Experimental Study of High Purity CO₂ Concentration from Syngas by a Dual-bed Six-step Pressure Swing Adsorption Process

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Abstract. With the industry development, the concentration of greenhouse gas increases year by year. Consequently, how to reduce the emission of greenhouse gas has become an important issue all over the world. This research is the experimental study of concentrating high purity CO₂ from syngas after oxy-fuel combustion by a dual-bed six-step pressure swing adsorption (PSA) process. The composition of feed gas used in the process was simulated as 95% CO₂ with N₂ balanced. We chose UOP 13X zeolite as the adsorbent according to the adsorption capacity and selectivity of CO₂ over N₂ comparing to other adsorbents studied. The breakthrough and desorption curves were discussed by changing different feed flow rate and temperature. Next the carbon dioxide was purified by a dual-bed six-step PSA process. After exploring the effects of variables on performance of PSA process, we found the best operating conditions for obtaining high purity carbon dioxide among our experiments. The best operating conditions are feed pressure 3.45 atm, countercurrent depressurization pressure 0.48 atm and purge to feed ratio 0.105. The experimental results of best conditions are 99.94% purity and 42.84% recovery of carbon dioxide at bottom product, energy consumption 0.304 GJ/tonne CO₂ and productivity 0.136 kg CO₂/kg adsorbent-h.

1. Introduction
With the rapid growth of economy, the requirement of fossil fuels increases dramatically. Although fossil fuels play a dominant role in global energy systems, there are also negative impacts, being the main source of greenhouse gases, especially CO₂. To balance the role of energy in social and economic development, the world needs to reduce CO₂ emissions. The 21st Conference of the Parties (COP21) to the United Nations Framework Convention on Climate Change (UNFCCC) set the objective to limit global warming to less than 2°C and announced a new legally Paris Agreement to replace the Kyoto Protocol[1]. Due to the legal validity of this agreement, the signatories show their determination to solve global warming.

In order to reduce carbon dioxide emissions, we can concentrate high purity CO₂ and let it become the high value-added product such as the carbonated beverage manufacturing, freezing, welding and wafer cleaning[2]. There are several major technologies to capture carbon dioxide, such as absorption, cryogenic separation, membrane separation, high temperature solid looping systems and adsorption[3].
Among these technologies, pressure swing adsorption (PSA) is one of the most known and established industrial processes for gas separation because of the low energy requirements, low capital investment cost, and simplicity of operation which makes it very competitive.

We developed a PSA process to purify carbon dioxide from syngas after oxy-fuel combustion. The feed of syngas composition was simplified as a mixture of 95% CO₂ and 5% N₂, and UOP 13X zeolite was used as the adsorbent. In our last study[4], we used a single-bed four-step PSA process to purify CO₂ and the purity and recovery of CO₂ were 99.34% and 30.69%, respectively. However, CO₂ purity with more than only 99% doesn’t have high economic value. Therefore, in this study, based on the breakthrough curve and desorption curve experiments, we carries out the dual-bed six-step PSA process to purify carbon dioxide and explore various variables to find the optimum operating conditions to obtain more valuable high purity (> 99.9%) and recovery (> 40%) of carbon dioxide.

2. Experimental description
The typical syngas compositions[5] were H₂, CO, CO₂, CH₄, H₂O and a small amount of N₂ and Ar. After the syngas passes through the oxy-fuel combustion and water removal, the output gas concentration of CO₂ was about 95% - 97.4%. Adsorption amount and adsorption isotherm were obtained by using Micro-Balance Thermo Cahn D-200. Breakthrough curves, desorption curves and PSA process experiments were performed by adsorption bed. The concentration of outlet gas was detected by Thermo Fisher Scientific Trace-1300 GC. The dual-bed six-step PSA process is shown as Figure 1 and the steps are pressurization, adsorption, cocurrent depressurization, countercurrent depressurization, purge and idle respectively. The experiments started with a set of basic experiment, and the operating conditions are shown in Table 1.

| Operating conditions                      | Value       |
|------------------------------------------|-------------|
| Feed composition                         | 95% CO₂, 5% N₂ |
| Feed pressure                            | 3.45 atm    |
| Countercurrent Depressurization pressure | 0.17 atm    |
| Operating temperature                    | 358 K       |
| Pressurization time                      | 150 s       |
| Adsorption time                          | 20 s        |
| Cocurrent Depressurization time          | 250 s       |
| Countercurrent Depressurization time     | 150 s       |
| Purge time                               | 20 s        |
| Idle time                                | 250 s       |

![Figure 1. Schematic diagram of dual-bed six-step PSA process.](image-url)
3. Results and Discussion

3.1. Adsorbent selection
We discuss the adsorbents from different companies, such as COSMO 5A, UOP 5A, COSMO 13X, and UOP 13X respectively, and then calculate the selectivities by Equation (1) with feed concentration 95% CO2 and 5% N2 at different feed pressure: 1, 1.5, 2 and 2.35 atm at various temperature.

\[ \alpha_p = \left( \frac{y_{CO_2,pure}}{y_{N_2,pure}} \right)_{feed} \]

Because the adsorption amount of CO2 on COSMO 13X and UOP 13X is higher than that on COSMO 5A and UOP 5A at 1 atm. Also, the selectivity of COSMO 13X is higher than that of UOP 13X at 298 K, but the selectivities of COSMO 13X are lower than those of UOP 13X at other temperatures. Most of all, the selectivity of UOP 13X usually increases along with temperature. The range of operating temperature can be wider when the CO2 is purified with 13X zeolite, so that we choose UOP 13X zeolite as the adsorbent in this experiment.

From Figure 2, it can be seen that the highest selectivity of UOP 13X is at 398 K and the second highest is at 358 K at total pressure 1 atm. However, with the increase of total pressure, the selectivity at 358 K is close to that at 398 K. In addition, the CO2 adsorption capacity at 358 K is higher than that at 398 K. The higher adsorption amount will be beneficial to the improvement of the bottom product CO2 purity in dual-bed PSA process, so that it can be predicted that 358 K is a suitable operating temperature for the dual-bed six-step PSA experiment.

3.2. Comparison of different operating conditions for breakthrough curve and desorption curve

3.2.1. Effect of feed flow rate on breakthrough curve.
Figure 3 shows that the breakthrough curve of CO2 at 2 atm and 358 K with different feed flow rate. The flow rates are 0.498 L/min and 1.511 L/min respectively. As observed from the figure, when the flow rate increases, the feed amount of CO2 increases, resulting in a faster breakthrough in the adsorption bed.

3.2.2. Effect of bed temperature on breakthrough curve.
As the bed temperature increases, the adsorption amount of CO2 decreases. Therefore, the time for adsorption bed to achieve breakthrough reduces, resulting in a faster breakthrough in the adsorption bed.

3.2.3. Effect of feed flow rate on desorption curve
Figure 4 shows that the breakthrough curve of CO2 at 2 atm and 358 K with different feed flow rate. The flow rates are 0.498 L/min and 1.511 L/min respectively. When the He flow rate increases, the feed amount of He increases, resulting in decreasing the concentration of CO2 in gas phase and increasing desorption rate of CO2.
3.2.4. Effect of bed temperature on desorption curve
Since desorption is an endothermic reaction, carbon dioxide desorption is faster at high temperatures. Therefore, at higher bed temperature, the dimensionless concentration would decline more until the dimensionless concentration of CO$_2$ reaches 0.

![Figure 3. CO$_2$ breakthrough curves at 358 K with different feed flow rate.](image1)

![Figure 4. CO$_2$ desorption curves at different temperature with feed flow rate 0.498 L/min.](image2)

3.3. Dual-bed six-step PSA process
To separate high purity CO$_2$ from syngas after oxy-fuel combustion, dual-bed six-step PSA process is used. There are many operating variables discussed, and the main experimental results are as following:

3.3.1. Effect of countercurrent depressurization pressure
As shown in Figure 5, with the increase of countercurrent depressurization pressure, the purity of CO$_2$ of bottom product increases and the recovery decreases. When the countercurrent depressurization pressure increases, the bottom product of adsorption bed discharges less, so that the recovery of bottom product decreases. The lower countercurrent depressurization pressure it is, the more amount of N$_2$ the bed emits at the bottom. Therefore, the CO$_2$ purity of bottom product decreases.

3.3.2. Effect of feed pressurization / countercurrent depressurization step time
As shown in Figure 6, with the increase of feed pressurization / countercurrent depressurization step time, the purity of CO$_2$ of bottom product decreases slightly and the recovery increases significantly. At the beginning of countercurrent depressurization step, the amount of CO$_2$ released from the bottom of the bed is relatively high, but it becomes lower as the step time goes by. Therefore, the CO$_2$ purity of bottom product decreases with the increase of feed pressurization / countercurrent depressurization step time. As the feed pressurization/ countercurrent depressurization step time increases, the increasing ratio of the bottom product amount is greater than that of the feed amount, so that the CO$_2$ recovery of bottom product increases.

3.3.3. Effect of cocurrent depressurization / idle step time
As shown in Figure 7, with the increase of cocurrent depressurization/ idle step time, the purity of CO$_2$ of bottom product increases and the recovery decreases. When the cocurrent depressurization time increases, N$_2$ as weakly adsorbed gas would be discharged from the top of bed, so that the CO$_2$ purity of bottom product at the following step increases. However, the longer the cocurrent depressurization time is, the more amount of CO$_2$ emits from the top of bed, resulting in a decrease in the CO$_2$ recovery of bottom product.
3.3.4. Effect of feed pressure
As shown in Figure 8, with the increase of feed pressure, the purity of CO₂ of bottom product increases and the recovery decreases. As the feed pressure increases, the molar feed flow rate increases which makes the utilization rate of the adsorbent and the adsorption amount of CO₂ increase, so that the CO₂ purity of bottom product increases. As the feed pressure increases, the increasing ratio of the bottom product amount is less than that of the feed amount, so that the CO₂ recovery of bottom product decreases.

3.3.5. Effect of adsorption / purge step time
As shown in Figure 9, with the increase of adsorption/ purge step time, the purity of CO₂ of bottom product remains nearly the same and the recovery decreases. As the adsorption/ purge step time increases, there is more CO₂ being adsorbed at adsorption step and being discharged at purge step. However, the CO₂ purity of bottom product is close to 100%, so that the change of purity is not significant. As adsorption/ purge step time increases, the increasing ratio of the bottom product amount is less than that of the feed amount, so that the CO₂ recovery of bottom product decreases.

3.3.6. Effect of operating temperature
As shown in Figure 10, with the increase of the operating temperature, the purity of CO₂ of bottom product goes up first and then down, and the recovery increases. From section 3.1, among the temperature region from 328K to 368K, the selectivity of UOP 13X is the highest at 358 K, 368 K is the second, and 328 K is the lowest. The higher selectivity is beneficial to the increase of purity of bottom product. Therefore, the CO₂ purity of bottom product is the highest at 358 K. As the operating temperature increases, the increasing ratio of the bottom product amount is greater than that of the feed amount, so that the recovery increases.

3.3.7. Effect of purge to feed ratio
As shown in Figure 11, with the increase of purge to feed ratio (P/F ratio), the purity of CO₂ of bottom product goes up first and then down, and the recovery increases. When the P/F ratio increases from 0.073 to 0.105, the adsorbent bed regenerates well which is beneficial to the adsorption of next cycle, so that the CO₂ purity of bottom product increases. When the P/F ratio increases further from 0.105 to 0.152, not only CO₂ but also N₂ is purged to the bottom, so that the CO₂ purity of bottom product decreases. As the P/F ratio increases, the increasing ratio of the bottom product amount is greater than that of the feed amount, so that the recovery of bottom product increases.
4. Conclusion
This research experimentally studied the simulated gas (95% CO$_2$, 5% N$_2$) from syngas after oxy-fuel combustion by PSA process. By the analysis of the adsorption amount and the selectivity of CO$_2$ to N$_2$ over different adsorbents, we chose UOP 13X zeolite as the adsorbent due to its high adsorption amount and the selectivity of CO$_2$ to N$_2$ usually increasing with temperature. Breakthrough curves and desorption curves were discussed by changing the feed flow rate and the bed temperature. In the breakthrough experiment, it could be known that when the feed flow rate increased or the operating temperature increased, the adsorption bed would reach breakthrough faster. In the desorption experiment, it could be known that when the feed flow rate of helium gas increased, or the operating temperature increased, the adsorbent in the adsorption bed had a better desorption.
CO₂ from the feed of syngas after oxy-fuel combustion was purified by a dual-bed six-step PSA process. After a series of experiments, we found that the best operating conditions among the experiments, as shown in Figure 12, are feed pressure 3.45 atm, cocurrent depressurization pressure 1.25 atm, bed temperature 358 K, countercurrent depressurization pressure 0.48 atm, feed pressurization/ countercurrent depressurization step time 150 s, adsorption/ purge step time 20 s, cocurrent depressurization/ idle step time 250 s, and purge to feed ratio 0.105. The experimental results of final conditions are 99.94% purity and 42.84% recovery of CO₂ at bottom product, with an energy consumption of 0.304 GJ/ tonne CO₂ and a productivity of 0.136 kg CO₂/ kg adsorbent-h.

Figure 12. Schematic diagram of best results among the experiments for CO₂ capture from syngas after oxy-fuel combustion and dehydration as feed stream.

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