ECONOMICAL CO_2 CAPTURE FROM FOSSIL FLUE UTILIZATION

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Lucrarea prezintă un studiu experimental privind reţinerea CO_2 din gazele de ardere prin aplicarea unui procedeu de adsorbţie (PSA). Pentru reţinerea CO_2 s-a utilizat un amestec care simulează gazele de ardere (azot şi dioxid de carbon). Pentru adsorbţie s-au folosit adsorbanţi selectivi (zeolit-X, carbon molecular, carbon activ). Procesul PSA constă în trei straturi de adsorbţie. Procesul a fost testat prin variaţia presiunilor de operare. Ca un rezultat tipic, se poate obţine o puritate înaltă a CO_2 (≈99%) în condiţiile în care gradul de reţinere din gazele de ardere este cuprins în intervalul 50 % - 65 % (pentru o concentraţie a CO_2 în gazele de ardere în intervalul 15 – 25 %). Pentru un proces PSA în două trepte, se poate obţine o puritate a CO_2 de 99 %, dar cu un grad de reţinere sensibil mai mare (> 80 %). Rezultatele obţinute dovedesc că reţinerea prin procesul PSA a CO_2 din gazele de ardere rezultate din arderea combustibililor fosili este o soluţie eficientă, care poate contribui la reducerea emisiei acestui gaz în atmosferă şi implicit la obţinerea unui mediu înconjurător mai curat.

This paper presented an experimental study for CO_2 capture from flue gas by pressure swing adsorption process (PSA). Capture of carbon dioxide from a binary mixture (N_2/CO_2) 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_2 (≈99%) can be produced with recoveries of 50% and 65% from feed gases containing 15-25 vol. % CO_2 respectively. By the other process of two stage PSA, CO_2 can be concentrated from feed gas to product of 99% with much higher capture (>80%).The obtained results prove that the capture of CO_2 from the fossil fuel industry by PSA process is to find cost-effective solutions that will reduce the release of CO_2 into the atmosphere and can contribute to cleaning of environment.

Keywords: CO_2, PSA, Adsorption, Pollution, Environment

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1. Introduction

The emission of carbon dioxide (CO_2) 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_2 and other pollutants into the atmosphere [2-5].

For the purpose of CO_2 separation from flue gas, three separation techniques using absorption, adsorption and membranes are available [6-8]. Up to now CO_2 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_2 from flue gas streams because of the high operating costs and the sensitivity of chemical agents. Therefore a new alternative process for CO_2 separation is adsorption. It is easy to separate and recover CO_2 when the concentration of the gas emission is more than 25%. In case of the power plant, the CO2 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 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 [4-6].The CO_2 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_2 to high purity from flue gas, but at a low recovery ratio.

In this paper, two CO_2 PSA processes are examined. One PSA consists of three adsorption beds charged with zeolite 5A and a binary gas mixture (CO_2/N_2) containing 15 and 25% of CO_2 was tested to obtain CO_2 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_2 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 shows in Fig. 1.

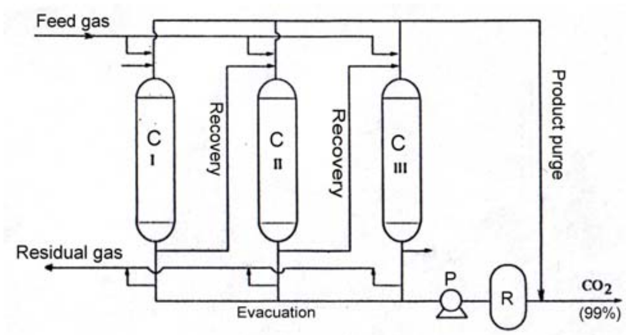

Fig. 1. Schematic diagram of a PSA unit with three adsorption columns: C-adsorption column; P-vacuum pump; R-gas reservoir

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.

<table>
<tr><td>C I</td><td>PR</td><td colspan="2">AD</td><td>CD</td><td>PE</td><td colspan="3">Product Purge</td><td></td><td colspan="4">Vacuum</td><td>PE</td></tr>
<tr><td>C II</td><td colspan="4">Product Purge</td><td></td><td colspan="3">Vacuum</td><td>PE</td><td>PR</td><td colspan="2">AD</td><td>CD</td><td>PE</td></tr>
<tr><td>C III</td><td colspan="4">Vacuum</td><td>PE</td><td>PR</td><td>AD</td><td>CD</td><td>PE</td><td colspan="4">Product Purge</td><td></td></tr>
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Fig. 2. Simplified flow schedule for CO_2 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 Fig. 2). Step (AD)-adsorption: In this step the feed gas is passed through the adsorption column and the equilibrium separation of CO_2/N_2 occurs within the adsorption column.The effluent gas rich in N_2 is vented as residual gas. This step continues until the the CO_2 concetration 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_2 present within void volume and adsorbed phase flows out to the effluent stream. The CO_2 is recovered from the gas coming from the other column undergoing purge step, of which CO_2 concentration is higher than that of feed gas. After the recovery step, a portion of product gas is used to replace N_2 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_2 is obtained and a portion of the evacuated gas is used for purge step. Part of the CO_2 was stored in the product reservoir for a product purge gas and the remaining CO_2 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_2/85% N_2 and 25% CO_2/75% N_2) was tested the recovery of CO_2. As the operating parameters were examined, the pressure level of adsorption and the evacuation steps followed. The amount of purge gas is controlled to obtain the 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_2 purity in product stream. The CO_2 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_2 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 Fig. 2. The product purity was obtained by varying the purge gas amount. The feed gas (15%CO_2/85% N_2) fed during adsorption and pressurization steps were about 10 Nl / min. The effect of adsorption pressure on the PSA performance is shown in Fig. 3.

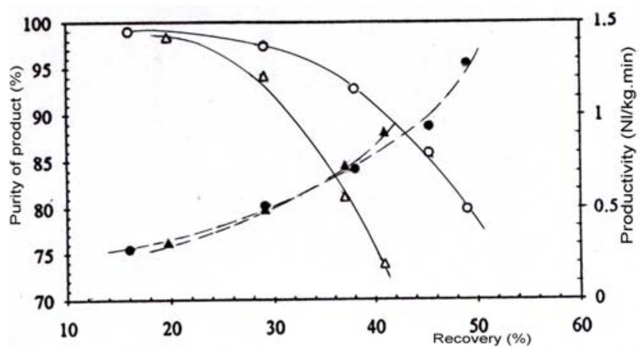

Fig. 3. Effect of adsorption pressure P_A on PSA system performance; the symbols represent: (o and ●) P_A-1.8 atm; (Δ and ▲)P_A-1.1 atm; continue line-product purity; dotted line-productivity

It can be seen that a high feed pressure is favorable for CO_2 recovery since a higher purity of CO_2 product gas can be obtained at a higher adsorption pressure. For a high adsorption pressure a larger amount of CO_2 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_2 were measured according to the flow rate. Pressurization and adsorption times were set to 70 sec and 145 sec at 4.7 Nl / min of feed flow rate, 35 sec and 180 sec at 10Nl/min and 25 sec and 185 sec at 15.2 Nl/min and 25 sec and 190 sec at 20 Nl/min respectively (run 4-7). CO_2 purity did not increase above 10Nl/min of feed flow rate as shown in Fig. 4.

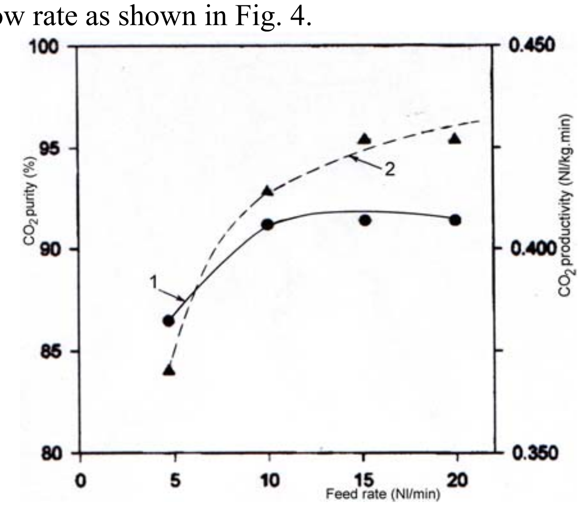

Fig. 4. Effect of total feed rate on the purity and recovery of CO_2: 1) CO_2 purity as a function of feed rate; 2) CO_2 productivity as a function of feed rate.

CO_2 productivity increased up to 15 Nl / min of a feed flow rate. When the adsorption time was constant, increasing feed flow rate caused high CO_2 purity due to the increase of the adsorption zone.

3.3. Effect of CO_2 mole fraction in the feed gas

The CO_2 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_2, while 25% of CO_2. The present CO_2 PSA was tested for two different gas mixtures containing 15 and 25 % of CO_2. Fig. 5 shows the experimental results obtained at the conditions of P_A = 1.1 atm and P_V = 0.05 atm. The feed gas flow rates were maintained at the average values of about 12 and 9Nl/min for 15 and 25% CO_2 feed, respectively. In the case of the high concentration CO_2 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_2 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_2 in the effluent stream ranges from 4-6% vol. which is vented as residual gas.

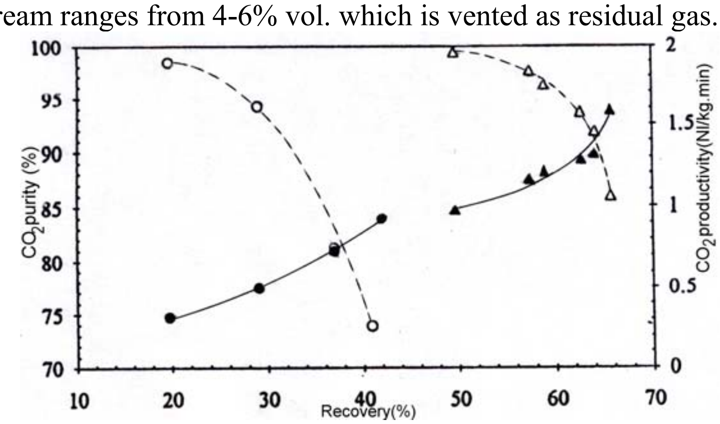

Fig. 5. Effect of CO_2 mole fraction in feed gas; the symbols: (o and ●) represent 15 vol.% CO_2; (Δ and ▲) represent 25 vol.% CO_2; dotted line represent the product purity and continue line represent the productivity

In order to increase the recovery ratio of the process, the process has to be improved to reduce the total amount of CO_2 present in the effluent of the adsorption step.

3.4. Effect of pressure equalization

The purity and recovery of CO_2 were also measured according to the change of the pressure equalization time, Fig. 6.

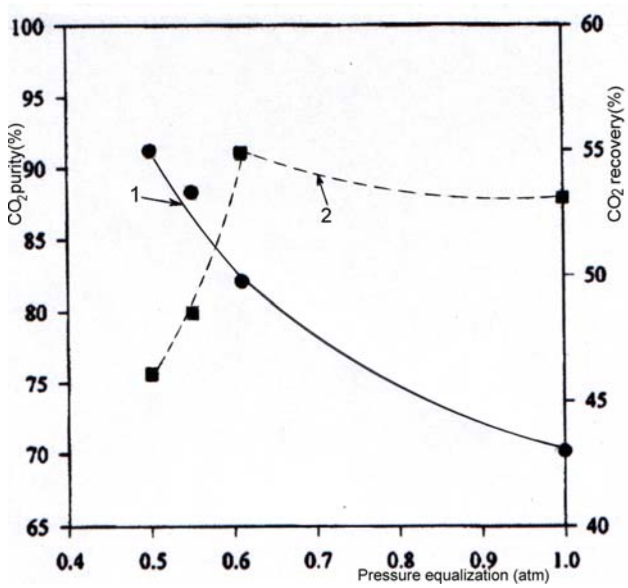

Fig. 6. Effect of final pressure of pressure equalization step on the purity and recovery of CO2: 1) CO_2 purity as a function of pressure equalization; 2) CO_2 productivity as a function of pressure equalization

The flow rate was fixed at 10Nl/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_2 was increased as the equalization pressure was decreased as shown in Fig. 6. The recovery of $CO_2$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_2 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_2, 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_A was held at 1.1 atm. The experimental results are shown in Fig. 7. A decrease in evacuation pressure results in a high productivity and recovery for a fixed product purity. As the adsorption isotherm of CO_2 on zeolite 5A has a highly favorable shape, a slight decrease in evacuation pressure increases the effective adsorption amount in the cycle and consequently the productivity of the process in cyclic operation.

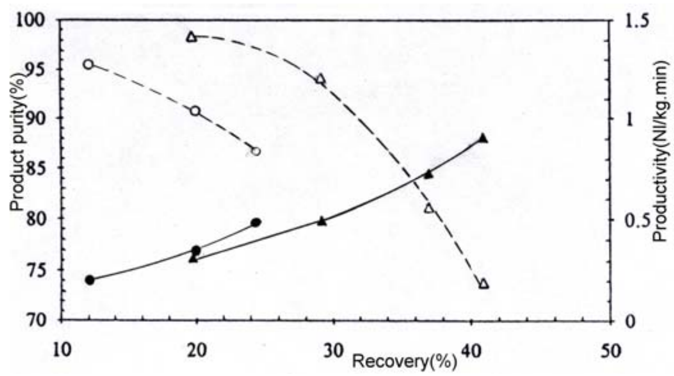

Fig. 7. Effect of evacuation pressure P_E on product purity and productivity; the symbols: (o and ●) represent P_E =0.09 atm; (Δ and ▲) represent P_E =0.07 atm; dotted line –product purity; continue line-productivity

3.6. Effect of product purge

The purity and recovery of CO_2 according to the changes of the product purge time was shown in Fig. 8 at the condition that total flow rate was 10Nl/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_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.

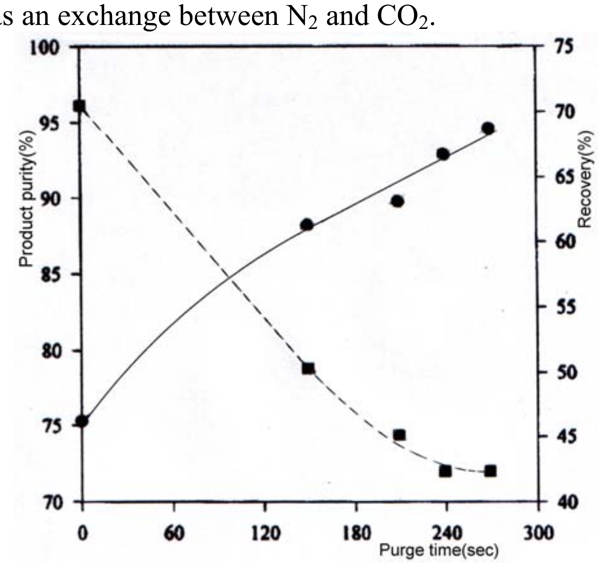

Fig. 8. Effect of product purge step on the purity and recovery of CO_2; the symbols: (●) and continue line represent the purity of CO_2; (■) and dotted line represent the recovery of CO_2

3.7. Cyclic behavior of adsorption column

The adsorption heat of CO_2 and N_2 on zeolite 5A was 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_2.

The recovery ratio was inferior to 50% when CO_2 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_2, 99% of CO_2 was produced at high recovery of 84%.

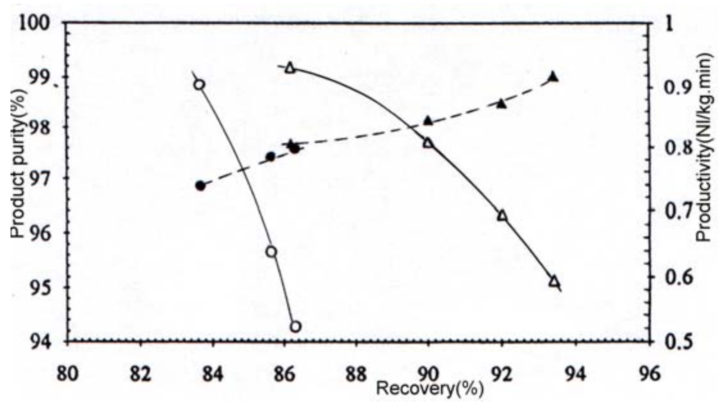

Fig. 9. Performance of two stage PSA process; the symbols: (o and ●) represent 15 vol. % CO_2; (Δ and ▲) represent 25 vol. % CO_2; continue line represent the product purity; dotted line represent the productivity

Fig. 9 represents the typical results of two stage PSA process operation for two feed gases: 15 and 25 vol. % CO_2 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_2 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_2 from binary gas mixtures simulating a flue gas were studied. The process performances were influenced by the operating parameters. As the adsorption isotherm of CO_2 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_2 in feed, while for the low concentrated feed gas (15 vol % CO_2) it was produced CO_2 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_2 purity. The maximum CO_2 purity obtained was 99 vol. %.

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