsorption pressure ( $P_A$ ) by introducing the feed gas from the top of the column. The final pressure  $P_A$  of this step was 1. 8 and 1. 1 atm., respectively ( see Figure 2),. Step (AD)-adsorption :In this step the feed gas is passed through the adsorption column and the equilibrium separation of CO<sub>2</sub>/N<sub>2</sub> occurs within the adsorption column.The effluent gas rich in N<sub>2</sub> is vented as residual gas. This step continues until the the CO<sub>2</sub> concentration front propagates to a desired position within the adsorption column. Step (CD)-cocurrent depressurization. In the case of the cycle sequence , the adsorption column is depressurized to near atmosphere pressure, so that the following recovery and purge steps may occur at low pressure. During this step the weak adsorptive N<sub>2</sub> present within void volume and adsorbed phase flows out to the effluent stream. The CO<sub>2</sub> is recovered from the gas coming from the other column undergoing purge step , of which CO<sub>2</sub> concentration is higher than that of feed gas. After the recovery step, a portion of product gas is used to replace N<sub>2</sub> remaining within the column. By using a vacuum pump, the gas is evacuated through the bed end to the lowest pressure level in the cycle. During this step a high purity of CO<sub>2</sub> is obtained and a portion of the evacuated gas is used for purge step. Part of the CO<sub>2</sub> was stored in the product reservoir for a product purge gas and the remaining CO<sub>2</sub> was obtained as a product. This gas was connected to the gas chromatograph for the analysis. The process continued the next cycle.

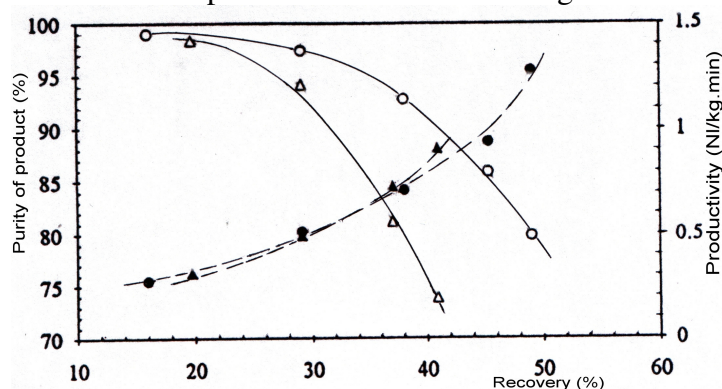
### 3.Results and discussions

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 product. The productivity was defined by the amount of a gas in the product per unit adsorbent and unit time. Using the cycle sequence presented above and two feed gas mixtures ( 15%CO<sub>2</sub>/85% N<sub>2</sub> and 25% CO<sub>2</sub>/75% N<sub>2</sub>) was tested the recovery of CO<sub>2</sub>. As the operating parameters were examined the pressure level of adsorption and the evacuation steps. The amount of purge gas is controlled to obtain a desired product purity. Experimentally a steady state was decided by way of a stabilized bed temperature and product purity. At least 15 to 20 cycles were required to attain a steady state of PSA operation. PSA performances at a steady state are expressed in terms of product recovery for a given CO<sub>2</sub> purity in product stream. The CO<sub>2</sub> purity was measured by a GC analyzer in the gas stream coming out of the storage reservoir when the pressure of this reservoir reaches the maximum value. The differences in purity and recovery at various conditions came from the effect of N<sub>2</sub> adsorption.

### 3.1. Effect of adsorption pressure

The pressure level of the adsorption step was kept at 1.8 and 1.1 atm with the process following the cycle sequences from Figure 2. The product purity was obtained by varying the purge gas amount. The feed gas ( 15%CO<sub>2</sub>/85% N<sub>2</sub> ) fed during adsorption and pressurization steps was about 10 NI / min. The effect of adsorption pressure on the PSA performance is shown in Figure 3.

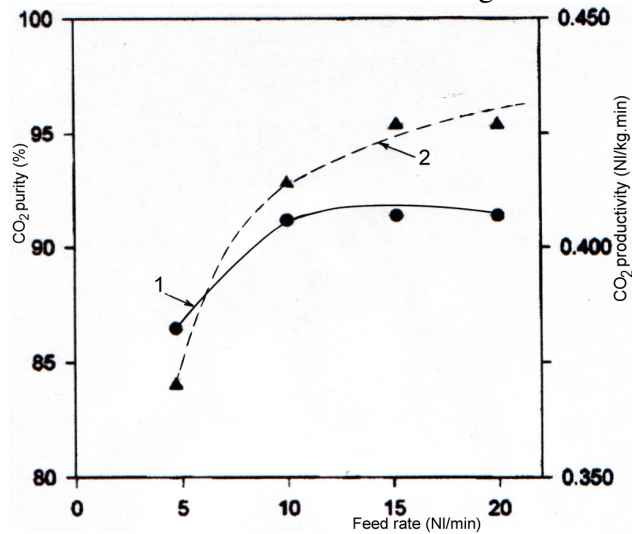


**Figure 3.** Effect of adsorption pressure  $P_A$  on PSA system performance. Symbols represents:(o and ●)  $P_A$ -1.8 atm; ( $\Delta$  and  $\blacktriangle$ ) $P_A$ -1.1 atm; continue line-product purity; dotted line-productivity

It can be seen that a high feed pressure is favorable for CO<sub>2</sub> recovery since a higher purity of CO<sub>2</sub> product gas can be obtained at a higher adsorption pressure. For a high adsorption pressure a larger amount of CO<sub>2</sub> in the feed gas is adsorbed within the bed and hence the process operation results in high productivity for a desired purity.

### 3.2. Effect of feed flow rate

In order to find out optimum feed flow rate for the process, purity and recovery of CO<sub>2</sub> were measured according to the flow rate. Pressurization and adsorption times were set to 70 sec and 145 sec at 4.7 NI / min of feed flow rate, 35 sec and 180 sec at 10NI/min and 25 sec and 185 sec at 15.2 NI/min and 25 sec and 190 sec at 20 NI/min respectively ( run 4-7). CO<sub>2</sub> purity did not increase above 10NI/min of feed flow rate as shown in Figure 4.



**Figure 4.** Effect of total feed rate on the purity and recovery of CO<sub>2</sub>: 1) CO<sub>2</sub> purity as a function of feed rate; 2) CO<sub>2</sub> productivity as a function of feed rate.

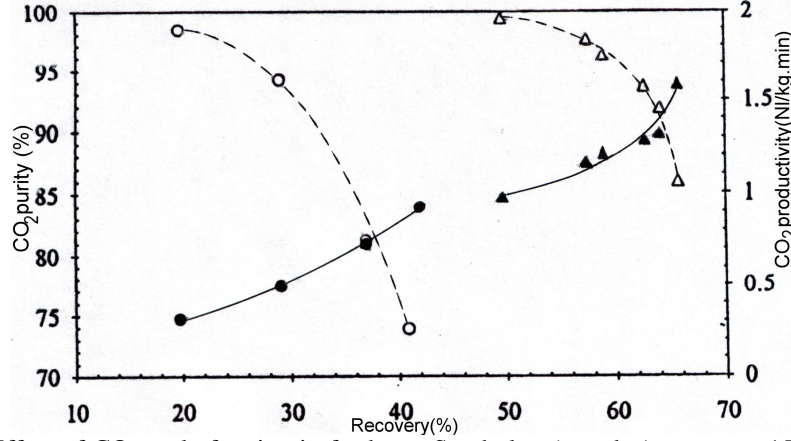
CO<sub>2</sub> productivity increased up to 15 NI / min of a feed flow rate. When the adsorption time was constant, increasing feed flow rate caused high CO<sub>2</sub> purity due to the increase of the adsorption zone.

### 3.3. Effect of CO<sub>2</sub> mole fraction in the feed gas

The CO<sub>2</sub> mole fraction in the flue gas stream varies depending on the sources. The flue gas coming out of the power generation plant using fossil flue contains around 10% of CO<sub>2</sub>, while 25% of CO<sub>2</sub>. The present CO<sub>2</sub> PSA was tested for two different gas mixtures containing 15 and 25 % of CO<sub>2</sub>. Figure 5 shows the experimental results obtained at the conditions of P<sub>A</sub> = 1.1 atm and P<sub>V</sub> = 0.05 atm. The feed gas flow rates were maintained at the average values of about 12 and 9NI/min for 15 and 25% CO<sub>2</sub> feed, respectively. In the case of the high concentration CO<sub>2</sub> in the feed gas the effective adsorption amount is high and higher productivity is obtained. The present process shows a fairly good performance for the feed gas containing 25% CO<sub>2</sub> feed. However for the low concentrated flue gas, the process performance should be ameliorated to raise the



recovery ratio. During the adsorption step the average mole fraction of CO<sub>2</sub> in the effluent stream ranges from 4-6% vol which is vented as residual gas.

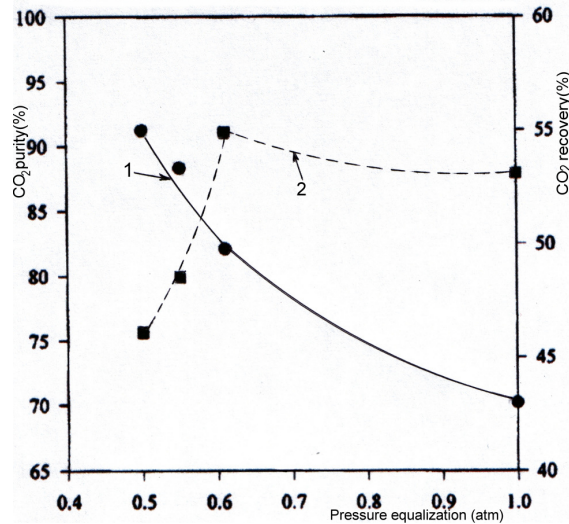


**Figure 5.** Effect of CO<sub>2</sub> mole fraction in feed gas. Symbols : (o and ●) represent 15 vol.% CO<sub>2</sub> ; (Δ and ▲) represent 25 vol.% CO<sub>2</sub>; dotted line represent the product purity and continue line represent the productivity

In order to increase the recovery ratio of the process ,the process has to be improved to reduce the total amount of CO<sub>2</sub> present in the effluent of the adsorption step.

### 3.4. Effect of pressure equalization

The purity and recovery of CO<sub>2</sub> were also measured according to the change of the pressure equalization time , Figure 6.

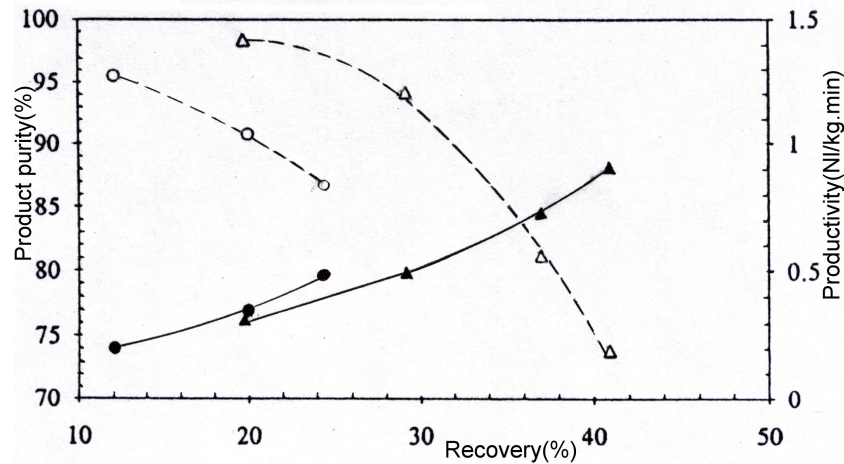


**Figure 6.** Effect of final pressure of pressure equalization step on the purity and recovery of CO<sub>2</sub> 1) CO<sub>2</sub> purity as a function of pressure equalization; 2) CO<sub>2</sub> productivity as a function of pressure equalization .

The flow rate was fixed at 10NI/min. Adsorption pressure was also fixed at 1.8 atm. Final pressure equalization step was controlled by equalization and pressurization time. In this experimental condition, the pressure of both columns was fully equalized over 10 sec of pressure equalization time. The purity of CO<sub>2</sub> was increased as the equalization pressure was decreased as shown in Figure 6. The recovery of CO<sub>2</sub> 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 CO<sub>2</sub> could be adsorbed on zeolite 5A during the next product purge step because of increasing pressure drop between column pressure and atmospheric pressure.

### 3.5. Effect of evacuation pressure

For the feed gas containing 15 vol.% CO<sub>2</sub>, operations at two evacuation pressures ( 0.05 and 0.09 atm) were made to investigate the effects of this parameter on the process performances. The adsorption pressure P<sub>A</sub> was held at 1.1 atm. The experimental results are shown in Figure 7. A decrease in evacuation pressure results in a high productivity and recovery for a fixed product purity. As the adsorption isotherm of CO<sub>2</sub> on zeolite 5A has a highly favorable shape, a slight decrease in evacuation pressure increases the effective adsorption



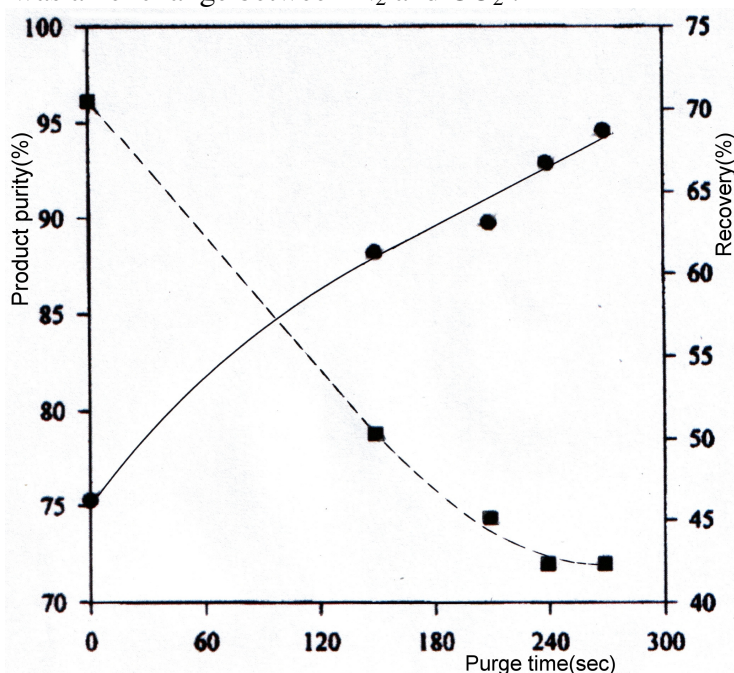
**Figure 7.** Effect of evacuation pressure P<sub>E</sub> on product purity and productivity. Symbols : (o and ●) represent P<sub>E</sub> =0.09 atm; (Δ and ▲) represent P<sub>E</sub> =0.07 atm; dotted line –product purity; continue line-productivity

amount in the cycle and consequently the productivity of the process in cyclic operation.

### 3.6. Effect of product purge

The purity and recovery of CO<sub>2</sub> according to the changes of the product purge time was shown in Figure 8 at the condition that total flow rate was 10NI/min, pressurization time was 30 sec, adsorption time was 270 sec, depressurization time was 10 sec, pressure equalization time was 15 sec and vacuum desorption time was 210 sec.

The increase of the product purge time increased the product purity and decreased the product recovery. At the product purge time of 270 sec, the CO<sub>2</sub> 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<sub>2</sub> and CO<sub>2</sub>.



**Figure 8.** Effect of product purge step on the purity and recovery of CO<sub>2</sub>. Symbols: (●) and continue line represent the purity of CO<sub>2</sub>; (■) and dotted line represent the recovery of CO<sub>2</sub>

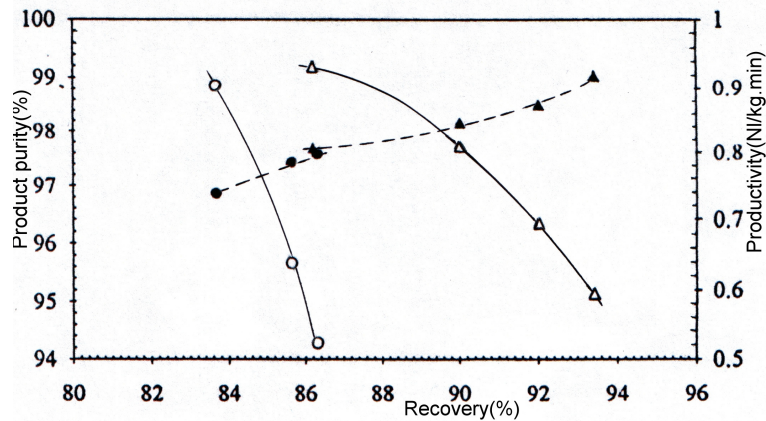
### 3.7. Cyclic behavior of adsorption column

The adsorption heat of CO<sub>2</sub> and N<sub>2</sub> on zeolite 5A were estimated at 36 and 25 kJ/mol from the adsorption isotherms of pure component. During the cyclic operation at a steady state a temperature variation occurs: decrease in temperature during the evacuation step and increase in temperature during the adsorption. During the evacuation step, by decreasing the column pressure down to 0.05 atm, the temperature decreases due to the desorption of CO<sub>2</sub>.

The recovery ratio was inferior to 50% when CO<sub>2</sub> was concentrated from the feed gas described above to a product of 99%. The main reason for the low



recovery was the insufficient regeneration of the adsorption column. However, by lowering the evacuation pressure, the regeneration rate could be ameliorated as discussed above, but it is directly related to the product cost-vacuum. Incorporation of the purge step by flowing a part of the effluent gas coming from the column undergoing an adsorption step, results in a significant improvement of the process performance. This operation was performed in unit II of two stage PSA. Even for a feed gas containing 15 vol.% CO<sub>2</sub>, 99% of CO<sub>2</sub> was produced at high recovery of 84%.



**Figure 9.** Performance of two stage PSA process. Symbols: (o and ●) represent 15 vol.% CO<sub>2</sub>; (Δ and ▲) represent 25 vol.% CO<sub>2</sub>; continue line represent the product purity; dotted line represent the productivity .

Figure 9 represents the typical results of two stage PSA process operation for two feed gases: 15 and 25 vol.% CO<sub>2</sub> in feed. It can be seen that 99% purity was obtained with recovery of about 84%. In the case of the operation of unit II, CO<sub>2</sub> content in the effluent gas coming out of the adsorption step could be reduced at 0.7 to 1.5%, and consequently a high recovery could be obtained.

#### 4. Conclusions

Two different PSA processes for the recovery CO<sub>2</sub> from a binary gas mixtures simulating a flue gas were studied. The process performances were influenced by the operating parameters. As the adsorption isotherm of CO<sub>2</sub> on zeolite 5A has a favorable shape and the vacuum evacuation pressure had an important role on the productivity and recovery performances.

The PSA unit with three adsorption columns showed a good performance for 25 vol% CO<sub>2</sub> in feed, while for the low concentrated feed gas (15 vol % CO<sub>2</sub>) it was produced CO<sub>2</sub> with high purity but with a low recovery. The PSA process

with three bed was operating including and pressure equalization and product purge step. The purity was increased as the increase of the adsorption time, the product purge and the vacuum desorption time. The decrease of the pressure after the pressure equalization increased the CO<sub>2</sub> purity. The maximum CO<sub>2</sub> purity obtained was 99 vol.% .

## REFERENCES

- [1] *Yong, Z., V. Mata, A.E. Rodrigues*, Adsorption of Carbon Dioxide on Basic Alumina at High Temperatures," *J. Chem. Eng. Data*, 45, (2000). 1093-1095 ;
- [2] *Yong, Z., V. Mata, A.E. Rodrigues*, Adsorption of Carbon Dioxide onto Hydrotalcite-like Compounds (HTlcs) at High Temperatures, *Ind. Eng. Chem. Res.*, 40, (2001),204-209;
- [3] *Yong, Z., V. Mata, A.E. Rodrigues*, Adsorption of Carbon Dioxide at High Temperature – A Review, *Separ. Purif. Technol.*, 26, (2002) 195-205;
- [4] *Olajossy, A., A. Gawdzik, Z. Budner, J. Dula*, Methane Separation from Coal Mine Methane Gas by Vacuum Pressure Swing Adsorption, *Trans. IChemE.*, 81, (2002) 474-482;
- [5] *Reynolds, S.P., A.D. Ebner, and J.A. Ritter*, New Pressure Swing Adsorption Cycles for Carbon Dioxide Sequestration, *Adsorption*, 11, (2005) 531-536;
- [6] *Na, B., H. Lee, K. Koo, H.K. Song*, Effect of Rinse and Recycle Methods on the Pressure Swing Adsorption Process to Recover CO<sub>2</sub> from Power Plant Flue Gas Using Activated Carbon, *Ind. Eng. Chem. Res.*, 41, (2002) 5498-5503;
- [7] *Ding, Y. and E. Alpay*, (2000).Equilibria and Kinetics of CO<sub>2</sub> Adsorption on Hydrotalcite Adsorbent, *Chem. Eng. Sci.*, 55, (2000) 3461-3474 ;
- [8] *Caldeira, K., A.K. Jain, and M.I. Hoffert*, Climate Sensitivity Uncertainty and the Need for Energy Without CO<sub>2</sub> Emission, *Science*, 299, (2003),2052-2054;